# THE SYNTHESIS AND REACTIVITY OF SOME HYDROCARBYL COMPLEXES OF MANGANESE, RHENIUM AND IRON

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by

JO-ANN MARGARET ANDERSEN (née GARNER)
B.Sc (Hons)

Department of Chemistry
University of Cape Town
Rondebosch 7700
South Africa

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## ABSTRACT

An extensive series of n-alkyl derivatives of manganesepentacarbonyl have been synthesized, *viz.* $[Mn(R)(CO)_5]$ ($R = CH_3$ to $n\text{-}C_9H_{19}$; $n\text{-}C_{11}H_{23}$ to $n\text{-}C_{18}H_{37}$). Only the methyl, ethyl and n-propyl derivatives have been reported previously. The majority of these compounds were synthesized *via* thermal decarbonylation of the acyl precursors, $[Mn(COR)(CO)_5]$ (most of these acyl compounds were new). A second synthetic pathway involved the direct reaction of $Na[Mn(CO)_5]$ with the appropriate n-alkyl bromide, RBr ($R = n\text{-}C_{12}H_{25}$; $n\text{-}C_{14}H_{29}$; $n\text{-}C_{16}H_{33}$; $n\text{-}C_{18}H_{37}$). The stability of most of these compounds, especially the longer chain derivatives, is remarkable when compared to ethyl manganesepentacarbonyl, which is notoriously unstable. Reactivity studies show that the longer chain alkyl compounds undergo alkyl migration more slowly than the shorter chain species; this is proposed as the reason for their much higher stability. Rate studies on the reactions of these alkyl compounds with a nucleophile ($PPh_3$) indicate that both steric and electronic factors play a role in determining reactivity patterns. In general, electronic factors were found to be more important for the short chain alkyl compounds (up to $C_3$), steric effects were dominant for the medium chain alkyl groups ($C_4$ to $C_7$) and thereafter a combination of both effects was in operation. The products of these reactions were, in all cases, the compounds *cis*-$[Mn(COR)(CO)_4(PPh_3)]$. The rates of decarbonylation of the acyl compounds $[Mn(COR)(CO)_5]$ have been measured for $R = CH_3$ to $n\text{-}C_9H_{19}$; $n\text{-}C_{11}H_{23}$; $n\text{-}C_{13}H_{27}$; $n\text{-}C_{15}H_{31}$; $n\text{-}C_{17}H_{35}$.

Selected alkyl compounds of the type $[Mn(R)(CO)_5]$ were found to be intermediates in a hydroformylation process. Thus, reaction of $[Mn(R)(CO)_5]$ with synthesis gas ($CO/H_2$) gave either (a) exclusively n-alcohols, $RCH_2OH$ (no aldehydic species were detected) in tetrahydrofuran, or (b) alkoxycarbonyl compounds, $[Mn\{CO(O)CH_2R\}(CO)_5]$, in hexane.

In a separate experiment, $[Mn_2(CO)_{10}]$ was observed to be a hydroformylation catalyst for the conversion of 1-hexene to 1-heptanol in tetrahydrofuran (again, no aldehyde was detected). A mechanism is proposed which accounts for the different products obtained in different solvents.

A series of binuclear compounds, $[(CO)_5Mn(CH_2)_nMn(CO)_5]$, ($n = 4$ to 8,10) has also been synthesized by thermal decarbonylation of the appropriate diacyl precursors.

To compare the effects of changing the metal, a similar series of n-alkyl rheniumpentacarbonyl compounds, $[Re(R)(CO)_5]$ ($R = C_2H_5$ to n-$C_{18}H_{37}$) was synthesized (the ethyl derivative is known). The syntheses were accomplished either by thermal decarbonylation of the acyl compounds $[Re(COR)(CO)_5]$ ($R = C_2H_5$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$) or by the direct reaction of $Na[Re(CO)_5]$ with RBr ($R =$ n-$C_{10}H_{21}$; n-$C_{12}H_{25}$; n-$C_{14}H_{29}$; n-$C_{16}H_{33}$; n-$C_{18}H_{37}$). The series of binuclear compounds $[(CO)_5Re(CH_2)_nRe(CO)_5]$ ($n = 4$ to 10) was also synthesized. The $n = 4$ to 8 and $n = 10$ compounds were synthesized by thermal decarbonylation of the acyl compounds and the $n = 9$ compound was prepared by direct reaction of $Na[Re(CO)_5]$ with 1,9 dibromononane. The mononuclear alkyl compounds ($[Re(R)(CO)_5]$) were observed to undergo reaction with triphenylphosphine to form the phosphine-substituted alkyl species, *viz.* *cis*-$[Re(R)(CO)_4(PPh_3)]$. No evidence for acyl intermediates was found.

An isomer of the propanediyl compound $[(CO)_5Mn(CH_2)_3Mn(CO)_5]$ is the cyclic carbene complex *eq*–$[(CO)_5MnMn(CO)_4(L)]$ where $L = {=}\overline{CCH_2CH_2CH_2O}$, *i.e.* 2-oxacyclopentylidene. This compound and five other related cyclic carbene complexes ($L = {=}\overline{CCH_2CH_2CH(CH_3)O}$, ${=}\overline{CCH_2CH(CH_3)CH_2O}$, ${=}\overline{CC(CH_3)_2CH_2CH_2O}$, ${=}\overline{CCH_2CH_2CH_2CH_2O}$ and ${=}\overline{CCH_2CH_2CH_2CH(CH_3)O}$) have been prepared. Crystal structures are reported for the compounds with $L = {=}\overline{CCH_2CH_2CH_2O}$, ${=}\overline{CCH_2CH_2CH(CH_3)O}$, ${=}\overline{CCH_2CH_2CH_2CH_2O}$ and

$=\overline{CCH_2CH_2CH_2CH(CH_3)O}$. The latter two are the first crystal structures to be reported for complexes containing the 2-oxacyclohexylidene ligand. Reactions of these compounds which we report include (a) the exchange of $\alpha$-protons of the carbene ring for methyl groups and (b) exchange of the $\alpha$-protons for deuterium. Rate constants were obtained for this latter process.

The substituted benzyl compounds $[Mn(CH_2C_6H_4X)(CO)_5]$ (X = o-Br, m-Br, p-Br, o-$NO_2$, m-$NO_2$, p-$NO_2$, p-$CH_3$ and H), $[CpFe(CH_2C_6H_4X)(CO)_2]$(X = o-Cl, m-Cl, p-Cl, o-Br, m-Br, p-Br, o-$CH_3$, m-$CH_3$, p-$CH_3$ and H), $[CpFe(CH_2CH_2C_6H_5)(CO)_2]$ and $[CpFe(CH_2CH_2CH_2C_6H_5)(CO)_2)]$, the majority of which are new, were synthesized by us and their reactivity investigated. The manganese compounds were found to undergo a relatively facile $PPh_3$-induced alkyl migration to form the compounds *cis*-$[Mn(COCH_2C_6H_4X)(CO)_4(PPh_3)]$. None of the iron benzyl compounds of the type $[CpFe(CH_2C_6H_4X)(CO)_2]$ reacted with $PPh_3$, even at elevated temperatures or after addition of an oxidant ($AgBF_4$). The phenylethyl and phenylpropyl derivatives did however undergo reaction to form the species $[CpFe\{CO(CH_2)_nC_6H_5\}(CO)_2]$(n = 2,3).

# PUBLICATIONS

The following work from this thesis has already been presented:

**PAPERS:**

1. "Synthesis of dimanganese nonacarbonyl cyclic carbene complexes and molecular structures of two of them", J. M. Garner, A. Irving and J. R. Moss, Organometallics, 9 (1990) 2836.

2. "Alkylmanganese pentacarbonyls", J. M. Andersen and J. R. Moss, J. Organomet. Chem., 439 (1992) C25.

3. A comparison of some complexes of the type *eq*-[$Mn_2(CO)_9L$] where L is a cyclic carbene ligand with a five- or six-membered ring and the molecular structures of two complexes containing six-membered carbene rings", J. M. Andersen, S. J. Archer, J. R. Moss and M. L. Niven, Inorg. Chim. Acta, 1993, *in press*.

**CONFERENCE CONTRIBUTIONS:**

1. Poster titled "Synthesis and reactivity of transition metal aryl compounds", J. M. Garner, J. R. Moss and E. M. Zulu, presented at "Inorganic 88", Gordon's Bay, RSA (1988).

2. Poster titled "Binuclear manganese cyclic carbene complexes", J. M. Garner, A. Irving and J. R. Moss, presented at the 30th Convention of the South African Chemical Institute, Johannesburg, RSA (1989).

3. Poster titled "Dimanganese cyclic carbene complexes: confirmation of the structure of King's complex, $[Mn_2(CO)_9(C_4H_6O)]$", J. M. Garner, A. Irving and J. R. Moss, accepted for presentation at the First International Conference on the Chemistry of the Early Transition Metals, Brighton, United Kingdom (1989).

4. Poster titled "Transition metal carbene compounds", J. M. Garner, A. Irving and J. R. Moss, presented at "Inorganic 90", Golden Gate, RSA (1990).

5. Poster titled "A comparison of the structures of some transition metal carbene compounds", S. J. Archer, J. M. Garner, A. Irving, K. R. Koch and J. R. Moss, presented at the XXVIII International Conference on Coordination Chemistry, Gera, Germany (1990).

6. Lecture titled "The synthesis, structure and reactivity of transition metal carbene complexes and their relevance to catalysis", presented by J. M.

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7. Lecture titled "The synthesis, structure and reactivity of long chain alkyl manganese species; their catalytic relevance and some unusual properties" presented by J. M. Andersen at Catalysis and Catalytic Processing 1990, Golden Gate, RSA (1991).

8. Poster titled "Carbonylation studies involving manganese alkyl species", J. M. Andersen and J. R. Moss, presented at the International Symposium on Transition Metals in Organic Synthesis, Bristol, United Kingdom (1992).

9. Poster titled "New studies on the CO insertion reaction in alkyl manganesepentacarbonyl complexes", J. R. Moss and J. M. Andersen, presented at the 8th International Symposium on Homogeneous Catalysis, Amsterdam, The Netherlands (1992).

10. Poster titled "Conversion of 1-alkenes to alcohols using a manganese carbonyl catalyst", J. M. Andersen and J. R. Moss, accepted for presentation at Catalysis and Catalytic Processing 1993, Gordon's Bay, RSA (1993).

# ABBREVIATIONS

Å = angstrom
ax = axial
i-Bu = iso-butyl group
t-Bu = tertiary-butyl group
ca = approximately
COSY = correlated spectroscopy
Cp = cyclopentadienyl group = $\eta^5$-$C_5H_5$
dec = decomposed
DMSO = dimethylsulfoxide
DSC = differential scanning calorimetry
eq = equatorial
eqn = equation
Et = ethyl group
ether = diethyl ether
Fig = figure
Fp = irondicarbonyl cyclopentadienyl = $[CpFe(CO)_2]$
h = hours
HETCOR = heteronuclear correlation
I∞ = intensity at time = infinity
It = intensity at time = t
IR = infrared (vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad)
L, $L_n$ = ligand(s)
m- = meta position on benzene ring
M = transition metal
$M^+$ = molecular ion
$^m/_e$ = mass to charge ratio
Me = methyl group
mol = moles
mp = melting point
n = normal

NMR = nuclear magnetic resonance (m = multiplet, c = complex signal, qu = quintet, q = quartet, tr = triplet, d = doublet, s = singlet, br = broad)

o- = ortho position on benzene ring

p- = para position on benzene ring

Ph = phenyl group

ppm = parts per million

i-Pr = iso-propyl group

Pr = propyl group

$PR_3$ = tertiary phosphine

R = alkyl group

Rp = rutheniumdicarbonyl cyclopentadienyl = $[CpRu(CO)_2]$

RT = room temperature

s = seconds

$t_{\frac{1}{2}}$ = half-life of reaction

THF = tetrahydrofuran

TMS = tetramethylsilane

vs = versus

**NOTE:** COMPOUND, FIGURE AND EQUATION NUMBERS ARE VALID WITHIN EACH INDIVIDUAL CHAPTER ONLY

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# CHAPTER 1

# A REVIEW OF ALKYL AND ACYL MANGANESE AND RHENIUM PENTACARBONYL COMPOUNDS - THEIR SYNTHESIS, STRUCTURE AND REACTIVITY

## 1.1 **PERSPECTIVE**

The study of transition metal alkyl compounds is an ever-growing field in organometallic chemistry. This is, in part, because of the proposed intermediacy of such species in a variety of heterogeneous and homogeneous catalytic reactions. These reactions include, among others, the Fischer-Tropsch synthesis and the hydroformylation and polymerization of olefins. One of the key mechanistic steps proposed in these catalytic reactions is migratory insertion into a metal-carbon bond. Owing to the industrial and commercial importance of these reactions, the search for stoichiometric systems in which this step can be observed directly has been one of great endeavour. One of the simplest types of alkyl complexes which have been used as models for catalytic intermediates and which undergo reactions that are of prime importance in many catalytic processes are the complexes $[Mn(R)(CO)_5]$ (R = alkyl) (and to a lesser extent $[Re(R)(CO)_5]$). Alkyl manganese- and rheniumpentacarbonyl compounds are also considered to be important from a theoretical viewpoint in that they contain both the alkyl group and carbon monoxide in an activated form.

The synthesis of methyl manganesepentacarbonyl, $[Mn(CH_3)(CO)_5]$ was a highly signficant event in organometallic chemistry as it was the first stable transition metal carbonyl alkyl compound to be reported [1]. Since then, alkyl compounds of virtually every transition metal in the periodic table have been reported. Despite this wealth of new and intriguing compounds, the relatively simple methyl manganesepentacarbonyl remains to date the most well-studied transition metal alkyl compound in terms of structure and reactivity. Surprisingly though, very little is known about higher alkyl derivatives of manganesepentacarbonyl. Ethyl and n-propyl manganesepentacarbonyl have been synthesized [2], but were found to be extremely unstable, decomposing even under vacuum, in the dark at -10°C [3]. It was therefore assumed that derivatives with longer alkyl chains would be even more unstable and presumably this has deterred even the most determined researcher from investigating this field any further. In Chapters 2 and 3 of this thesis we describe results on our studies of higher homologues of $[Mn(R)(CO)_5]$.

## 1.2 SYNTHESIS

### 1.2.1 SYNTHESIS OF $[Mn(R)(CO)_5]$ and $[Mn(COR)(CO)_5]$

The method first used to prepare $[Mn(CH_3)(CO)_5]$ and $[Mn(COCH_3)(CO)_5]$[1] is still today the most common route to carbonyl-containing alkyl and acyl compounds of manganese. This route involves the preparation of $[Mn(CO)_5]^-$ *in situ* (most commonly by reductive cleavage of $[Mn_2(CO)_{10}]$ over a sodium/mercury amalgam to give $Na[Mn(CO)_5]$), which then acts as a nucleophile to displace a halide ion from either an alkyl or an acyl halide. Thus, the syntheses of $[Mn(CH_3)(CO)_5]$ and $[Mn(COCH_3)(CO)_5]$ are effected as shown in equations (1) and (2) respectively.

$$[Mn(CO)_5]^- + CH_3I \longrightarrow [Mn(CH_3)(CO)_5] + I^- \qquad (1)$$

$$[Mn(CO)_5]^- + CH_3COCl \longrightarrow [Mn(COCH_3)(CO)_5] + Cl^- \qquad (2)$$

The synthesis of methyl manganesepentacarbonyl has also been effected by the reaction of $[Mn(H)(CO)_5]$ with diazomethane [2] (equation 3).

$$[Mn(H)(CO)_5] + CH_2N_2 \longrightarrow [Mn(CH_3)(CO)_5] + N_2 \qquad (3)$$

However, this reaction is much less efficient than the synthesis using methyl iodide.

The manganesepentacarbonyl anion is usually used in the form of the sodium salt, $Na[Mn(CO)_5]$, however, other electropositive metals have been used, for example, $Li^+$ and $K^+$ [4]. The species $[Mn(MgBr)(CO)_5]$ [5], $Tl[Mn(CO)_5]_3$, $Hg[Mn(CO)_5]_2$ and $Cd[Mn(CO)_5]_2$[6] have also been found to react with alkyl halides to give alkyl manganesepentacarbonyl species. The reaction of the thallium complex, however, can be complicated since there is concurrent reduction of thallium (equation. 4). The mercury and cadmium complexes react satisfactorily with methyl iodide.

$$Tl[Mn(CO)_5]_3 + 2RX \longrightarrow TlX + 2\,[Mn(R)(CO)_5] + [Mn(X)(CO)_5] \qquad (4)$$
$(R = CH_3,\ CH_3CO,\ C_6H_5CO)$

Another synthetic route involves the treatment of the pentacarbonyl halides $[Mn(X)(CO)_5]$ with an organic derivative of magnesium or lithium, *e.g.* the treatment of $[Mn(Br)(CO)_5]$ with benzylmagnesium chloride gives the benzyl derivative $[Mn(CH_2Ph)(CO)_5]$ [2] and the reaction of $[Mn(Br)(CO)_5]$ with phenyllithium gives $[Mn(Ph)(CO)_5]$[7]. However, this type of reaction suffers from the disadvantages of $[Mn_2(CO)_{10}]$ formation and low product yields.

Relatively few alkyl halides react with $[Mn(CO)_5]^-$ to form $[Mn(R)(CO)_5]$ derivatives [8], due in part to the low nucleophilicity of the manganesepentacarbonyl anion [9]. Mention should be made of the fact that Cotton and Markwell [10] have reacted $[Mn(CO)_5]^-$ with a series of substituted benzyl bromides to give the corresponding substituted benzyl manganesepentacarbonyl derivatives $[Mn(CH_2C_6H_{5-n}X_n)(CO)_5]$ in high yield. This will be discussed in detail in Chapter 5. Virtually all acyl chlorides will react with $[Mn(CO)_5]^-$ to form the acyl derivatives $[Mn(COR)(CO)_5]$. Thus, numerous acyl derivatives have been prepared, including: COR = COPh [1], $CO(CH_2)_4CH_3$[11], $COCH_2CH_2Ph$[10, 12], $COCH_2CH_3$[13] and $COCH_2Ph$[14].

These acyl derivatives may be stabilised by resonance structures such as Fig. 1, in which the manganese — acyl carbon bond has appreciable double bond character (as in manganese carbonyl itself)[8].

$$R - \overset{\overset{\displaystyle O^-}{|}}{C} = \overset{+}{Mn}(CO)_5$$

**Fig. 1** A Resonance Structure for $[Mn(COR)(CO)_5]$

The rarity and instability of acyl derivatives of non-transition metals such as tin emphasizes the importance of structures analogous to Fig. 1 in stabilising acyl derivatives of transition metals.

The facile decarbonylation (equation 5) of these acyl derivatives permits the preparation of many aryl and alkyl derivatives of manganese not obtainable by reaction of $[Mn(CO)_5]^-$ with aryl or alkyl halides.

$$[Mn(COR)(CO)_5] \longrightarrow [Mn(R)(CO)_5] + CO \qquad (5)$$

Thus, the phenyl derivative [Mn(Ph)(CO)$_5$], the p-tolyl derivative [Mn(p-CH$_3$C$_6$H$_4$)(CO)$_5$] and the phenylethyl derivative [Mn(CH$_2$CH$_2$Ph)(CO)$_5$] were prepared from the benzoyl [1], p-toluoyl [15] and phenylpropionyl [12] derivatives, respectively. In many cases, this decarbonylation reaction is reversible, for example, methyl manganesepentacarbonyl reacts with carbon monoxide at room temperature to give acetyl manganesepentacarbonyl in good yield [15]. This very facile carbonylation process for manganesepentacarbonyl alkyls may in fact be the reason for the high instability of ethyl and n-propyl manganesepentacarbonyl [8]. That ethyl and propyl manganesepentacarbonyl undergo facile carbonylation has been demonstrated by Calderazzo and Cotton [17] and Cawse *et al.* [14]. The first reported synthesis of [Mn(C$_2$H$_5$)(CO)$_5$] (from the reaction of Na[Mn(CO)$_5$] with ethyl iodide) was in 1958 by Hieber and Wagner [2] who maintained that the compound existed as colourless needle-like crystals melting at 58°C. However, when Green and Nagy repeated this reaction [3], they found that the product of the reaction reported by Hieber and Wagner was in fact propionyl manganesepentacarbonyl ([Mn(COC$_2$H$_5$)(CO)$_5$]), not ethyl manganesepentacarbonyl, which they found to be a thermally unstable, air-sensitive yellow oil which froze to a solid mass at -20°C. The first reported synthesis of [Mn(COC$_2$H$_5$)(CO)$_5$] was by Coffield *et al.* in 1957 [16].

There appears to be some discrepancy in the literature as to the reasons for the instability of [Mn(C$_2$H$_5$)(CO)$_5$]. Several reports ascribe the instability to a very facile ß-hydride elimination process [2,4,18,19]. In fact, ref 19 makes the following statement: "... the ß-hydride elimination reaction dominates the chemistry of alkyl ligands". However, a ß-hydride elimination reaction would result in the formation of [Mn(H)(CO)$_5$] (which could decompose to [Mn$_2$(CO)$_{10}$]) and ethylene, yet it is propionyl manganesepentacarbonyl, not ethylene, which is one of the observed decomposition products of $[Mn(C_2H_5)(CO)_5]$. Gismondi and Rausch thermally degraded $[Mn(C_2H_5)(CO)_5]$ (at room temperature) and they sublimed crystals of $[Mn(COC_2H_5)(CO)_5]$ from the residue [13]. Bearing in mind the high carbonylation rate for $[Mn(C_2H_5)(CO)_5]$ it seems reasonable to conclude that ethyl manganesepentacarbonyl probably decomposes by facile carbonylation (to propionyl manganesepentacarbonyl) rather than by ß-hydride elimination. A mechanism as outlined in Scheme 1 could be in operation for the thermal decomposition of $[Mn(C_2H_5)(CO)_5]$.

$$[Mn(C_2H_5)(CO)_5] \xrightarrow{S} [Mn(COC_2H_5)(CO)_4(S)]$$

$$\longrightarrow [Mn(C_2H_5)(CO)_4(S)] \quad + \quad CO$$

$$\downarrow$$

decomposition

and

$$[Mn(COC_2H_5)(CO)_4(S)] \quad + \quad CO \longrightarrow [Mn(COC_2H_5)(CO)_5] \quad + \quad S$$

(S = Solvent)

Scheme 1 Decomposition of $[Mn(C_2H_5)(CO)_5]$

Thus, the carbonylation reaction for $[Mn(C_2H_5)(CO)_5]$ is so facile that carbon monoxide liberated during the initial decomposition of some of the ethyl manganesepentacarbonyl is able to carbonylate some of the remaining $[Mn(C_2H_5)(CO)_5]$ to the propionyl derivative. The decomposition of n-propyl manganesepentacarbonyl is expected to follow the same pathway.

Because of the unstable nature of ethyl and n-propyl manganesepentacarbonyl, very little work has been done on them and no work at all has been done on higher n-alkyl derivatives. Work of this nature should prove to be very valuable since in many catalytic reactions it is $C_3$ and higher alkyl fragments which are involved. If the instability of $[Mn(C_2H_5)(CO)_5]$ and $[Mn(C_3H_7)(CO)_5]$ is indeed due to high carbonylation rates and not ß-hydride elimination, then higher alkyl derivatives could prove to be relatively stable if they were found to be less susceptible to the carbonylation reaction than $[Mn(C_2H_5)(CO)_5]$. Indeed, this is found to be the case and is the scope of much of this thesis (see chapters 2 and 3).

A brief mention should be made of the fact that $[Mn(R)(CO)_5]$ compounds, where R is a secondary or tertiary alkyl group, also appear to be very unstable. Thus, reactions between $Na[Mn(CO)_5]$ and secondary or tertiary alkyl halides give $[Mn_2(CO)_{10}]$ and hydrocarbons as products rather than $[Mn(R)(CO)_5]$ compounds [8]. For example, treatment of $Na[Mn(CO)_5]$ with tropylium bromide gives ditropyl and $[Mn_2(CO)_{10}]$ [20] instead of the σ-cycloheptatrienyl derivative, $[Mn(C_7H_7)(CO)_5]$.

While mononuclear manganesepentacarbonyl alkyl compounds continue to receive considerable attention, interest is also starting to develop in binuclear compounds. Binuclear and cluster species may be more accurate approximations of a catalyst surface than their mononuclear analogues. However, the reactions of binuclear compounds may not be as predictable as for mononuclear species, since there is no corresponding library of fundamental processes on which to model transformations at complexes with more than one metal centre. It could be that the same fundamental processes outlined for mononuclear systems will hold for binuclear metal complexes, (acting either in parallel or separately at each metal centre), but another possibility is that new primary processes unique to polynuclear metal centres may be required to explain the observed transformations. Thus, a hydrocarbyl ligand bridging two metals may undergo a rearrangement that is not possible for mononuclear species.

The first binuclear manganesepentacarbonyl species reported were the acyl species $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$ and $[(CO)_5MnCO(C_6H_4)COMn(CO)_5]$, synthesized by Nesmeyanov *et al.* in 1963 [21], who reacted $Na[Mn(CO)_5]$ with the appropriate acyl chlorides to give the required products in good yield. In 1968, Kraihanzel and Herman followed suit with the synthesis of $[(CO)_5MnCO(CH_2)_5COMn(CO)_5]$ (and $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$) [22] (also from the treatment of $Na[Mn(CO)_5]$ with acyl chlorides). After 1968, interest in these compounds seemed to wane, and the next report only appeared in 1983, from Raab *et al.* [23], who reported the syntheses of $[(CO)_5MnCH_2CH_2Mn(CO)_5]$ and $[(CO)_5MnCH_2CH_2Re(CO)_5]$ (a heterobimetallic compound). However, they adopted a slightly different synthetic strategy: the tetrafluoroborato complex formed by treating $[Mn(CH_3)(CO)_5]$ with $Ph_3CBF_4$ was reacted with ethylene to give $[Mn(C_2H_4)(CO)_5]^+BF_4^-$ and nucleophilic addition of $[M(CO)_5]^-$ (M = Mn,Re) gave the hydrocarbyl bridged compound $[(CO)_5MnCH_2CH_2M(CO)_5]$. Mapolie *et al.* then reported the synthesis of μ(1,4)-butanediylbis(manganesepentacarbonyl), *i.e.* $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$ [24], formed *via* decarbonylation of the acyl species (which was synthesized by treatment of $[Mn(CO)_5]^-$ with adipoyl chloride). In 1990, the same group extended this synthetic pathway to the preparation of $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ (n = 5, 6) [25].

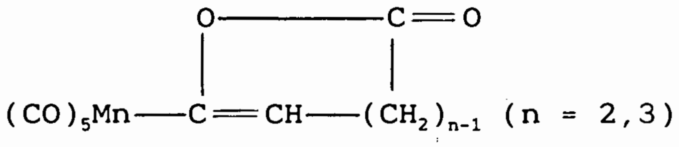
Sheeran *et al.* [11] have also reported the preparation of $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$ from the reaction of $[Mn(CO)_5]^-$ with adipoyl chloride and they also report the reaction of $[Mn(CO)_5]^-$ with sebacoyl chloride (equation 6).

$$2Na[Mn(CO)_5] + ClCO(CH_2)_8COCl \longrightarrow [(CO_5MnCO(CH_2)_8COMn(CO)_5] + 2NaCl \qquad (6)$$

The most recent report of a binuclear species came from Lindner and Pabel [26], who reacted the potassium salt, $K[Mn(CO)_5]$, with the bistriflate, $T_fO-(CH_2)_3-OT_f$ to give the propylene-bridged compound (equation 7).

$$2K[Mn(CO)_5] \quad + \quad F_3CSO_2O\text{-}(CH_2)_3\text{-}OSO_2CF_3 \longrightarrow$$
$$[(CO)_5Mn(CH_2)_3Mn(CO)_5] + 2K(OSO_2CF_3) \qquad (7)$$

In an attempt to prepare the acyl precursor to the above compound (and the ethylene bridged compound), Kraihanzel and Herman in 1968 [22], reacted $Na[Mn(CO)_5]$ with glutaryl chloride (and succinyl chloride). However, what they eventually isolated were not the desired bimetallic acyl species but compounds with an unusual ring structure.



1

Acid hydrolysis of the ring system gave the acids $[Mn(CO)_5\{CO(CH_2)_nCO_2H\}]$.

Mention should be made of the reaction of $[Mn(CO)_5]^-$ with 1,3-dibromopropane [27]. This reaction was initially suggested to give, not the propylene-bridged compound, but a product with an unusual "ring structure" (see Fig. 2), with a then-unprecedented type of manganese-hydrogen bond, formed by partial donation of one of the three unbonded electron pairs in the manganese d-orbitals to the relatively positive hydrogen atom

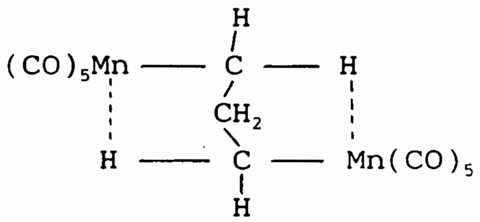


**Fig. 2** Proposed Product of the Reaction of $Br(CH_2)_3Br$ with $[Mn(CO)_5]^-$ [27]

This type of interaction is now becoming fairly well known in organometallic chemistry and is termed an "agostic interaction" [19]. A similar product was obtained from the reaction of 1,3-dibromobutane with $[Mn(CO)_5]^-$.

By careful analysis of NMR data, Casey subsequently suggested that these compounds were cyclic carbene complexes (Fig. 3) containing a manganese-carbon double bond [28].

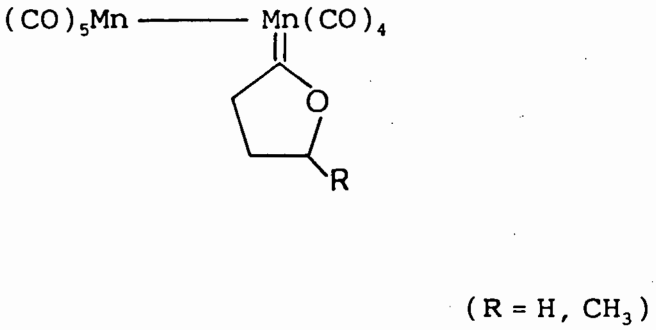


**Fig. 3** Product of the Reaction of $Br(CH_2)_3Br$ with $[Mn(CO)_5]^-$ [28]

Crystal structures on these two compounds have recently been reported [29], which confirmed Casey's suggestion.

### 1.2.2 SYNTHESIS OF $[Re(R)(CO)_5]$ and $[Re(COR)(CO)_5]$

The first report of a rheniumpentacarbonyl alkyl derivative was that of Hieber and Braun [30] in 1959 who reported the synthesis of methyl rheniumpentacarbonyl (equation 8).

$$Na[Re(CO)_5] + CH_3I \longrightarrow [Re(CH_3)(CO)_5] + NaI \qquad (8)$$

The same group then followed up on this report with the synthesis of $[Re(COCH_3)(CO)_5]$, $[Re(COPh)(CO)_5]$, $[Re(Ph)(CO)_5]$ and $[Re(CH_2Ph)(CO)_5]$ [31]. The same synthetic route as previously used was applied *i.e.* the reaction of $[Re(CO)_5]^-$ with the appropriate alkyl or acyl halide, except for

$[Re(Ph)(CO)_5]$ which was formed by thermal decarbonylation of $[Re(COPh)(CO)_5]$ (equation 9).

$$[Re(COPh)(CO)_5] \xrightarrow{120^\circ C} [Re(Ph)(CO)_5] + CO \qquad (9)$$

Then, in 1963, Davison *et al.* [32] reported the synthesis of ethyl rheniumpentacarbonyl from the treatment of $[Re(CO)_5]^-$ with ethyl iodide (equation 10).

$$Na[Re(CO)_5] + C_2H_5I \longrightarrow [Re(C_2H_5)(CO)_5] + NaI \qquad (10)$$

$[Re(C_2H_5)(CO)_5]$ was also found to be much less susceptible to carbonylation than $[Mn(C_2H_5)(CO)_5]$ and was therefore considerably more stable. The reaction between $[Re(C_2H_5)(CO)_5]$ and CO(100 atm.) was still not complete after 1 hour at 100°C [32]. In 1985, Warner and Norton reported an alternative synthesis of $[Re(C_2H_5)(CO)_5]$; they reacted $Na[Re(CO)_5]$ with excess ethyl tosylate to give the desired product [33]. This report also included the synthesis of isobutyl rheniumpentacarbonyl from treatment of $Na[Re(CO)_5]$ with isobutyltosylate.

Nesmeyanov and co-workers have reported the synthesis of several substituted phenyl rheniumpentacarbonyl compounds. In 1967, they reported the syntheses of $[Re(p\text{-}XC_6H_4CO)(CO)_5]$ and $[Re(p\text{-}XC_6H_4)(CO)_5]$ (X = Cl, Br, I) [34] and in 1968 followed this up with the syntheses of $[Re(o\text{-}, m\text{-} \text{ and } p\text{-}CH_3C_6H_4CO)(CO)_5]$, $[Re(m\text{-} \text{ and } p\text{-}CH_3C_6H_4)(CO)_5]$ [35], $[Re(o\text{-}, m\text{-} \text{ and } p\text{-}ClC_6H_4CO)(CO)_5]$ and $[Re(o\text{-}, m\text{-} \text{ and } p\text{-}ClC_6H_4)(CO)_5]$ [36]. Bent *et al.* have implied that they have prepared a series of substituted benzyl rheniumpentacarbonyl compounds [37].

As is the case with manganese, interest is starting to develop in binuclear hydrocarbyl-bridged complexes of rhenium.

Thus, the following compounds have been prepared: (a) $[(CO)_5ReCO(C_6H_4)CORe(CO)_5]$ (m- and p-) and $[(CO)_5Re(C_6H_4)Re(CO)_5]$ (m- and p-) (from the reaction of $[Re(CO)_5]^-$ with the relevant acyl chlorides, and decarbonylation of the acyl derivatives) [38]; (b) $[(CO)_5ReCH_2CH_2Re(CO)_5]$ (by the nucleophilic attack of $[Re(CO)_5]^-$ on $[Re(C_2H_4)(CO)_5]^+BF_4^-$) [39]; (c) $[(CO)_5ReCH_2\text{-}CH(CH_3)Re(CO)_5]$ (by the nucleophilic attack of $[Re(CO)_5]^-$ on $[Re(CH_2{=}CHCH_3)(CO)_5]^+BF_4^-$) [23]; (d) $[(CO)_5ReCO(CH_2)_4\text{-}CORe(CO)_5]$ and $[(CO)_5Re(CH_2)_4Re(CO)_5]$ (from the reaction of $[Re(CO)_5]^-$ with adipoyl chloride and subsequent decarbonylation of the acyl derivative) [25], and (e) $[(CO)_5Re(CH_2)_3Re(CO)_5]$ (from the treatment of $[Re(CO)_5]^-$ with the bistriflate $TfO\text{-}(CH_2)_3\text{-}OTf$ (equation 11)) [25].

$$2Na[Re(CO)_5] + F_3CSO_2O\text{-}(CH_2)_3\text{-}OSO_2CF_3 \longrightarrow [(CO)_5Re(CH_2)_3Re(CO)_5] + 2\,Na(OSO_2CF_3) \qquad (11)$$

A brief mention must be made of the high temperatures required to decarbonylate rheniumpentacarbonyl acyl species to the corresponding alkyl derivatives (usually over 100°C). Because rhenium-carbon bonds are considerably stronger than manganese-carbon bonds [40], temperatures 30-70°C higher than those required for decarbonylation of manganesepentacarbonyl acyl species are needed for the decarbonylation of the analogous rhenium compounds.

New work on $[Re(R)(CO)_5]$ compounds (and the binuclear analogues $[(CO)_5Re(CH_2)_nRe(CO)_5]$) is described in Chapter 4 of this thesis.

## 1.3 STRUCTURE

The molecular structures and bonding of manganese- and rheniumpentacarbonyl alkyl (and acyl) species have received considerable attention over the years, mainly because they contain a simple σ-bond between a transition metal and an organic alkyl group. The structures of the methyl compounds [Mn($CH_3$)($CO$)$_5$] and [Re($CH_3$)($CO$)$_5$] have been investigated by a wide variety of techniques, including X-ray [41], electron [42, 43], and incoherent inelastic neutron diffraction [41], vibrational [41, 44-47] and NMR spectroscopy [32,48-52].

### 1.3.1 Diffraction Studies

The gas phase electron diffraction study of [Mn($CH_3$)($CO$)$_5$] showed the compound to have a $C_{4v}$ symmetry with a manganese-methyl carbon bond length of 2.185Å [43] (hydrogen positions were not located). A separate gas phase electron diffraction study of [Re($CH_3$)($CO$)$_5$] gave a rhenium-methyl carbon bond length of 2.308Å [42]. A problem arose when the X-ray crystal structure of [Mn($CH_3$)($CO$)$_5$] was attempted [41]. Results showed that the solid phase was almost entirely orientationally disordered; each of the six co-ordination sites around the manganese atom was found to be occupied by, on average, about 5/6 of a carbonyl ligand and 1/6 of a methyl ligand. The superimposed methyl and carbonyl carbon atoms could not be resolved, thus no significant bond lengths or angles could be obtained. However, the X-ray diffraction data did indicate that [Mn($CH_3$)($CO$)$_5$] crystallizes in the orthorhombic space group *Pcmn* with four molecules per unit cell located at $C_s$ sites (the disorder was confirmed by Raman measurements which showed that at least some orientational disorder persisted even at 10K[41]). The problem of the hydrogen positions not being located by the electron diffraction experiments can be overcome by a study of the C-H stretching region of the [M($CHD_2$)($CO$)$_5$] species (M = Mn,Re), from whose isolated C-H stretching frequencies bond lengths and HCH angles may be predicted by the use of correlation graphs [41].

The vibrational studies conducted by Andrews *et al.* [41] for [Mn($CH_3$)($CO$)$_5$] show that the manganese-methyl carbon stretching frequency occurs at a lower value than most of the manganese-carbonyl carbon stretching frequencies. Together with the lower $CH_3$ versus CO oscillator mass, this was taken as indicative of a weaker force constant for the Mn-$CH_3$ versus Mn-CO stretch (force constants and bond lengths are often used as related, though not identical, measures of bond strength). Andrews *et al.* also discussed the idea that, in addition to the manganese-methyl carbon σ-bond, π back-bonding from the filled metal d orbitals into the methyl C-H antibonding σ* orbitals may occur. This hypothesis, known as hyperconjugation, was used to explain the high geminal $J_{HD}$ NMR coupling constant in $[Mn(CH_2D)(CO)_5]$ [53]. Reverse hyperconjugation is well known in perfluoroalkyl metal complexes and leads to lowering of the asymmetric C-F stretching frequency in $[Mn(CF_3)(CO)_5]$ by 150 $cm^{-1}$ [54]. A similar effect was observed in $[Mn(CH_3)(CO)_5]$, but smaller in magnitude due to the lower electronegativity of hydrogen versus fluorine [41].

Huang *et al.* have conducted a vibrational study of the effects of high external pressures on the structures and phase behaviours of $[Mn(CH_3)(CO)_5]$ and $[Re(CH_3)(CO)_5]$[47]. The vibrational data indicated that both $[Mn(CH_3)(CO)_5]$ and $[Re(CH_3)(CO)_5]$ undergo a phase transition (most probably second order); the manganese species at ~9 kbar and the rhenium species at ~22 kbar.

Avanzino *et al.* [55] have used X-ray photoelectron spectroscopy to study the effect of R (in $[Mn(R)(CO)_5]$) on the carbonyl stretching force constants. They determined gas-phase core binding energies of manganese, carbon and oxygen, as well as the atoms in R (R = H, $COCH_3$, $CH_3$, $CF_3$, $Mn(CO)_5$, Br, $Me_3Sn$), calibrated against the Ne 1s, Ne 2s and $N_2$ 1s lines [55]. The oxygen 1s and carbon 1s binding energies of a carbonyl group have been shown to be a good measure of the dπ——π* back-bonding to the carbonyl group

[56]. The above study showed that the manganese binding energies were linearly related to the carbon and oxygen binding energies. It had previously been assumed that, because of the delocalized nature of the dπ——π* bonding, changes in the π-acceptor nature of R would cause the charges on manganese, carbon and oxygen atoms to change by similar amounts but that, because of the well-known attenuation of electronegativity effects in σ-bonded systems, changes in the σ-donating ability of the ligand, R, would mainly affect the charge of the metal atom [55]. The fact that the changes in the binding energies of manganese, carbon and oxygen were found to be of similar magnitude forced the authors to admit that their initial assumption was wrong and that binding energy data alone is not sufficient to determine both the relative π-acceptor and σ-donor nature of R. The mutual proportionality of the manganese, carbon and oxygen binding energies was rationalized by assuming that only one property of R (σ-donor or π-acceptor character) was important in determining the degree of back-bonding to the carbonyl groups [55]. To determine which was the most important, Avanzino *et al.* structured the correlation of their data with different sets of ligand parameters believed to be measures of either σ-donor ability or π-acceptor ability [55]. It was concluded that changes in the degree of back-bonding to carbonyl groups are determined principally by changes in the σ-donor nature of R. Changes in the π-acceptor (or π-donor) ability of the R groups used in this study had very little effect on the CO groups, although the authors did comment on the fact that the relative unimportance of R-Mn π-bonding in the $[Mn(R)(CO)_5]$ compounds used in their study could have been due to the very weak π-acceptor and π-donor natures of ligands used compared to the relatively strong π-acceptor nature of a carbonyl group [55]. The theoretical rationale for an increase in π back-bonding to the carbonyl groups being associated with an increase in the σ-donor nature of R is based on the idea that an

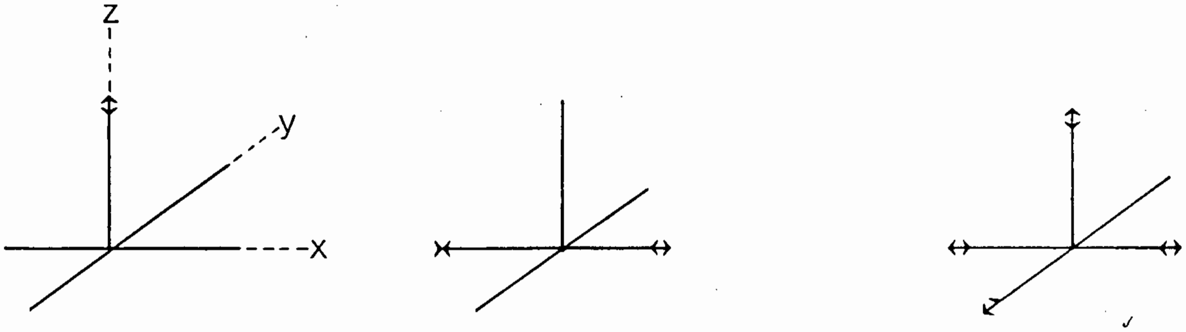
increase in electron density on the metal atom raises the energy of the metal dπ electrons and causes them to drift towards the carbonyl π* orbitals [57]. Thus the CO stretching frequencies of metal carbonyls decrease as the extent of π electron donation from the metal to the carbonyl group increases.

### 1.3.2 Infrared Studies

A monosubstituted metal carbonyl, $[M(R))(CO)_5](M = Mn,Re)$ has $C_{4v}$ symmetry, for which formal symmetry rules predict the following vibrations for the carbonyl groups [58]:

E : allowed, x, y polarized
$2A_1$ : allowed, z polarized
$B_1$ : forbidden

These vibrations are represented in Fig. 4.



$A_1$ E $A_1$

(only one component shown)

**Fig. 4** Allowed Vibrations (Carbonyl Stretching Region) For $[M(R)(CO)_5]$

The E vibration constitutes 4/5 of the total intensity of absorption. The two $A_1$ vibrations are made up of the stretching mode of the unique carbonyl group and the symmetrical breathing mode of the other four carbonyl groups. If these two $A_1$ modes did not couple to one another, the former would be allowed, accounting for the remaining 1/5 of the total intensity, while the latter would be almost forbidden. However, the two $A_1$ modes do interact, with some of the intensity of the strongly allowed mode being transferred to the other. These facts lead one to expect a very strong band, a band which is less strong by a factor of four, and a third much weaker band, which is in fact the pattern observed for most $[M(R)(CO)_5]$ (M = Mn,Re) species. For manganese, these bands typically occur at around 2115 $cm^{-1}$ (weak, $A_1$), 2012 $cm^{-1}$ (strong, E) and 1990 $cm^{-1}$(medium, $A_1$) (in hydrocarbon solvents) [50]. The corresponding values for rhenium are 2125 $cm^{-1}$($A_1$), 2110 $cm^{-1}$(E) and 1979 $cm^{-1}$ ($A_1$) [59].

However, the situation for acyl species $[M(COR)(CO)_5]$ (M = Mn,Re) is slightly different since the acyl group lacks even approximate axial symmetry (although there may be a symmetry plane including the R-CO-M group). This could lead to a small and possibly resolvable splitting of the intense E transition and, more important, to the appearance of the $B_1$ transition with low intensity. Thus, the appearance of a single, weak, extra band between the E and higher frequency $A_1$ bands for $[M(COR)(CO)_5]$ species is understandable [58] and is in fact observed for most acyl derivatives of manganese- and rheniumpentacarbonyl.

Typical band positions for manganese are 2112 $cm^{-1}$ (weak, $A_1$), 2050 $cm^{-1}$ (weak, $B_1$), 2010 $cm^{-1}$ and 2006 $cm^{-1}$ (strong, E; the splitting is in the region of 0 - 14 $cm^{-1}$, depending on the nature of R) 1999 $cm^{-1}$ (medium, $A_1$) and 1660 $cm^{-1}$ (weak, acyl band) [48] (in hydrocarbon solvents). Corresponding values for rhenium are 2134 $cm^{-1}$ ($A_1$), 2068 $cm^{-1}$ ($B_1$), 2018

$cm^{-1}$ and 2001 $cm^{-1}$ (E) and 1978 $cm^{-1}$ ($A_1$) and 1620 $cm^{-1}$ (weak, acyl) [59]. The magnitude of the splitting for the E transition and the intensity of the $B_1$ transition are not related; the latter is present with almost the same intensity in a variety of $[Mn(COR)(CO)_5]$ compounds [50].

The frequencies of the terminal carbonyl vibrations were also found to be relatively insensitive to the nature of R, although the halogen-substituted acyl manganesepentacarbonyl species proved to be an exception to this [60]. All the terminal CO stretching vibrations were shifted to higher frequencies due to the lowering of the electron density on manganese by the inductive effect of the halogen atoms.

In the ketonic region, usually only one single band is seen for the acyl carbonyl group *eg* for $[Mn(COC_2H_5)(CO)_5]$, but for $[Mn(COCMe_3)(CO)_5]$ and $[Mn(COCHMe_2)(CO)_5]$ two distinct bands were observed [48]. The $B_1$ transition can sometimes be observed for alkyl manganesepentacarbonyl species. Noack *et al.* [50] observed the $B_1$ band to be absent in a heptane solution of $[Mn(CH_3)(CO)_5]$, but it appeared in diethoxydiethyl ether (at 2044 $cm^{-1}$); thus, the solvent may interact with these complexes altering the symmetry sufficiently to bring about the appearance of the otherwise inactive $B_1$ band. A split in the band corresponding to the E transition was only observed for $[Mn(CH_2C_6H_5)(CO)_5]$. Thus, one can conclude that the number and intensity of the observed carbonyl stretching vibrations are in agreement with a slightly distorted $C_{4v}$ symmetry for alkyl and acyl manganese- and rheniumpentacarbonyls.

Long *et al.* [45] have recorded infrared spectra in the CH and CD stretching regions for various methyl manganese- and rheniumpentacarbonyl isotopomers (methyl = $CH_3$, $CD_3$, $CHD_2$, $CH_2D$). The spectra of these species were qualitatively interpreted in terms of a C-H stretching force constant which varies with the internal rotation angle of an essentially freely rotating methyl group. The C-H bands were found to be of average strength (those in $[Re(CH_3)(CO)_5]$ were slightly weaker) and bore an inverse relationship to the metal-methyl carbon bond strengths.

Long *et al.* then subsequently calculated an energy-factored force field for the carbonyl stretching vibrations in $[Mn(CH_3)(CO)_5]$ and $[Re(CH_3)(CO)_5]$, which included the $B_1$ fundamental [45]. An $A_1$ force field calculation for all vibrations showed that all the metal-carbonyl carbon bonds increase in strength from manganese to rhenium, while the methyl carbon-hydrogen bonds are weakened. The axial and equatorial metal-carbonyl carbon bonds in $[Re(CH_3)(CO)_5]$ are equal in strength, indicating a negligible trans effect on the part of the methyl ligand. This was interpreted in terms of equal and opposite π- and σ-trans effects, the former strengthening the axial rhenium-carbonyl carbon bond and the latter weakening it.

The infrared spectra of $^{12}CH_3$, $^{13}CH_3$, $^{12}CD_3$ and $^{13}CD_3$ isotopomers of $[Mn(CH_3)(CO)_5]$ and $[Re(CH_3)(CO)_5]$ in the gas phase down to 450 $cm^{-1}$ and in the solid at 78K down to 200 $cm^{-1}$ were also reported [44], in addition to the solid-phase Raman spectra (600 - 300 $cm^{-1}$) for $[Re(CH_3)(CO)_5]$ [44]. Andrews *et al.* have reported detailed Raman frequency data for $[Mn(CH_3)(CO)_5]$ [41]. A mention should be made of the observation of Bent *et al.* [37] that the higher energy $A_1$ band in a series of meta- and para-substituted $[M(CH_2\text{-}C_6H_{5-n}X_n)(CO)_5]$ (M = Mn,Re) complexes varied linearly with Hammett constants (as did the chemical shifts in the $^{55}Mn$ NMR). With a view that these spectroscopic parameters might reflect the electronic properties of the substituents rather more strongly than the steric influences, Bent *et al.* derived, for a number of ortho substituents, sets of Hammett constants and observed some degree of consistency [37].

### 1.3.3 NMR Studies

Surprisingly, very few studies on alkyl and acyl derivatives of manganese- and rheniumpentacarbonyl species report the use of NMR spectroscopy as a tool to probe their structure. The majority of studies have used NMR data for kinetic measurements [61, 62] or merely to obtain characterization data to aid in identification. The first detailed NMR study was that of Davison *et al.* [32] who obtained $^1$H NMR spectra of a series of $[M(R)(CO)_5]$ compounds ($M$ = Mn,Re; $R$ = H, $CH_3$, $C_2H_5$, $COC_2H_5$). They found that the chemical shifts of protons bonded directly to transition metals (*e.g.* in $[Mn(H)(CO)_5]$), when compared with the chemical shifts of hydrogen atoms bonded to main-group elements of low electronegativity (*e.g.* Sn; $SnH_4$, $\delta = 3.89$ ppm) [63], show that they are highly diamagnetically shielded by the transition metal. If this shielding was due to a large neighbour anisotropy effect by the transition metal, it was reasoned that a large contribution from this effect may be present in the alkyl derivatives. However, the $^1$H NMR spectra of the methyl and ethyl derivatives of manganese and rhenium showed that, as with non-transition metal alkyl compounds [32], the screening of the alkyl protons could not be adequately described on the basis of inductive and paramagnetic effects. Some evidence that this lack of correlation could be related to the close proximity of the metal to the alkyl group was shown by the introduction of a carbonyl group between the metal and the ethyl group - the spectra of the propionyl derivatives were very similar to those of a normal $C_2H_5CO$-$R'$ group. It was also noted that **M** was not merely a transition metal atom but a transition metal with CO groups attached, which could also have produced long-range screening contributions at the alkyl proton positions [32].

In general, $^1$H NMR data for manganese and rheniumpentacarbonyl alkyl and acyl compounds containing nonequivalent protons are in agreement with the expected electron coupled spin-spin interactions [50]. Somewhat more complicated spectra were obtained for R = $Me_2CCHCO$, p-$CH_3OC_6H_4CO$ and p-$FC_6H_4CO$. In general, proton resonances for alkyl groups σ-bonded to the manganesepentacarbonyl moiety range from -0.89 ppm to 7.23 ppm (R = $CH_3$ to $CF_2H$) (and for rhenium, -0.77 ppm to 1.77 ppm (R = $CH_3$ to $CH_2CH_3$)). The electronegativity of the fluorine atoms is important in determining the extent of the diamagnetic current, and consequently the decreased shielding of the protons. The proton resonances of the acyl derivatives of manganesepentacarbonyl, not containing fluorine, are at lower fields relative to the corresponding alkyl compounds, while in fluorine-substituted derivatives, the situation is reversed. Noack *et al.* have suggested that this could be due to an increase in manganese-carbon bond order for the fluorine-substitued species [50].

Calderazzo *et al.* [51] have measured $^{55}$Mn NMR spectra for various $[Mn(R)(CO)_5]$ compounds (R = H, $CH_3$,$CH_3CO$,$C_2H_5CO$, $Me_2CHCO$, $C_3H_7CO$, $C_6H_5CH_2CO$, p-$FC_6H_4CO$) and found the chemical shift (in ppm) to increase as the electron-donating ability of R increased.

Webb and Graham [52] have reported $^{13}$C NMR data for some $[Re(R)(CO)_5]$ compounds (R = $CH_3$,$CH_3CO$,$C_6H_5$,$C_6H_5CO$), which showed that the carbonyl carbon atoms *trans* to R are more shielded than those *cis* to R. Although there was found to be a linear relationship between the $^{13}$C chemical shift and the stretching force constant for *cis* carbonyls, there was no apparent correlation of the force constants with other features of the $^{13}$C NMR spectra. The acyl carbonyl carbon atom in $[Re(COCH_3)(CO)_5]$, with a chemical shift of 244 ppm, was found to be shifted upfield with respect to [CpFe-$(COCH_3)(CO)_2$] (δ = 254.4 ppm, [64]) and $[Mn(COCH_3)(CO)_5]$ (δ = 255 ppm, [65]). The resonance of the methyl carbon in $[Re(CH_3)(CO)_5]$, at -38.0 ppm, was more highly shielded than that of [$Mn(CH_3)(CO)_5$], at -9.4 ppm. All of the complexes studied by Webb and Graham gave satisfactory spectra in the carbonyl region at ambient temperature, especially [$Re(CH_3)(CO)_5$], for which the carbonyl peaks remained resolved even at elevated temperatures. The *cis* and *trans* carbonyl resonances were assigned on the basis of relative peak intensities; the *trans* carbonyl resonance was found to be upfield from the *cis* carbonyl resonance. When compared to $^{13}C$ NMR data known for [$Mn(R)(CO)_5$] species [66], it appears that the generally observed increase in shielding of carbonyl carbon atoms upon descending a periodic group (for transition metals) is in evidence for manganese and rhenium. The $^{13}C$ NMR spectrum of [$Mn(CH_3)(CO)_5$] exhibits a broad, unresolved singlet at 214 ppm [66] and only at -87°C does [$Mn(CH_2C_6H_5)(CO)_5$] exhibit two signals, at 211.1 ppm and 209.1 ppm, due to *cis* and *trans* carbonyls, respectively [67]. These values can be compared to those of 185.2 ppm and 181.3 ppm for the *cis* and *trans* carbonyls, respectively of [$Re(CH_3)(CO)_5$] [52]. Such a large upfield shift when descending a group cannot, however, be explained merely in terms of carbonyl stretching force constants. Webb and Graham made plots of Cotton-Kraihanzel carbonyl stretching force constants [68] versus $^{13}C$ NMR chemical shifts [52]. An excellent correlation was observed for the *cis* carbonyl carbon atoms, with the more highly shielded carbon atoms belonging to ligands of higher force constants. However, the correlation for the *trans* carbonyls was poor. Thus, changing chemical shifts of *trans* carbonyl carbon atoms in [$Re(R)(CO)_5$] compounds are not always reflected by changes in carbonyl force constants [52].

### 1.3.4 MASS SPECTRAL STUDIES

Very little mass spectral data is available for [$Mn(R)(CO)_5$] compounds, and almost none for the analogous [$Re(R)(CO)_5$] species. That which is available has mainly been reported as characterization data and not analyzed in any great depth. The only detailed study known is that of Mays and Simpson [69] who reported complete positive ion spectra of four complexes: $[Mn(CH_3)(CO)_5]$, $[Mn(C_6H_5)(CO)_5]$, $[Mn(CF_3)(CO)_5]$ and $[Mn(SO_2CH_3)(CO)_5]$. They obtained the results as shown in Table 1. The metal-containing ions were classified according to their mode of derivation (Scheme 2) from the molecular ion as follows: (i) loss of carbonyl groups; (ii) loss of R; (iii) loss of ligand fragments from the atom attached to manganese, and (iv) transfer of groups or atoms from R to manganese. Each process may involve more than one mechanism.

### (i) **Carbonyl Loss.**

This is a common feature of transition metal carbonyl compounds and occurs in a stepwise fashion. In the four species studied by Mays and Simpson, all ions of the type $[Mn(R)(CO)_n]^+$ (n = 0 - 5) were observed. For $[Mn(C_6H_5)(CO)_5]$, these ions accounted for some 80% of the metal-containing fragments. In the other three compounds, however, competing processes seemed to be more important.

### (ii) **Loss of R.**

Ions of the type $[Mn(CO)_n]^+$ (n = 0 - 5) were observed in all the spectra. Loss of R therefore competes with carbonyl loss.

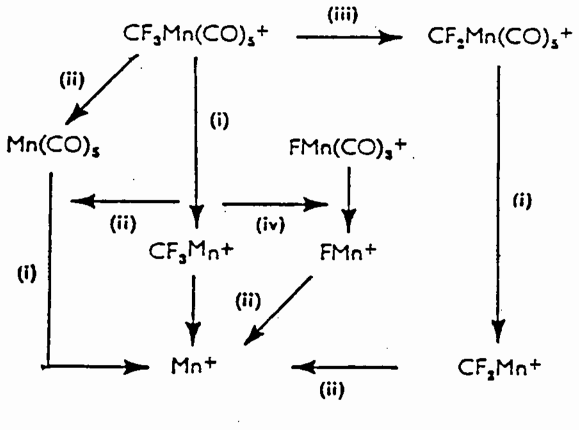
### (iii) **Loss of Ligand Fragments.**

A number of ions were observed in which the ligand (R) had been partially fragmented. The ease with which this occurs will depend on the relative energies of $[Mn(R)(CO)_n]^+$ and $[Mn(R')(CO)_n]^+$ (where R' is the fragmented ligand), as well as upon the neutral fragment released. All ions of this type were related to the molecular ion by virtue of the fact that the ligand fragment which was eliminated had originally been attached to an atom directly bonded to the manganese atom. Thus, $[Mn(CH_3)(CO)_5]$ gave the ions $[Mn(CH_3)(CO)_5]$ to $[Mn(C)(CO)_5]^+$.

(iv) **Transfer of Groups or Atoms to Manganese.**

In the conditions prevailing in the mass spectrometer, ions formed by carbene elimination are observed. Thus, ions of the type $[Mn(F)(CO)_n]^+$ ($n = 0-3$) were seen as major peaks in the mass spectrum of $[Mn(CF_3)(CO)_5]$. Weak peaks in the spectrum of $[Mn(CH_3)(CO)_5]$ at m/e 56 and 84 were assigned to $[MnH]^+$ and $[Mn(H)(CO)]^+$. This assignment was confirmed by comparison with the mass spectrum of $[Mn(CD_3)(CO)_5]$ [69]. For $[Mn(C_6H_5)(CO)_5]$ a peak due to $[MnH]^+$ was observed. This ion was thought of as arising from a different type of rearrangement, involving $[Mn(C_6H_5)(CO)_n]^+$. The complexes $[Mn(FC_6H_4)(CO)_5]$ (o-, m- and p-) were prepared in an attempt to gain more insight into the mechanism of this transfer. The results obtained indicated that the manganese-phenyl carbon bond was only partially retained during the transfer process [69].

The only mass spectra reported for alkyl rhenium-pentacarbonyl species are for the binuclear compounds, *viz.* *cis*-$[(CO)_5ReMn(CO)_4\{=C(OCH_3)CH_3\}]$[76], $[(CO)_5ReCH_2\text{-}CH(CH_3)Re(CO)_5]$[23] and $[(CO)_5Re(CH_2)_nRe(CO)_5]$



Scheme 2 Suggested Fragmentation Pathways for $[Mn(CF_3)(CO)_5]$[69]

$[Mn(CH_3)(CO)_5]$

| m/e | Ion | A |
|---|---|---|
| 210 | $CH_3Mn(CO)_5$ | 11 |
| 195 | $Mn(CO)_5$ | 10 |
| 182 | $CH_3Mn(CO)_4$ | 26 |
| 167 | $Mn(CO)_4$ | 13 |
| 154 | $CH_3Mn(CO)_3$ | 10 |
| 139 | $Mn(CO)_3$ | 14 |
| 126 | $CH_3Mn(CO)_2$ | 4 |
| 111 | $Mn(CO)_2$ | 16 |
| 98 | $CH_3MnCO$ | 6 |
| 97 | $CH_2MnCO$ | 2 |
| 96 | CHMnCO | 1 |
| 95 | CMnCO | 2 |
| 84 | HMnCO | 0.6 |
| 83 | MnCO | 27 |
| 70 | $CH_3Mn$ | 46 |
| 69 | $CH_2Mn$ | 17 |
| 68 | CHMn | 12 |
| 67 | CMn | 9 |
| 56 | HMn | 2 |
| 55 | Mn | 100 |

$[Mn(CF_3)(CO)_5]$

| m/e | Ion | A |
|---|---|---|
| 264 | $CF_3Mn(CO)_5$ | 100 |
| 245 | $CF_3Mn(CO)_5$ | 18 |
| 236 | $CF_3Mn(CO)_4$ | 3 |
| 217 | $CF_2Mn(CO)_4$ | 53 |
| 208 | $CF_3Mn(CO)_3$ | 14 |
| 195 | $Mn(CO)_5$ | 52 |
| 189 | $CF_2Mn(CO)_3$ | 16 |
| 180 | $CF_2Mn(CO)_2$ | 47 |
| 167 | $Mn(CO)_4$ | 6 |
| 161 | $CF_3Mn(CO)_2$ | 24 |
| 158 | $FMn(CO)_3$ | 10 |
| 152 | $CF_3MnCO$ | 17 |
| 139 | $Mn(CO)_3$ | 17 |
| 133 | $CF_2MnCO$ | 13 |
| 130 | $FMn(CO)_2$ | 7 |
| 124 | $CF_3Mn$ | 72 |
| 111 | $Mn(CO)_2$ | 48 |
| 105 | $CF_2Mn$ | 64 |
| 102 | FMnCO | 42 |
| 83 | MnCO | 29 |
| 74 | FMn | 39 |
| 69 | $CF_3$ | 25 |
| 55 | Mn | 52 |

$[Mn(C_6H_5)(CO)_5]$

| | | |
|---|---|---|
| 272 | $PhMn(CO)_5$ | 12 |
| 244 | $PhMn(CO)_4$ | 25 |
| 216 | $PhMn(CO)_3$ | 31 |
| 188 | $PhMn(CO)_2$ | 7 |
| 160 | PhMn(CO) | 17 |
| 132 | PhMn | 100 |
| 83 | MnCO | 3 |
| 56 | HMn | 3 |
| 55 | Mn | 36 |

$[Mn(SO_2CH_3)(CO)_5]$

| m/e | | A |
|---|---|---|
| 274 | $CH_3SO_2Mn(CO)_5$ | 3 |
| 259 | $SO_2Mn(CO)_5$ | 100 |
| 231 | $SO_2Mn(CO)_4$ | 2 |
| 210 | $CH_3Mn(CO)_5$ | 1 |
| 195 | $Mn(CO)_5$ | 96 |
| 190 | $CH_3SO_2Mn(CO)_2$ | 1 |
| 175 | $SO_2Mn(CO)_2$ | 2 |
| 167 | $Mn(CO)_4$ | 32 |
| 162 | $CH_3SO_2Mn(CO)$ | 2 |
| 147 | $SO_2MnCO$ | 2 |
| 139 | $Mn(CO)_3$ | 5 |
| 134 | $CH_3SO_2Mn$ | 3 |
| 119 | $SO_2Mn$ | 4 |
| 111 | $Mn(CO)_2$ | 3 |
| 87 | SMn | 1 |
| 83 | MnCO | 8 |
| 71 | OMn | 0.8 |
| 70 | $CH_3Mn$ | 2 |
| 56 | HMn | 0.5 |
| 55 | Mn | 10 |

Table 1 Mass Spectra of $[Mn(R)(CO)_5]$ Compounds (A = Relative Intensity) (Data from Ref. 69) (all ions have a single positive charge)

(n = 3,4)[25]. For the latter two compounds, molecular ions of low intensity were observed. $[(CO)_5Re(CH_2)_4Re(CO)_5]$ followed a similar fragmentation pattern to the analogous manganese compound [25], *viz.* (i) loss of CO from the parent ion; (ii) loss of the hydrocarbon bridge to form $[Re_2(CO)_{10}]^+$ and (iii) loss of a $[Re(CO)_5]$ fragment from the parent ion. However, for $[(CO)_5Re(CH_2)_3Re(CO)_5]$, the major decomposition pathway involved initial elimination of $C_3H_6$[25].

## 1.4 REACTIONS OF ALKYL AND ACYL MANGANESE AND RHENIUM PENTACARBONYL COMPOUNDS

### 1.4.1 ALKYL MANGANESEPENTACARBONYLS

Methyl manganesepentacarbonyl, $[Mn(CH_3)(CO)_5]$, and to a lesser extent other alkyl derivatives, are to date some of the most widely studied compounds in organotransition metal chemistry. The reactions that have been reported for these compounds are extensive; however, they can be divided into six main categories, namely

(1) reaction with neutral nucleophiles *e.g.* $PPh_3$,
(2) reaction with anionic nucleophiles, *e.g.* $I^-$,
(3) reaction with cationic species, *e.g.* $H^+$,
(4) reaction with transition metal hydrides, *e.g.* $[Re(H)(CO)_5]$,
(5) addition of Lewis acids, *e.g.* $AlCl_3$, and
(6) orthometallation reactions

Each of these categories will now be discussed separately, although it should be borne in mind that this account is by no means fully comprehensive since it would be beyond the scope of this thesis to provide a complete review of every reaction reported for $[Mn(R)(CO)_5]$ compounds. Consequently only several more important and representative reactions from each category have been selected for discussion.

### 1.4.1.1 Reaction of $[Mn(R)(CO)_5]$ with Neutral Nucleophiles

This is by far the most widely studied type of reaction for $[Mn(R)(CO)_5]$ compounds. The reaction usually involves the addition of the neutral nucleophile, L, with CO insertion/alkyl migration to form an acyl species, *i.e.*

$$[Mn(R)(CO)_5] + L \longrightarrow [Mn(COR)(CO)_4(L)] \qquad (12)$$

L is usually a tertiary phosphine ($PR_3$), an alkylated amine ($RNH_2$) or free carbon monoxide. Besides being a carbon-carbon bond forming reaction of fundamental importance, alkyl migration studies on transition metal alkyl species have essential applications in the field of catalysis, especially for the oxo or hydroformylation process [71], the Monsanto acetic acid synthesis [71] and the synthesis of ethylene glycol [72].

## Kinetics and Mechanism of Alkyl Migration

### A. Mechanistic Studies

Over the years various mechanisms have been proposed for the CO insertion/alkyl migration reaction, *e.g.* Calderazzo and Cotton's proposal [72] that an activated complex was formed by the direct combination of L (in this case CO) with $[Mn(CH_3)(CO)_5]$ without any solvent participation and had the following structure.

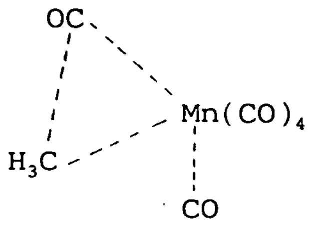
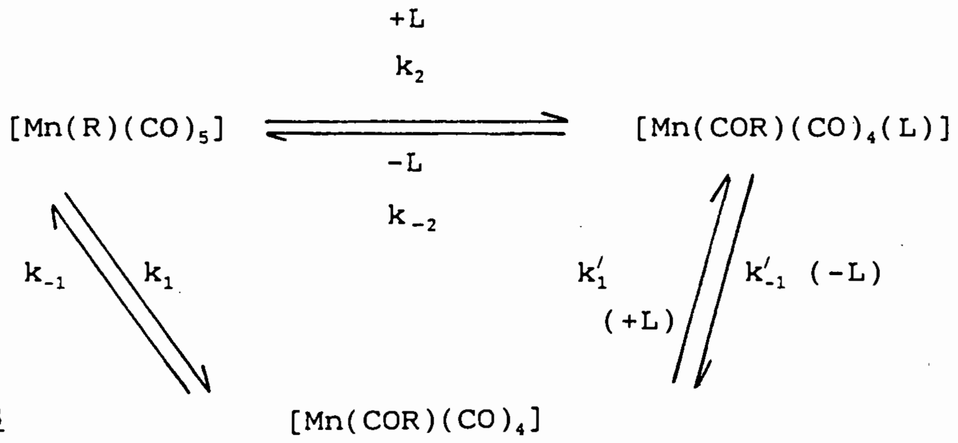


Fig. 5

However, it is now generally accepted that the reaction essentially proceeds by migration of the alkyl group, R, to an adjacent *i.e. cis* carbonyl group [4, 74] to form the coordinatively unsaturated species [Mn(COR)$(CO)_4$] (see Scheme 3). Coordination of the incoming ligand L then follows, to form [Mn(COR)$(CO)_4$(L)] compounds. That the reaction proceeds via alkyl migration rather than direct CO insertion into the metal-alkyl σ-bond has been demonstrated by labelling studies [75,76].

The following general kinetic scheme has been developed for the alkyl migration process in [Mn(R)$(CO)_5$] compounds:



Scheme 3

Thus, two pathways to the final product are available; (1) a second order pathway ($k_2$ [Mn(R)$(CO)_5$][L]) and (2) a two-step sequence *via* the coordinatively unsaturated intermediate [Mn(COR)$(CO)_4$]. In polar solvents, this intermediate may exist as a solvent hexacoordinated species, [Mn(COR)$(CO)_4$(S)]. In the absence of a suitably polar solvent, it is thought to adopt a square-based pyramidal conformation, with the acetyl ligand occupying a basal position, although a π-acyl derivative has also been proposed [77] which could take the following form:

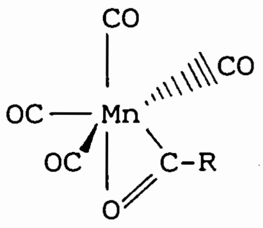
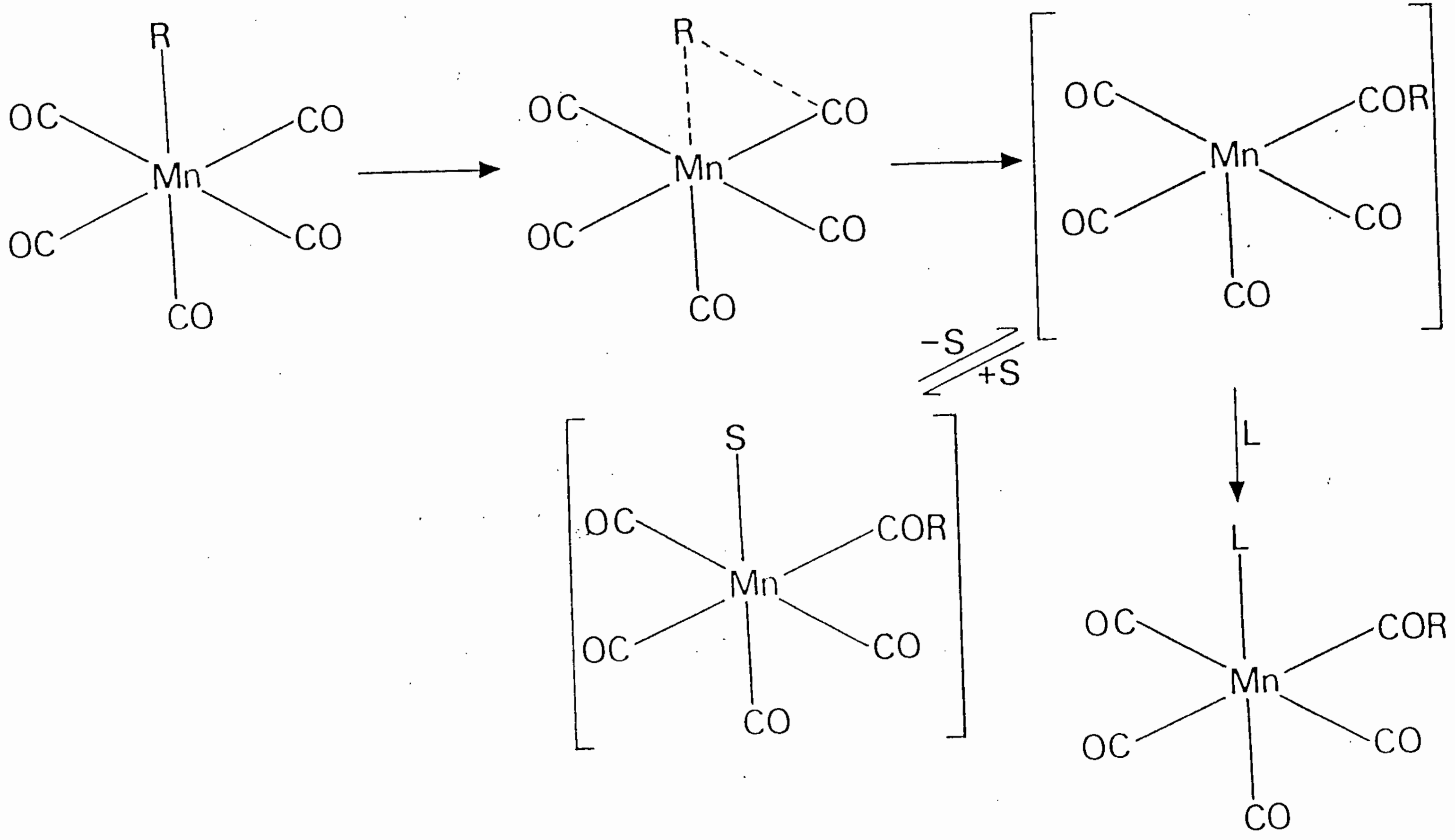


Fig. 6

The manganese-oxygen interaction is best described as $\sigma$-donation of the "$\pi$-type" lone pair orbital on the oxygen atom with vacant atomic orbitals on manganese. Although the $\eta^2$-interaction would be electronically favourable, the strain present in the metallacycle would serve to diminish any stabilization and thus the formation of a $\pi$- or $\eta^2$-acyl reactive intermediate would probably not be realized. It has also been calculated that the overlap match of fragment orbitals is significantly worse in the $\eta^2$- acyl species than in the square-based pyramidal intermediate [78]. However, a recent matrix isolation study by Horton-Mastin *et al.* [79] confirmed the square pyramidal structure. Thus, the two-step sequence ($k_1$ path) will proceed (*via* a 3—centred transition state) according to scheme 4.

Alkyl migration in $[Mn(R)(CO)_5]$ species is assumed to follow a concerted reaction pathway, *i.e.* concomitant bond breaking and bond forming [80]. Concerted reactions are characterized by low energies of activation [81] (low in that they are lower than the bond dissociation energies of the weakest bonds involved). Activation entropies are usually very small or negative, indicative of restricted motion resulting from the cyclic transition state [81]. Calderazzo and Cotton investigated the reaction of CO with $[Mn(CH_3)(CO)_5]$ and obtained an activation energy of 61.9 kJ. $mol^{-1}$ for the alkyl migration process [73]. This value is well below the reported bond dissociation energy of 184 kJ. $mol^{-1}$ for the manganese-methyl bond in $[Mn(CH_3)(CO)_5]$ [19], supporting a concerted mechanism, *i.e.* a 3-centred transition state.

The acyl compounds which are formed from the alkyl migration reaction initially adopt a *cis* geometry, but where the incoming ligand has a large steric profile they often isomerize to the *trans* form (see Fig. 7). This shows that the initial reaction is kinetically rather than thermodynamically controlled. A recent study, however,



Scheme 4 <u>Reaction of $RMn(CO)_5$ with L in a Two Step Sequence</u>
(S = Coordinating solvent)

reports an example where the incoming ligand initially enters *trans* to the acetyl group in a related [Mn(R)$(CO)_3(L_2)$] compound [82]. The isomerization process has been shown to occur *via* a dissociative intermolecular process, *i.e.* dissociation of L [83]. When L (in [Mn(COR)$(CO)_4$(L)]) is a very bulky group, the possibility of rotational isomerization also exists [84]. When the acyl compounds are decarbonylated, the alkyl products, [Mn(R)$(CO)_4$(L)], usually adopt a *cis* configuration.

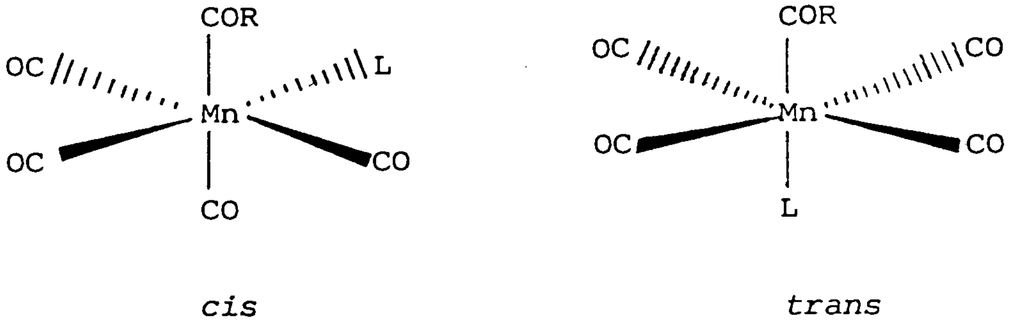


Fig. 7 *cis* and *trans* [Mn(COR)$(CO)_4$(L)]

## B. Effect of Solvent

In solvents of relatively high polarity, it has been intimated that a solvent molecule can coordinate to the coordinatively unsaturated intermediate, [Mn(COR)$(CO)_4$], to form a solvated hexacoordinate species (see Scheme 4), which effectively stabilizes the reactive intermediate [4,74,85]. A large, negative entropy of activation supports this suggestion [85]. It has been suggested that the cleavage of the manganese-alkyl bond is assisted by the solvent which then enters the coordination sphere of the metal. In a number of instances the reaction rate has been found to increase with an increase in polarity of the solvent, which was termed "solvent assistance". The direct influence of the solvent was investigated for the reaction of $PPhMe_2$ with $[CpMo(CH_3)(CO)_3]$[86]. A series of $\alpha$-substituted tetrahydrofurans was used and the reaction rate was found to increase in the order $THF > 2\text{-}CH_3THF >> 2,5\text{-}(CH_3)_2THF$. This series of solvents was used as they have similar dielectric constants, but as a result of the steric constraints of the $\alpha$-substituents, they have significantly different electron-donating abilities. Thus the acceleration of the alkyl migration reaction by polar solvents depends on the electron-donating ability of the solvent, rather than its dielectric constant. Several very elegant studies on the effect of the solvent on alkyl migration have been reported by Cotton and co-workers [74,87-89] who found electron-donating solvents to increase the rate of alkyl migration in substitued benzyl manganesepentacarbonyl compounds, $[Mn(CH_2C_6H_{5-n}X_n)(CO)_5]$ by stabilization of the coordinatively unsatured intermediate (see Scheme 4). In some instances, the solvent-coordinated intermediate was stable enough to be detected [74] and rate studies on the formation of this intermediate were performed. The following trend was observed : $DMSO > DMF > py > CH_3CN$. These results suggest that direct attack of the solvent at the metal centre is occurring as migration of the alkyl group to a carbonyl carbon atom is taking place [74]. In addition to influencing the reactivity, the coordinating ability of the solvent can affect the mechanism of alkyl migration. If a poorly co-ordinating solvent is used in conjunction with a good nucleophile, L, the $k_1$ path (see Scheme 3) can be suppressed and the $k_2$ path may dominate, dependent, of course, on the nature of the alkyl group, R. $[Mn(C_2H_5)(CO)_5]$ "decomposes" to $[Mn(COC_2H_5)(CO)_5]$ [13] in the absence of any solvent or external nucleophile, demonstrating that the migration of the ethyl group to a carbonyl carbon atom is an extremely facile process.

## C. Effect of Entering Ligand, L

This effect is very closely related to the nature of the solvent. If the solvent lacks coordinating ability, then alkyl migration proceeds *via* attack of L upon the alkyl compound ($k_2$ path, Scheme 3). However, in a coordinating solvent there will be competition between the reaction of the intermediate $[Mn(COR)(CO)_4(S)]$ with L to give the acyl product, $[Mn(COR)(CO)_4(L)]$ and its reversion to the alkyl, $[Mn(R)(CO)_5]$. If L is a strong enough nucleophile to capture the intermediate (solvated or not) then the $k_1$ path will prevail, alone or in conjunction with the $k_2$ path. Very little quantitative data is available on the effect of L, although a recent study was made by Cotton *et al.* [87] who reacted $[Mn(CH_2C_6H_5)(CO)_5]$ with a series of phosphines and found the rate of alkyl migration to increase with decrease in the Tolman electronic parameter, $\nu$ , of the phosphine [90] (*i.e.* with increase in electron donation). However, it is known that alkyl migration reactions of $[Mn(CH_3)(CO)_5]$ exhibit very little sensitivity towards L [85].

## D. Effect of Alkyl Group, R

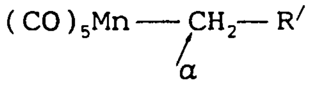
Although both the solvent and incoming nucleophile can affect the rate of alkyl migration considerably, the nature of R, the alkyl group, has a far greater influence. Both steric and electronic factors are important in determining the magnitude of this effect. Early studies have indicated the following trends in reactivity with different R groups: n-Pr>Et>Ph>$CH_3$>$CH_2F$>>$CF_3$ [17,84]. Somewhat more recent studies have substantiated these trends, and added to the list of alkyl groups : n-Pr>Et>$CH_2C_6H_{11}$>$CH_3CH_2OCH_3$>$CH_2$-$C_6H_5$>$CH_2CO_2H$ [14] and Et>>$CH_3$>$CH_2$Ph>Ph [17]. Thus, the rate of alkyl migration increases as the electron donating ability of the alkyl group in [Mn(R)(CO)$_5$] increases. It has been shown that [Mn(CH$_2$I)(CO)$_5$], [Mn(SiMe$_3$)(CO)$_5$] and [Mn(SiPh$_3$)(CO)$_5$] do not undergo the CO insertion/alkyl migration reaction [91-93]. These trends can be, and have been correlated with the Taft $\sigma^*$ inductive parameter of $R'$ in [Mn(CH$_2$R$'$)(CO)$_5$] [14]. The nature of the alkyl group was also found to have a significant effect on the alkyl migration reactions of a homologous series of n-alkyl manganesepentacarbonyl compounds [Mn(R)(CO)$_5$)] where (R = CH$_3$ to n-C$_9$H$_{19}$; n-C$_{11}$H$_{23}$ to n-C$_{18}$H$_{37}$) [94].

When changing the nature of R in [Mn(R)(CO)$_5$], the $\sigma$ or $\pi$ interactions (of R with Mn) may change. The $\sigma$ effect can be modelled by changing the energy of the donor orbital: the more electronegative R is, the lower its energy will be and thus the poorer a $\sigma$ donor it will be [95]. Thus electron withdrawing groups have higher calculated energies of activation and should retard, or even prevent, the migration process whereas electron donating groups have the opposite effect [10,14,96]. The order of the activation energies parallels the experimentally known reaction rates for the [Mn(R)(CO)$_5$] system [14,17,74,84]. In order to measure the migratory aptitudes of different alkyl groups onto a carbonyl group, Connor *et al.* obtained the following values of $\Delta$H for the reaction of CO with [Mn(R)(CO)$_5$] at 298K [97]:

| R | $\Delta$H (kJ mol$^{-1}$) |
|---|---|
| CH$_3$ | -(54±8) |
| C$_6$H$_5$ | -(63±8) |
| CF$_3$ | -(12±7) |

Table 2 $\Delta$H Values for the reaction of CO with [Mn(R)(CO)$_5$]

These results demonstrate conclusively that alkyl migration in $[Mn(CH_3)(CO)_5]$ is much more facile and exothermic than in $[Mn(CF_3)(CO)_5]$. Molecular orbital studies intimate that the decrease in rate of alkyl migration from $R = CH_3$ to $R = CF_3$ is not in fact connected with any strengthening of the manganese-carbon (alkyl) bond, but rather with a change in charge distribution on the carbon atom [98]. This will then reduce the liklihood of nucleophilic attack. The above studies also show that the negative charge on the α-carbon atom of the alkyl group (Fig. 8) decreases in the order $R' = CH_3 > H > F$



$$(CO)_5Mn\text{---}\underset{\alpha}{CH_2}\text{---}R'$$

**Fig. 8**

Axe and Marynick [96] gave a slightly different interpretation of the effect of the alkyl group, using acid-base considerations. The $Mn(CO)_5$ moiety possesses two different acidic sites (in the Lewis sense) namely, the transition metal centre and a carbonyl carbon atom. These correspond to a hybrid of metal 4d, 4s and 4p atomic orbitals and a carbonyl 2π* antibonding orbital, respectively. The antibonding orbital of the carbonyl group is of higher energy than the vacant metal hybrid orbital. R groups which are weakly basic, *e.g.* $CF_3$, have a stable lone pair orbital and will interact unfavourably with the higher energy CO 2π* orbital. More basic R groups have a more energetic lone pair orbital which is closer in energy to the vacant 2π* orbital and will, therefore, interact better than weakly basic alkyl groups. Indirect quantitative evidence for this acid-base relationship is found in the degrees of bonding and overlap populations in $[Mn(R)(CO)_5]$ both of which increase with increasing basicity of R [96].

### (i) Reaction of $[Mn(R)(CO)_5]$ with Tertiary Phosphines and Tertiary Phosphine Derivatives

Reactions of $[Mn(R)(CO)_5]$ compounds with tertiary phosphine ligands, $PR_3$, are extensive and range from the very early studies of Mawby *et al.* [99], Noack *et al.* [83] and Bannister *et al.* [100] to the far more recent studies of Mapolie and Moss [25] and Cotton *et al.* [87]. In the first study reported on this type of reaction, in 1964, Mawby *et al.* [99] reacted $[Mn(CH_3)(CO)_5]$ in THF at room temperature with $PPh_3$ and $P(OPh)_3$. The products of the reaction were the tertiary phosphine substituted acyl complexes, *cis*-$[Mn(COCH_3)(CO)_4(PR_3)]$. Although the $P(OPh)_3$ adduct was not isolated, it was claimed to have been detected spectroscopically. Similar results were subsequently obtained by other workers in the field [100-104]. These later results also demonstrated the presence of the *trans* isomer of the phosphine-substituted acyl products (which were isolated), formed by isomerization of the initial, kinetically favoured *cis* product. Noack *et al.* [83] made a very elegant study of the isomerization process. Bannister *et al.* [100] conducted a rather extensive study on the reaction of $[Mn(R)(CO)_5]$ (R = $CH_3$, $C_6H_5$) with a range of nucleophiles and obtained the results shown in Tables 3 and 4.

| Ligand, L | Product |
|---|---|
| $PPh_3$ | *cis/trans* - $[Mn(COCH_3)(CO)_4(L)]$ |
| $AsPh_3$ | *cis/trans* - $[Mn(COCH_3)(CO)_4(L)]$ |
| $SbPh_3$ | *cis* - $[Mn(COCH_3)(CO)_4(L)]$ |
| $P(OPh)_2Me$ | *cis* - $[Mn(CH_3)(CO)_3(L)_2]$ |
| $P(OPh)_3$ | *trans* - $[Mn(COCH_3)(CO)_3(L)_2]$ |

Table 3 Reaction of $[Mn(CH_3)(CO)_5]$ with Ligands

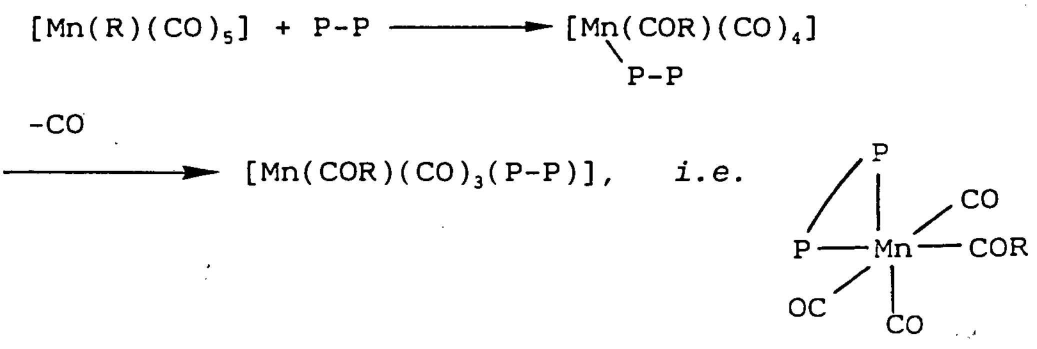
| Ligand, L | Product |
|---|---|
| $PPh_3$ | *cis* - $[Mn(C_6H_5)(CO)_4(L)]$ |
| $AsPh_3$ | *cis* - $[Mn(C_6H_5)(CO)_4(L)]$ |
| $SbPh_3$ | *cis* - $[Mn(C_6H_5)(CO)_4(L)]$ |
| $P(OMe)_3$ | *trans* - $[Mn(C_6H_5)(CO)_3(L)_2]$ |
| $P(OPh)_3$ | *trans*-$[Mn(C_6H_5)(CO)_3(L)_2]$ or<br>*trans* - $[Mn(COC_6H_5)(CO)_3(L)_2]^a$ |
| $P(OPh)_2Me$ | *trans* - $[Mn(C_6H_5)(CO)_3(L)_2]$ or<br>*trans* - $[Mn(COC_6H_5)(CO)_3(L)_2]^a$ |

Table 4 Reaction of $[Mn(C_6H_5)(CO)_5]$ with Ligands

([a] The authors did not determine which product was actually formed).

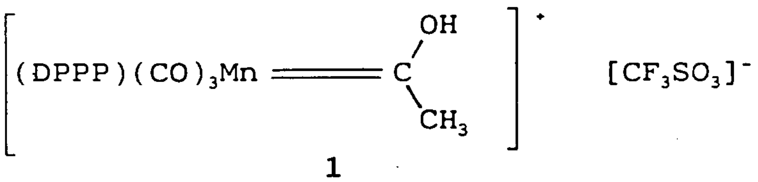
Thus, the reaction of $[Mn(CH_3)(CO)_5]$ and $[Mn(C_6H_5)(CO)_5]$ with phosphites gave disubstituted products. Similar results were obtained by subsequent studies on this type of reaction [24,61,62,105,106].

When $[Mn(R)(CO)_5]$ compounds are reacted with chelating ditertiary phosphines (denoted P-P), mono-substituted products are formed initially (Scheme 5) which then, in a second step, undergo an intramolecular substitution reaction with elimination of CO to give a chelate complex [107].



Scheme 5 Reaction of $[Mn(R)(CO)_5]$ with a Ditertiary Phosphine

This chelate complex may subsequently undergo decarbonylation. Thus, $[Mn(CH_3)(CO)_5]$ will react with $Ph_2P(CH_2)_nPPh_2$ (n = 1,2 or 3) (in a 2:1 molar ratio) to give *fac*-$[Mn(COCH_3)(CO)_3(diphos)]$ [100,107-109], which can decarbonylate to the alkyls of the same stereochemistry. A higher ratio of $[Mn(CH_3)(CO)_5]$ to $Ph_2PCH_2CH_2PPh_2$ results in the formation of $[\{Mn(COCH_3)(CO)_4\}_2\{Ph_2PCH_2CH_2PPh_2\}]$ [100,108] An exception to the above general process is the reaction of $[Mn(CH_3)(CO)_5]$ with 1,3-bis(diphenylphosphino)propane ($Ph_2P(CH_2)_3PPh_2$) in the presence of triflic acid, which gave *fac*-(1,3-bis(diphenylphosphino)propane)(methylhydroxycarbene)tricarbonyl manganese(I) triflate [110] *i.e.*



$$\left[(DPPP)(CO)_3Mn{=}C(OH)(CH_3)\right]^+ \quad [CF_3SO_3]^-$$

1

(where DPPP = bis(diphenylphosphino)propane)

The reaction of $[Mn(CH_3)(CO)_5]$ with chelating tridentate phosphorus ligands (denoted P-P-P) gives $[Mn(COCH_3)(CO)_2(P\text{-}P\text{-}P)]$ species (which can decarbonylate to the corresponding alkyl species)[111,112]. Equation 13 represents an example of this type of reaction [110].

$$[Mn(CH_3)(CO)_5] + (Me_2PCH_2CH_2)_2PPh \longrightarrow [Mn(COCH_3)(CO)_2\{(Me_2PCH_2CH_2)_2PPh\}] \quad (13)$$

**2**

Two of the most recent studies on reactions of $[Mn(R)(CO)_5]$ compounds with tertiary phosphines have been those of

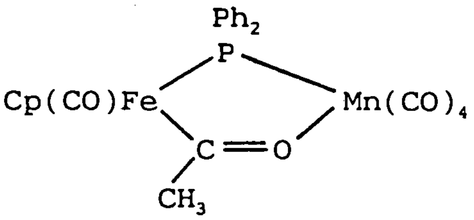
(a) Mapolie and Moss [25] who reacted the binuclear complexes $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ with $PR_3$ to give *cis, cis*-$[(PR_3)(CO)_4MnCO(CH_2)_nCOMn(CO)_4(PR_3)]$ ($n = 4-6$; $PR_3 = PPh_3$, $PPh_2Me$, $PPhMe_2$ and $PMe_3$), and

(b) Cotton *et al.* [87] who reacted a series of substituted benzyl manganesepentacarbonyl compounds with tertiary phosphines to give the products *cis*-$[Mn(COCH_2C_6H_{5-n}X_n)(CO)_4(PR_3)]$ (X = H, 2-Me, 2,4,6-$Me_3$, 2,4,6-i-$Pr_3$, 2-Cl, 3-Cl, 4-Cl; $PR_3 = PPh_3$, $PCy_3$). The difference in reactivity between $PPh_3$ and the much more reactive $PCy_3$ decreased as the size of the alkyl substituent on the benzene ring increased.

However, not all reactions of $[Mn(R)(CO)_5]$ compounds with phosphines give the expected products, thus mention should be made of three somewhat unusual reactions, all involving $[Mn(CH_3)(CO)_5]$ and tertiary phosphine derivatives:

(a) Rosen *et al.* [113] reacted $[Mn(CH_3)(CO)_5]$ with $[CpFe(CO)_2(PPh_2)]$ and isolated a heterobimetallic acetyl bridged complex $[CpFe(CO)(\mu\text{-}CO(CH_3))(\mu\text{-}PPh_2)\text{-}Mn(CO)_4]$) as the product (equation 14).

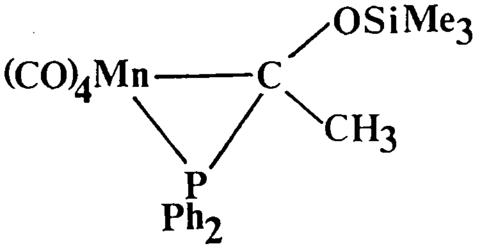
$$[Mn(CH_3)(CO)_5] + [CpFe(CO)_2(PPh_2)] \xrightarrow[22\,^{\circ}C]{THF}$$



(14)

**3**

(b) Vaughn *et al.* [114] reacted $[Mn(CH_3)(CO)_5]$ with $PPh_2(SiMe_3)$ to form the novel ylide complex, **4**



**4**

(c) Ressner *et al.* [115] reacted $[Mn(CH_3)(CO)_5]$ with $PPh_2CH_2Si(CH_3)_2CH_2PPh_2$ to give $[Mn(CO)_3\{CH_2Si(CH_3)_2\text{-}(CH_2PPh_2)_2\}]$ (**5**), formed by intramolecular activation of a C-H bond in a methylsilyl group by manganese.

(ii) Reaction of $[Mn(R)(CO)_5]$ with Carbon Monoxide

Reactions of $[Mn(R)(CO)_5]$ compounds with carbon monoxide have been studied extensively and in this case, only one product, *i.e.* the acyl species $[Mn(COR)(CO)_5]$ is formed (equation 15).

$$[Mn(R)(CO)_5] + CO \longrightarrow [Mn(COR)(CO)_5] \qquad (15)$$

Early studies [75,76] concentrated on the reaction of $[Mn(CH_3)(CO)_5]$ with labelled CO ($^{14}CO$ and $^{13}CO$) in order to probe the mechanism and stereochemistry of the alkyl migration reaction. It was these two studies which were instrumental in proving conclusively that the carbonylation reaction takes place *via* alkyl migration rather than by direct CO insertion. Subsequent studies involved the measurements of carbonylation rates (which will be discussed in detail in Chapter 3) in order to determine thermodynamic parameters (*e.g.* activation energy for the alkyl migration process) [73,116]. The variation in rate with change (steric and electronic) in R [14,17,76] for the reaction in equation 15 was investigated. The following order was found:

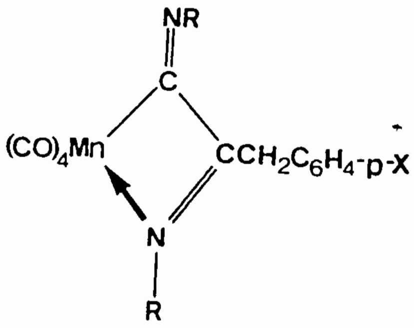
R = n-Pr>Et>$CH_2C_6H_{11}$>$C_6H_5$>$CH_3$>$CH_2OCH_3$>$CH_2C_6H_5$>$CH_2CO_2H$, and
R = $CH_3$>$CH_2F$>$CF_3$

The carbonylation of [Mn($CH_3$)(CO)$_5$] at high pressure (320 atm CO, 67°C in tetradecane) was reported [117]; the only product isolated was [Mn($COCH_3$)(CO)$_5$]. In another study, [Mn($CH_3$)(CO)$_5$] was reacted with CO (at 70°C) to give [Mn($COCH_3$)(CO)$_5$] with a rate constant, $k = 1.9 \times 10^{-5} s^{-1}$. This was compared to the rates for the reactions of *cis*-[Mn($CH_3$)(CO)$_4$($PR_3$)] with CO to give *cis*-[Mn($COCH_3$)(CO)$_4$($PR_3$)] ($PR_3$ = P(OPh)$_3$, $k = 3.6 \times 10^{-5} s^{-1}$; $PR_3$ = P(OMe)$_3$, $k = 2.3 \times 10^{-5} s^{-1}$). The similarity in these three rate constants implies a very small ligand effect, which was taken to indicate a transition state with very little unsaturation [116]. More recent studies [24,25] involved the carbonylation of [(CO)$_5$Mn($CH_2$)$_n$Mn(CO)$_5$] (under 1 atm. CO at room temperature) to give [(CO)$_5$MnCO($CH_2$)$_n$COMn(CO)$_5$](n = 4-6).

### (iii) Reaction of [Mn(R)(CO)$_5$] with Isocyanides and Amines

Another fairly common and well-documented reaction of [Mn(R)(CO)$_5$] compounds is that with alkyl isocyanides, RNC (which are isoelectronic with CO) or alkyl amines, $RNH_2$.

The usual product is the isocyanide or amine substitued acyl species, $[Mn(COR)(CO)_4(L)]$ (formed by alkyl migration). The first study reported on this type of reaction was that of Keblys and Filbey [118] who reacted $[Mn(R)(CO)_5]$ (R = $CH_3$,$C_6H_5$) with $NH_3$ and aliphatic and aromatic amines (($C_6H_{11}$)$NH_2$,$Me_2NH$,($C_6H_5$)$NH_2$) to give *cis*-$[Mn(COR)(CO)_4$-(amine)]. The subsequent study of Mawby *et al.* [99], using $[Mn(CH_3)(CO)_5]$ gave the same results (except for the reaction with n-methylcyclohexylamine, which did not go to completion). They also made the observation that the reaction was solvent-dependent. Thus, solvent-assisted migration of the methyl group occured in polar solvents, *e.g.* in nitromethane the reaction was first-order in $[Mn(CH_3)(CO)_5]$, whereas in hexane it was first-order in $[Mn(CH_3)(CO)_5]$ and in amine. Kraihanzel and Maples [104] also repeated these results and made the additional observation that the amine-substitued acyl products, $[Mn(COR)(CO)_4$(amine)] were difficult to decarbonylate. Kuty and Alexander [119] reported the reactions of $[Mn(R)(CO)_5]$ (R = $CH_3$,$CH_2C_6H_5$ and p-$NO_2C_6H_4CH_2$) with alkylated isocyanides, R$'$NC (R$'$ = $CH_3$, t-$C_4H_9$, n-$C_4H_9$ and $C_6H_{11}$) to give the acyl isocyanide adduct $[Mn(COR)(CO)_4(CNR')]$ (a mixture of *cis* and *trans*), except for $[Mn(p\text{-}NO_2C_6H_4CH_2)(CO)_5]$, which was observed to not undergo any reaction. A more recent study by Motz *et al.* [120] involved the very interesting reaction of $[Mn(p\text{-}XC_6H_4CH_2)(CO)_5]$ (X = Cl,$OCH_3$) with p-tolylisocyanide (p-$CH_3C_6H_4CH_2NC$) in the presence of PdO to give the double isocyanide-inserted products $[Mn\{C(=N\text{-}p\text{-}tolyl)C(=N\text{-}p\text{-}tolyl)CH_2C_6H_4\text{-}p\text{-}X\}(CO)_4]$, 6 (see Fig. 10) and also $[Mn\{C(=CH(C_6H_4\text{-}p\text{-}Cl))N(p\text{-}tolyl)C(NH\text{-}p\text{-}tolyl)\}(CO)_4]$, 7, for X = Cl (which is the product of intramolecular attack by an imino nitrogen atom on a coordinated p-tolyl isocyanide).



(R = p-tolyl; X = Cl,OMe)

Figure 9 Structure of 5

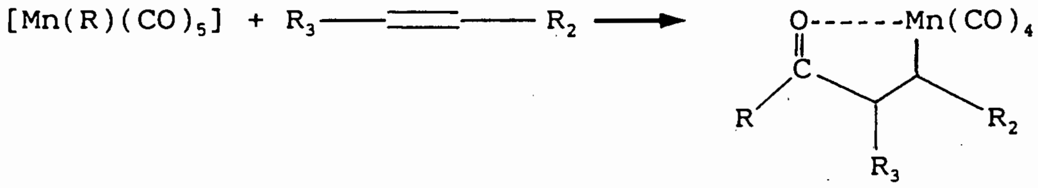
(iv) Reaction of $[Mn(R)(CO)_5]$ With Other Neutral Nucleophiles

Besides the numerous studies already mentioned on the reactions of $[Mn(R)(CO)_5]$ with phosphines, amines, isocyanides and carbon monoxide, there have been extensive investigations into the reactions of $[Mn(R)(CO)_5]$ compounds with other neutral donor ligands, a brief description of which now follows.

(a) Reaction with Alkenes and Alkynes

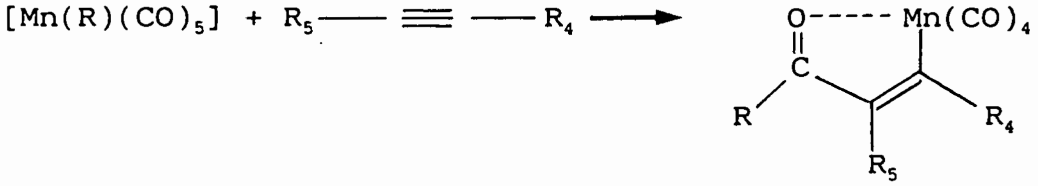
This usually results in alkyl migration of R in $[Mn(R)(CO)_5]$ and subsequent insertion of the alkene or alkyne *via* addition of the acyl species across the olefinic (or alkynyl) linkage.

An extensive study of this general reaction was executed by DeShong *et al.* [121], who reacted $[Mn(R)(CO)_5]$(R = $CH_3$,$CH_2Ph$,CH=$CHCH_3$) with a variety of substituted alkenes and alkynes to give substituted manganacycles (the unsymmetrical alkenes and alkynes exhibited a high degree of regioselectivity).



**8** (16)

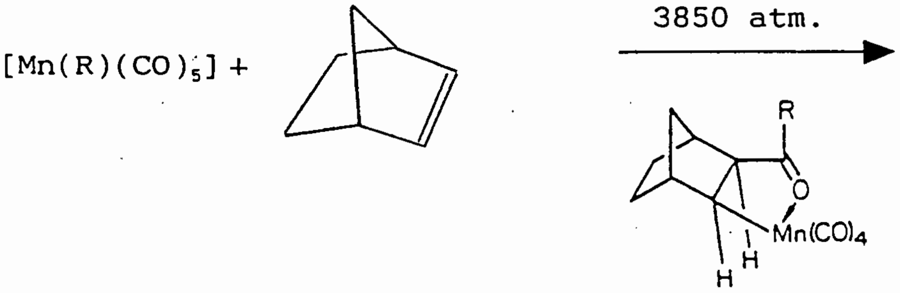
and



**9** (17)

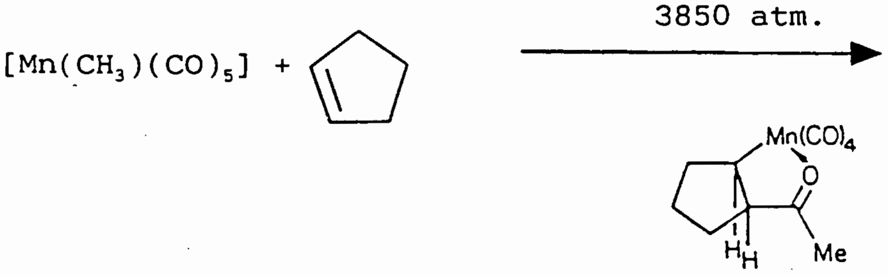
These manganacycles are valuable intermediates in the preparation of organic compounds, *e.g.* the adducts obtained from alkynes were demetallated under acidic conditions to give E-enones, and photochemical demetallation of the alkene-derived manganacycles gave ketones.

The reaction of $[Mn(R)(CO)_5](R = CH_3, CH_2Ph)$ with norbornylene occurs *via* sequential insertion of CO and the olefin [122].



**10** (18)

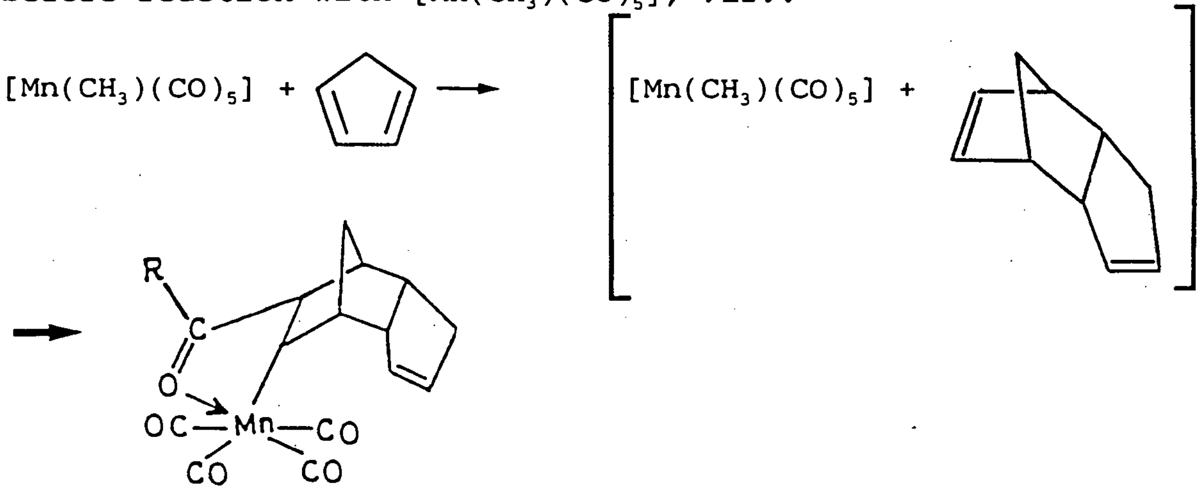
The reaction of $[Mn(CH_3)(CO)_5]$ with cyclopentene [123] proceeds in a similar manner.



(19)

**11**

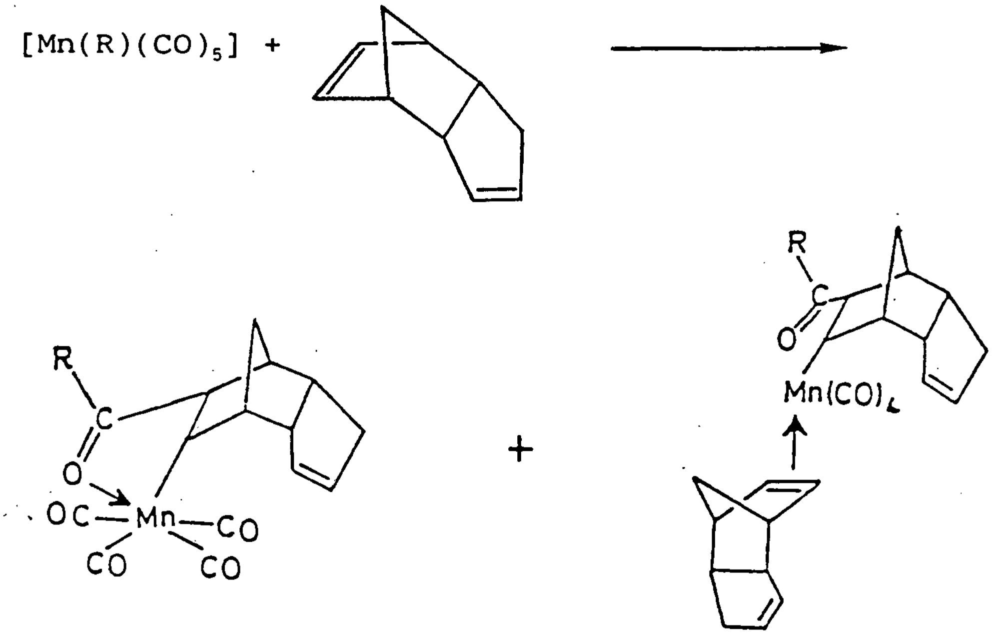
Booth *et al.* [123] carried out the reaction of $[Mn(CH_3)(CO)_5]$ with cyclopentadiene and found the reaction to be so slow that dimerization of cyclopentadiene occurred before reaction with $[Mn(CH_3)(CO)_5]$, *viz.*:



12 (20)

$(R = CH_3)$

The reaction of $[Mn(R)(CO)_5]$ $(R = CH_3, Ph)$ with dicyclopentadiene directly, however, also gave a 1:2 adduct, *viz.*:



12 13 (21)

The reaction of $[Mn(CH_3)(CO)_5]$ with norbornadiene which gave a mixture of the 1:1 and 1:2 adducts was also reported in this study.

Other studies with different olefins and alkynes gave the same type of products [124-127].

### (b) Reaction with Synthesis Gas *i.e.* $CO/H_2$

The conversion of carbon monoxide and hydrogen to organic chemicals by transition metal complexes is the goal of much current research, including applications for the field of catalysis and model or stoichiometric studies. These may result in an improved understanding of metal catalysts and allow development of catalytic systems which will display greater selectivity and activity towards synthesis gas conversion.

The first report on the reaction of synthesis gas with alkyl manganesepentacarbonyl species can be considered to be that of King *et al.* in 1978 [117]. Although they did not use syngas (an equimolar mixture of CO and $H_2$) they reacted $[Mn(CH_3)(CO)_5]$ with CO (320 atm., 67°C), resulting in the formation of the acyl compound, $[Mn(COCH_3)(CO)_5]$. They then reacted this with $H_2$ (313 atm., 95°C) (after releasing the CO pressure) to yield $[Mn_2(CO)_{10}]$ and acetaldehyde (a very small amount of formaldehyde was also detected).

In 1979 Dombek [72] investigated the reactions of $[Mn(R)(CO)_5](R = H, CH_3, CH_2OCH_2CH_3, CH_2OC(O)CMe_3)$ with synthesis gas (6.79 atm. $H_2$, 2.04 atm. CO) in sulfolane at 75°C. Acetaldehyde was the only organic product from the reaction of $[Mn(CH_3)(CO)_5]$ with syngas, however, when $[Mn(CH_3)(CO)_5]$ was reacted with $H_2$ only (6.79 atm.), ethanol was the only organic product. A high yield of alcohol was also obtained from the reaction of $[Mn(CH_2OCH_2CH_3)(CO)_5]$ with $H_2$, indicating that the hydroxymethylation of the alkyl group with $H_2$ under pressure is a general process and the $\alpha$-oxygen atom does not have a great influence on the reaction . When this reaction, *i.e.* with $H_2$ only, was repeated with the addition of $CH_3CHO$, the aldehyde was catalytically hydrogenated to $CH_3CH_2OH$ by $[Mn(CH_3)(CO)_5]$. Dombek proposed that the reaction proceeded *via* a complexed aldehyde species, and the presence of CO inhibited the hydrogenation of this intermediate. Dombek accounted for the discrepancy between his work and King's previous observation that only the aldehyde, not the alcohol, was obtained from the reaction of $[Mn(COCH_3)(CO)_5]$ and $H_2$ under more forcing conditions by the proposal that the acyl complex may release CO upon reaction with $H_2$. Small amounts of CO may also have remained in solution from the formation, *in situ*, of the acyl complex from $[Mn(CH_3)(CO)_5]$ and CO which may inhibit the hydrogenation of the aldehyde to the alcohol.

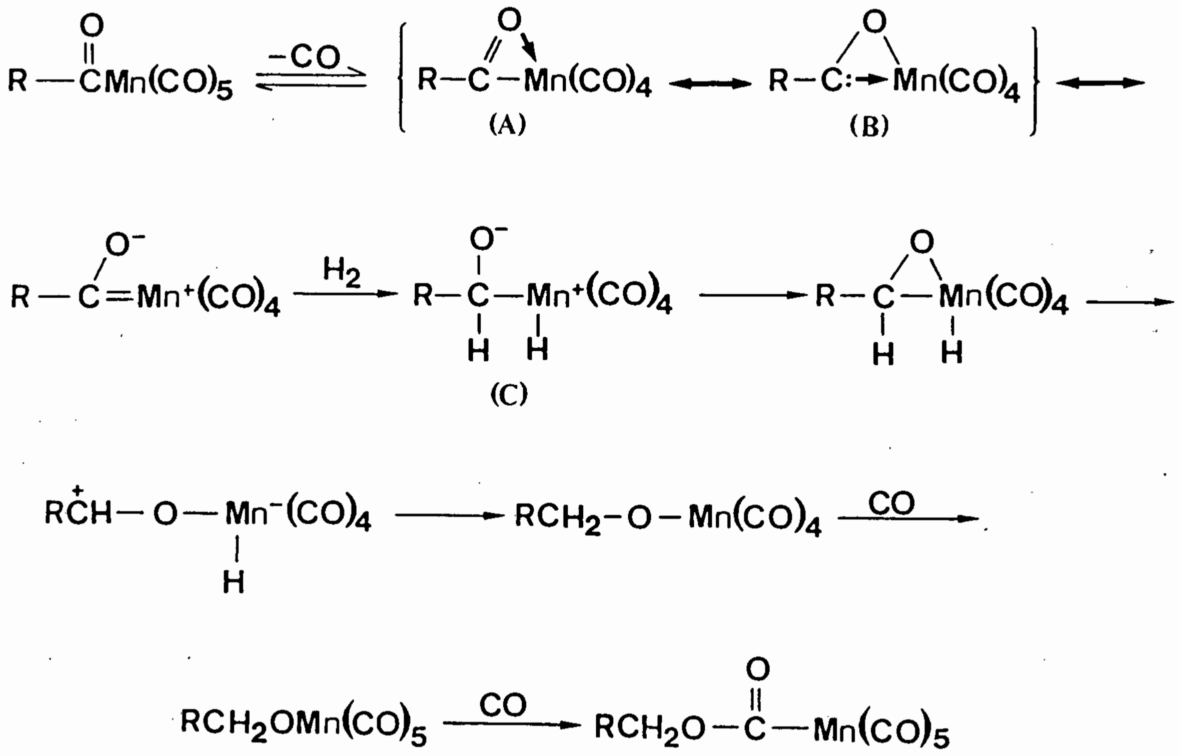
Freudenberger and Orchin, in 1982 [126] found that synthesis gas can become incorporated into $[Mn(COR)(CO)_5]$ compounds (in hexane) to give alkoxycarbonyl species:

$$[Mn(COR)(CO)_5] \xrightarrow[163\ \text{atm.}]{H_2/CO} \underset{\mathbf{14}}{[Mn\{OC(O)CH_2R\}(CO)_5]} \qquad (22)$$

(R = $CH_2Ph$, $CH_2CH_2Ph$)

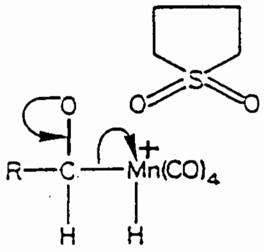
The reaction terminated at this point; the alkoxycarbonyl was inert towards further insertion of CO and $H_2$.

In contrast, the same reactions in sulfolane gave only the aldehydes, RCHO. The following mechanism for the formation of the alkoxycarbonyl species was proposed:



Scheme 6 Mechanism for the Formation of $[Mn\{OC(O)CH_2R\}(CO)_5]$ [126]

In sulfolane, intermediate (C) may be prevented from forming a manganese-oxygen bond by interaction with a molecule of solvent (structure D), collapsing instead to give the aldehyde.



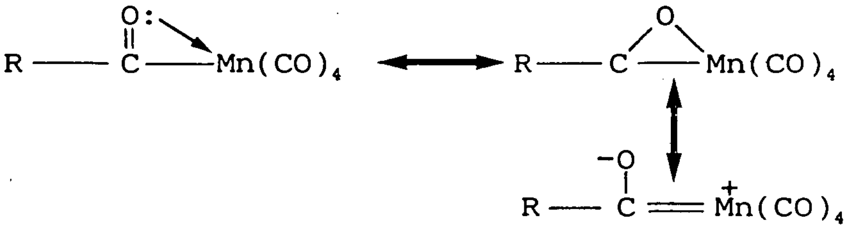
(D)

Fig. 10 Solvent Stabilized Intermediate in Sulfolane

Reaction of the corresponding alkyl species, $[Mn(R)(CO)_5]$ ($R = CH_2Ph$, $CH_2CH_2Ph$) gave similar results, *e.g.* reactions of $[Mn(CH_2Ph)(CO)_5]$ with $CO/H_2$ in sulfolane gave $PhCH_2CHO$ and reaction of $[Mn(CH_2CH_2Ph)(CO)_5]$ with $CO/H_2$ in hexane gave $[Mn\{OC(O)(CH_2)_3Ph\}(CO)_5]$. Reaction of $[Mn(CH_2Ph)CO)_5]$ with $H_2$ in sulfolane gave the alcohol, $PhCH_2CH_2OH$.

A later study by Orchin's group in 1986 [127] extended this reaction to a wider range of $[Mn(COR)(CO)_5]$ compounds ($R = CH_3$, $(CH_2)_4CH_3$, $p\text{-}CH_3C_6H_4$), including the binuclear compounds $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$ and $[(CO)_5MnCO(CH_2)_8COMn(CO)_5]$ and obtained similar results *i.e.* formation of an alkoxycarbonyl species in hydrocarbon solvents. They also carried out a labelling study with $[Mn(p\text{-}CH_3C_6H_4{}^{13}CO)(CO)_5]$ and found that the original acyl group in the reactant was reduced exclusively to the methylene group of the product.

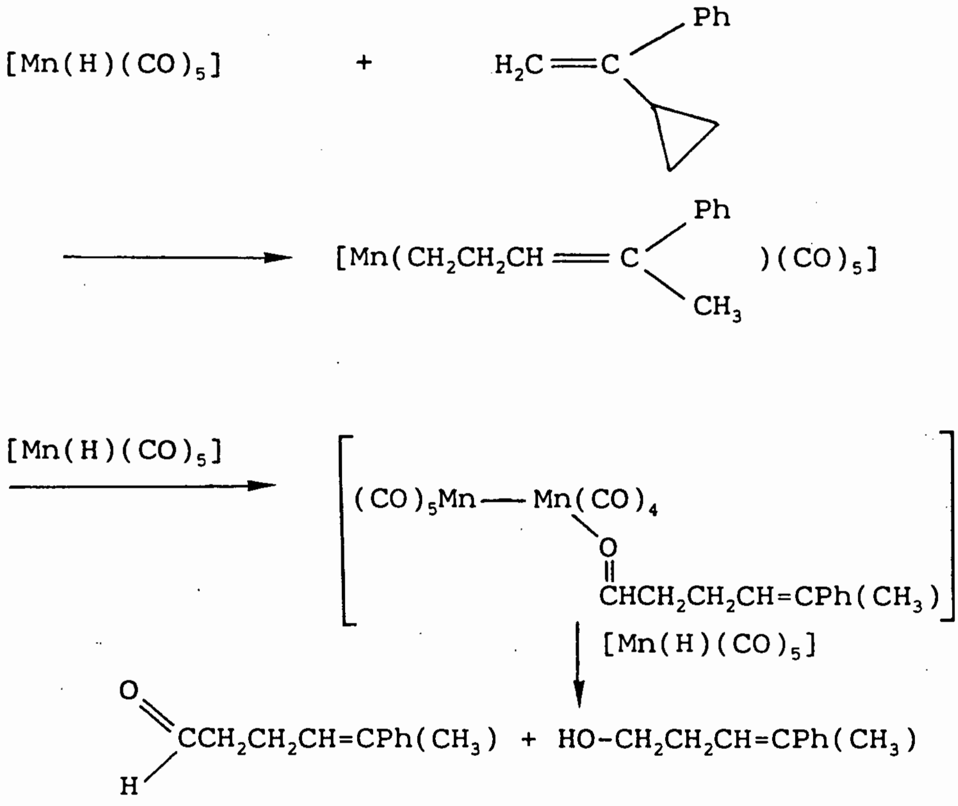
The formation of an acylmanganese tetracarbonyl species was proposed as an intermediate, which could adopt a carbenoid structure, as shown in Scheme 7 [127].



Scheme 7 Resonance Forms of the $[Mn(COR)(CO)_4]$ Intermediate

A more recent study is reported by Mapolie and Moss [25] who reacted $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$ with $CO/H_2$ (40 atm. at 70°C in THF) to give the diol, $HOCH_2(CH_2)_4CH_2OH$, as the only isolable organic product. Similar results were obtained from the reaction of synthesis gas with $[(CO)_5Mn(CH_2)_5Mn(CO)_5]$ and $[(CO)_5Mn(CH_2)_6Mn(CO)_5]$, *i.e.* diol formation [128]. The most recent study is that of Ahmed *et al.* [129]

who reacted benzyl manganesepentacarbonyl, $[Mn(CH_2Ph)(CO)_5]$, with PhC≡CPh in the presence of CO and $H_2$ and observed the formation of an aldehyde and $[Mn_2(CO)_{10}]$ *via* an unstable acyl intermediate. Mention should also be made of a very recent report by Bullock and Rappoli [130], which, although it does not involve reaction with synthesis gas, may have important implications in this field. Their study involved the use of $[Mn(H)(CO)_5]$ to induce ring-opening hydroformylation in cyclopropylstyrene (CPS) *via* an intermediate mononuclear alkyl manganesepentacarbonyl complex (Scheme 8).



$[Mn_2(CO)_{10}]$ was the organometallic product

Scheme 8 Reaction of $[Mn(H)(CO)_5]$ with CPS

Varying ratios of alcohol to aldehyde were formed, depending on reaction conditions. It was observed that CO inhibited the hydroformylation process, resulting instead in hydrogenated products. An analogous reaction using 2-

cyclopropylpropene instead of CPS produced higher amounts of alcohol compared to aldehyde. After a reaction time of 3 days, all the aldehyde had been consumed, giving a mixture of the alcohol complex $[Mn_2\{\eta^1\text{-}HO(CH_2)_3CH{=}CMe_2\}(CO)_9]$ and the free alcohol.

### (c) $SO_2$ Insertion

Unlike CO insertion, which occurs *via* alkyl migration, $SO_2$ insertion is believed to occur by the initial electrophilic attack of $SO_2$ at the $\alpha$-carbon atom of the alkyl group. The $[Mn(CO)_5]$ moiety is displaced as a cationic species onto an oxygen atom of the sulfinato group. However, these oxygen-bonded sulfinate complexes easily isomerize to the more thermodynamically stable S-sulfinato species. Thus,

$$[Mn(R)(CO)_5] + SO_2 \longrightarrow [Mn(SO_2R)(CO)_5] \qquad (23)$$

$(R = CH_3, C_2H_5, CH_2Ph, Ph;$ [131])

$SO_2$ cannot be eliminated from these complexes [132]. Reactions of $\eta^1$-allyl manganesepentacarbonyls, $[Mn(CH_2CH{=}CHR)(CO)_5]$ also give manganese-S-sufinates, however, these reactions occur with rearrangement of the allyl group [133], as shown in equation 24.

$$[Mn(CH_2CH{=}CHR)(CO)_5] + SO_2 \longrightarrow [Mn(SO_2CHRCH{=}CH_2)(CO)_5] \qquad (24)$$

The reaction of $SO_2$ with propargyl complexes, $[Mn(CH_2\text{-}C{\equiv}CR)(CO)_5]$ $(R = H, CH_3, C_6H_5)$ leads to a different type of product: cyclization of the propargyl group and $SO_2$ takes place [134].

$[Mn(SO_2R)(CO)_5]$ compounds can in turn react with a variety of ligands, resulting in carbonyl substitution [135], for example

$$[Mn(SO_2R)(CO)_5] + PPh_3 \longrightarrow [Mn(SO_2R)(CO)_4(PPh_3)] + CO \qquad (25)$$

## (d) Reaction with Other Organometallic Species

Reaction of $[Mn(CH_3)(CO)_5]$ with $\eta^5$-(cyclopentadienyl)-carbonyltriphenylphosphinerhodium and -iridium results in carbon-phosphorus bond cleavage in the triphenylphosphine complexes and isolation of bridged diphenylphosphido-heterodinuclear metal complexes [136].

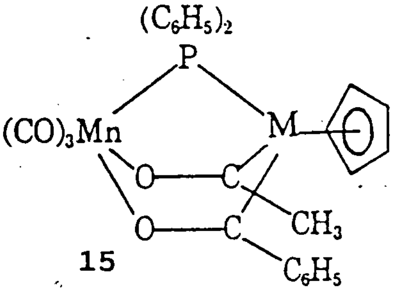
$$[Mn(CH_3)(CO)_5] + [CpM(CO)(PPh_3)] \longrightarrow$$

$$\underset{\mathbf{15}}{[CpM\text{-}\mu\text{-}\{C(C_6H_5)O\}\text{-}\mu\text{-}\{CMeO\}\text{-}\mu\text{-}\{PPh_2\}Mn(CO)_5]}$$

$$+ \underset{\mathbf{16}}{[Cp\{M\text{-}\mu\text{-}(PPh_2)\text{-}Mn(CO)_4\}]} \qquad (26)$$

$$(M = Ir, Rh)$$

The structures of the two products were proposed as follows:



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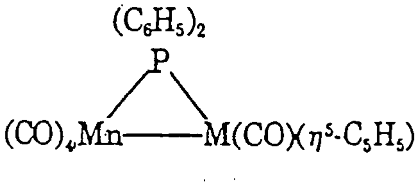
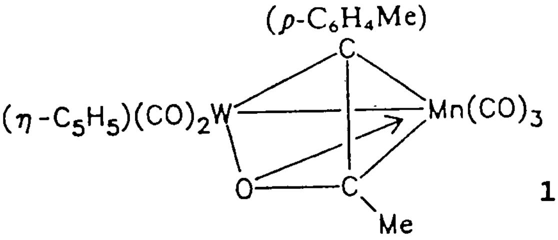


**16**

A recent study by Hart *et al.* [137] reported the reaction of $[Mn(CH_3)(CO)_5]$ with $[CpW\{\equiv C(p\text{-}MeC_6H_4)\}(CO)_2]$ to give the MnW complex **17** (in equation 27).

$$[Mn(CH_3)(CO)_5] + [CpW\{\equiv C(p\text{-}MeC_6H_4)\}(CO)_2] \longrightarrow$$



**17**

(27)

The structure of **17** was confirmed by X-ray analysis. The combination of the acyl and alkylidyne moieties took place through carbon-carbon bond coupling to give the bridging $C(p\text{-}MeC_6H_4)C(O)Me$ ligand which formally donates six electrons. The reaction of $[Mn(CH_3)(CO)_5]$ with acetylferrocene yields tetracarbonyl-2-(acetyl)ferrocenyl manganese [138].

### (e) Miscellaneous Reactions with Other Neutral Nucleophiles

There are numerous other reactions of $[Mn(R)(CO)_5]$ compounds with other neutral nucleophiles not mentioned so far which have been reported. However, these reactions do not really fall within the scope of this thesis and hence only a brief mention will be made of them. They include (1) the reaction of $[Mn(R)(CO)_5]$ with $CS_2$ to give dithiocarboxylate complexes [139,140]; (2) the reaction of $[Mn(CH_3)(CO)_5]$ with boranes to produce hydrocarbons [141]; (3) the reaction of $[Mn(CH_3)(CO)_5]$ with tetrafluoroethylene to give the fluorocarbon-inserted product [142]; (4) the reaction of $[Mn(CH_3)(CO)_5]$ with benzylmethylketone to give $[Mn(CO)_3\{\eta^5\text{-}CHC_6H_5CMeCH(CH_2C_6H_5)O\}]$ [143]; (5) the reaction of $[Mn(CH_2C{=}CPh)(CO)_5]$ with $N(CO)(SO_2Cl)$ resulted in cyclization of the propargyl group and insertion of $N(CO)(SO_2Cl)$ [144] and (6) the reaction of $[Mn(CH_3)(CO)_5]$ with N-sulfinylsulfonamides and sulfurbis(sulfonylimides) to give the inserted chelate products [145].

### 1.4.1.2 Reaction of $[Mn(R)(CO)_5]$ with Anionic Nucleophiles

This reaction most commonly proceeds *via* alkyl migration followed by nucleophilic attack at the now coordinatively unsaturated manganese atom. For example, the reaction of $[Mn(CH_3)(CO)_5]$ with lithium iodide is known [102] (equation 28).

$$[Mn(CH_3)(CO)_5] + LiI \longrightarrow [Mn(COCH_3)(I)(CO)_4]Li \qquad (28)$$

The same type of products result from the reaction of $[Mn(CH_3)(CO)_5]$ with $OCH_3^-$, $SCN^-$, $CN^-$ [102]. The reaction of $[Mn(CH_3)(CO)_5]$ with germyl lithium species gave anionic compounds (equation 29) which were either isolated as tetraethyl ammonium salts or alkylated to give carbene complexes [146].

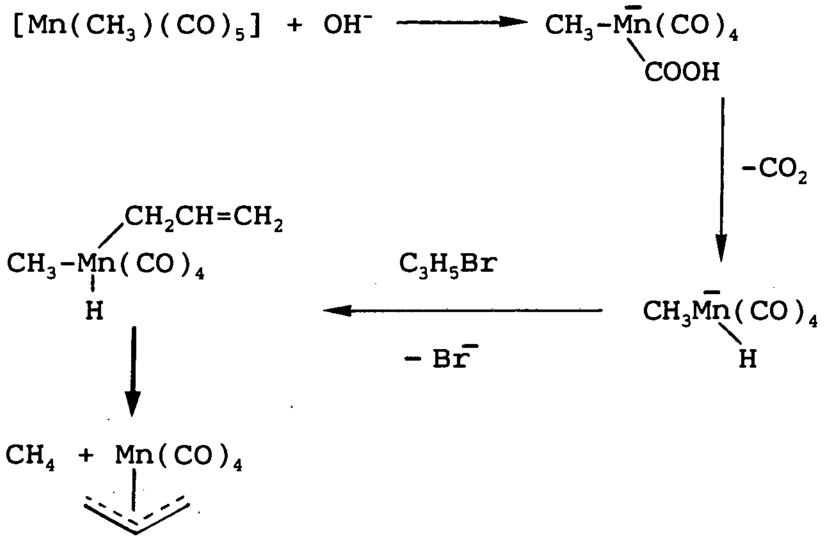
$$[Mn(CH_3)(CO)_5] + R_3GeLi \longrightarrow [Mn(COCH_3)(GeR_3)(CO)_4]Li \qquad (29)$$

($R_3$ = $Ph_3$ or Me,Ph,1-naphthyl)

The reaction of $[Mn(CH_3)(CO)_5]$ with $X^-$ (X = H or $OCH_3$) was investigated (equation 30) with a view to protonating the expected acyl anionic species. However, the isolated product was a trinuclear hydride, not a carbene complex [147].

$$[Mn(CH_3)(CO)_5] + X^- \longrightarrow [Mn_3H_3(CO)_{12}] \qquad (30)$$

The reaction of $[Mn(CH_3)(CO)_5]$ with the hydroxide ion, followed by allyl bromide led to the formation of $[Mn(\eta^3\text{-}C_3H_5)(CO)_4]$ and reductive elimination of $CH_4$ [148] as shown in Scheme 9.



Scheme 9 Reaction of $[Mn(CH_3)(CO)_5]$ with $OH^-$ and $C_3H_5Br$

The reaction of $[Mn(CH_3)(CO)_5]$ with $X^-$($X$ = Cl,Br or I) leads to the formation of halogenoanions which can be protonated to give hydroxycarbenes [150]:

$$\begin{tikzcd}[Mn(CH_3)(CO)_5] + X^- \arrow[r] & [Mn(COCH_3)(X)(CO)_4]^- \arrow[d, "H_3PO_4"] \\ & \textit{cis}\text{-}[Mn\{C(OH)CH_3\}(X)(CO)_4]\end{tikzcd} \qquad (31)$$

Reaction of $[Mn(CH_3)(CO)_5]$ with either manganese- or rheniumpentacarbonyl anions followed by $CH_3OSO_2F$ gives bimetallic carbene complexes $[(CO)_5MMn\{C(OCH_3)CH_3\}(CO)_4]$ (M = Mn,Re) [70]. The reaction of $[Mn(CH_3)(CO)_5]$ with $Ph_3CBF_4$ gives the species $[Mn(FBF_3)(CO)_5]$, which can subsequently be converted to the binuclear manganese complex $[(CO)_5MnCH_2CH_2Mn(CO)_5]$ [23].

A recent study by Wang and Atwood [149] involved the reaction of $[Mn(R)(CO)_5]$ (R = $CH_3$,$CH_2Ph$,Ph) with $[CpFe(CO)_2]^-$ The reaction resulted in transfer of R to $[CpFe(CO)_2]^-$ and generation of $[Mn(CO)_5]^-$. The reactions were found to be first order in $[CpFe(CO)_2]^-$ and in $[Mn(R)(CO)_5]$. A dependence on R was observed: $CH_2Ph>CH_3>Ph$; this is consistent with a nucleophilic attack mechanism.

### 1.4.1.3 Reaction of $[Mn(R)(CO)_5]$ with Cationic Species

This type of reaction usually results in cleavage of the manganese-alkyl carbon bond. Thus, the reaction of $[Mn(CH_3)(CO)_5]$ with sulfuric or hydrochloric acid produces methane [151] (equation 32).

$$[Mn(CH_3)(CO)_5] + HA \longrightarrow [Mn(A)(CO)_5] + CH_4 \qquad (32)$$

(HA = $H_2SO_4$,HCl)

The reaction is believed to occur *via* oxidative addition of the acid followed by reductive elimination of $CH_4$ [151].

A study by Motz *et al.* [12] involved reacting a variety of $[Mn(R)(CO)_5]$ compounds with acids ($CF_3SO_3H$ or $HBF_4$) to give the expected cleavage products (equation 33).

$$[Mn(R)(CO)_5] + HA \longrightarrow [Mn(A)(CO)_5] + RH \qquad (33)$$

The rate of manganese-alkyl carbon bond cleavage was found to increase in the order R = $H, CH_3, Ph, p\text{-}CH_3C_6H_4$, $p\text{-}BrC_6H_4$, $p\text{-}CF_3C_6H_4 > CH_2Ph > p\text{-}ClC_6H_4CH_2 = p\text{-}CH_3OC_6H_4CH_2 >> PhCH_2CH_2$. All reactions were slower with $HBF_4$ than with $CF_3SO_3H$.

Another study, by Butts *et al.* [152], was carried out on the reaction of $[Mn(CH_3)(CO)_5]$ with various acids in the presence of CO (equation 34).

$$[Mn(CH_3)(CO)_5] + HA + CO \longrightarrow [Mn(COCH_3)(CO)_5] + HA \qquad (34)$$

Thus, the acid was observed to increase the rate of alkyl migration. The order of increase in rate was HA = $CF_3CO_2H > CCl_2HCO_2H > CClH_2CO_2H$ (with HA = HBr, manganese-carbon bond cleavage occurred to give $[Mn(Br)(CO)_5]$ and $CH_4$).

The $\eta^1$-allyl complex $[Mn(CH_2CH{=}CH_2)(CO)_5]$ also reacts with strong acids to give the expected cleavage products [153] (equation 35).

$$[Mn(CH_2CH{=}CH_2)(CO)_5] + HA \longrightarrow [Mn(A)(CO)_5] + CH_3CH{=}CH_2$$
$$(HA = HCl, HNO_3, H_2SO_4, CF_3CO_2H) \qquad (35)$$

as does the binuclear compound $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$ [24] (equation 36).

$$[(CO)_5Mn(CH_2)_4Mn(CO)_5] + 2HCl \longrightarrow 2[Mn(Cl)(CO)_5] + n\text{-}C_4H_{10} \qquad (36)$$

The gas phase reaction of $[Mn(CH_3)(CO)_5]$ with various proton donors ($BH^+$) has been reported [154]. The products of the reaction were found to depend on the nature of B.

The reaction of ethyl manganesepentacarbonyl with $Ph_3CBF_4$ results in ß-hydride abstraction, resulting in a complex with coordinated ethylene as a ligand [3] (equation 37).

$$[Mn(CH_2CH_3)(CO)_5] + Ph_3CBF_4 \longrightarrow [Mn(CH_2{=}CH_2)(CO)_5]BF_4 \qquad (37)$$

Manganese-alkyl carbon bond cleavage can also be accomplished with the use of halogens [25,155].

### 1.4.1.4 Reaction of $[Mn(R)(CO)_5]$ with Transition Metal Hydrides

This reaction usually results in the formation of di- or polynuclear complexes. For example, the reaction of $[Mn(CH_3)(CO)_5]$ with various transition metal hydrides has been reported [33] (equations 38,39).

$$[Mn(CH_3)(CO)_5] + M\text{-}H \xrightarrow{CH_3CN} [MMn(CH_3CN)(CO)_4] + CH_3CHO \qquad (38a)$$

$(M\text{-}H = [Re(H)(CO)_5],\ [CpW(H)(CO)_3])$

$$[Mn(CH_3)(CO)_5] + [Os(H)_2(CO)_4] \xrightarrow{CH_3CN} [\{Os(H)(CO)_4\}\{Mn(CH_3CN)(CO)_4\}_2] \qquad (38b)$$

$$[Mn(CH_3)(CO)_5] + [Re(H)(CO)_5] \xrightarrow{C_6H_6} [(H)MnRe_2(CO)_{14}] + CH_3CHO \qquad (39)$$

Thus, in coordinating solvents the metal-containing products are solvated dinuclear complexes and in non-coordinating solvents they are polynuclear hydrides formed by coordination of a second equivalent of hydride (the vacant coordination site is created on manganese).

The reaction of $[Mn(R)(CO)_5]$ with $[Mn(H)(CO)_5]$ in non-co-ordinating solvents results in the formation of $\eta^1$-aldehyde complexes [156](equation 40).

$$[Mn(R)(CO)_5] + [Mn(H)(CO)_5] \longrightarrow [Mn_2(\eta^1\text{-}RCHO)(CO)_9] \qquad (40)$$
$(R = CH_3, p\text{-}CH_3C_6H_4, CH_2CH_2CH{=}C(Ph)(CH_3))$

Nearly all previously reported aldehyde complexes were formed by adding a free aldehyde to a metal complex containing a weakly bound ligand. In this case, the aldehyde was formed during the reaction. The alkyl (R) and carbonyl groups derived from $[Mn(R)(CO)_5]$. Other examples of $[Mn_2(\eta^1\text{-aldehyde})(CO)_9]$ complexes are known [157-159].

The reductive elimination of $[Mn(R)(CO)_5]$ by $[Mn(H)(CO)_5]$ can yield either RH or RCHO compounds, depending on the reaction conditions [160,161] (equations 41,42).

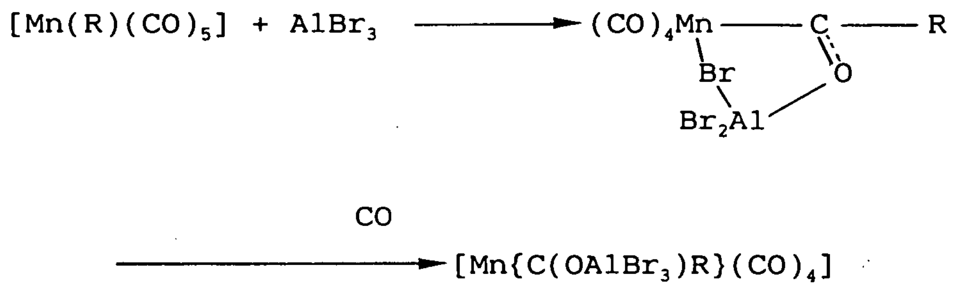
$$[Mn(R)(CO)_5] + [Mn(H)(CO)_5] \xrightarrow{C_6H_6} [Mn_2(CO)_{10}] + RH \qquad (41)$$

$$[Mn(R)(CO)_5] + [Mn(H)(CO)_5] \xrightarrow[C_6H_6,\ CO]{CH_3CN\ \text{or}} [Mn_2(CO)_{10}] + RCHO \qquad (42)$$

$(R = p\text{-}CH_3OC_6H_4CH_2, CH_2C_6H_5)$

### 1.4.1.5 Reaction of $[Mn(R)(CO)_5]$ with Lewis Acids

One of the earliest reports concerning this type of reaction came from Shriver's group [162], who reacted $[Mn(R)(CO)_5]$ with $AlBr_3$ (Scheme 10).



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(R = $CH_3$, $CH_2Ph$)

Scheme 10 Reaction of $[Mn(R)(CO)_5]$ with $AlBr_3$

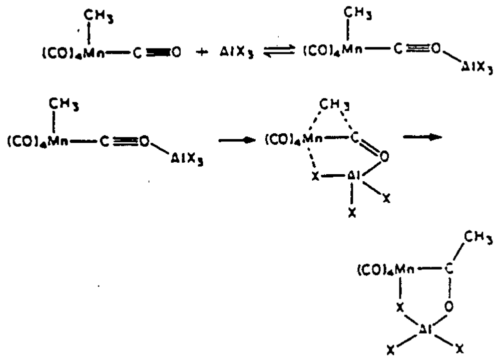
Thus, the incoming CO ligand in the final stage of the reaction has replaced the bromine ligand in the coordination sphere of manganese. Similar results were obtained using $AlCl_3$ and $BF_3$ in place of $AlBr_3$ ($[Mn\{C(OMX_3)R\}(CO)_4]$ compounds will undergo rapid elimination of $MX_3$ in the presence of $H_2O$ to form $[Mn(COR)(CO)_5]$ compounds). Thus, the purpose of the Lewis acid is to facilitate alkyl migration by providing an electron-rich atom to fill the vacant coordination site. The Lewis acid, therefore, does not merely increase the rate of reaction with CO, it actually induces a CO insertion, even in the absence of carbon monoxide, providing an alternative reaction route by way of two intermediate steps.

Richmond *et al.* [163] have reported the Lewis acid assisted carbonylation of $[Mn(CH_3)(CO)_5]$ with $AlBr_3$, $AlCl_3$, $AlCl_2Et$ and $AlClEt_2$ in order to obtain kinetic data. With $AlCl_3$ and $AlBr_3$, the reaction had reached completion within the time of mixing, so the rate constants could not be obtained. However, the reactions of $AlCl_2Et$ and $AlClEt_2$ were slightly slower and yielded the following results: $AlCl_2Et$, $k_{OBS}$ = 10 mol.s$^{-1}$ and $AlClEt_2$, $k_{OBS}$ = 0.37 mol.s$^{-1}$ It was proposed that $AlCl_2Et$ and $AlClEt_2$ underwent redistribution, *viz.*:

$$3AlCl_2Et \rightleftharpoons 2AlCl_3 + AlEt_3$$

$$3AlClEt_2 \rightleftharpoons AlCl_3 + 2AlEt_3$$

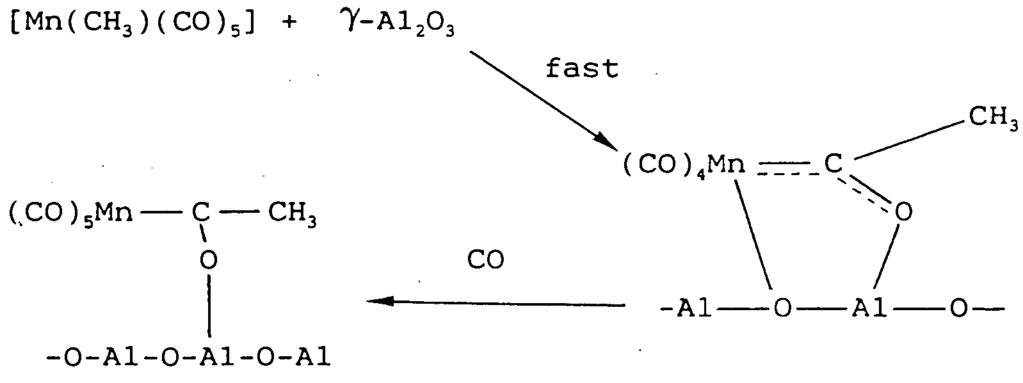
The mechanism shown in Scheme 11 was proposed for the coordination of the Lewis acid to [Mn($CH_3$)($CO$)$_5$]



Scheme 11 Mechanism for Lewis Acid Coordination

Nolan *et al.* [164] measured the enthalpy of reaction for the formation of [Mn{C(OAlBr$_3$)($CH_3$)}($CO$)$_4$] from $Al_2Br_6$ and [Mn($CH_3$)($CO$)$_5$] and reported a value of $\Delta H = -167.4$ kJ.mol$^{-1}$. It was noted, however, that this figure was based on reaction with 0.5 equivalents of $Al_2Br_6$ and that calculations based on reaction with $AlBr_3$ would require addition of -55.6 kJ.mol$^{-1}$ to the above $\Delta H$ value.

Correa *et al.* [165] reported the acceleration of the carbonylation reaction by $\gamma$-alumina, also *via* formation of a cyclic adduct (Scheme 12)



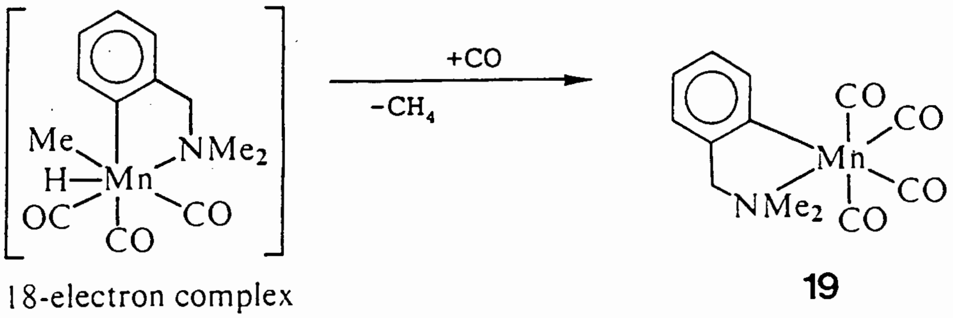
Scheme 12 Reaction of [Mn($CH_3$)($CO$)$_5$] with $\gamma$-alumina

Theoretical studies indicate that when the Lewis acid coordinates to the carbonyl oxygen, it activates that group towards alkyl migration [166]. The formation of the oxygen-acid bond lowers the energy of the carbonyl π* orbital, thus making the ligand a better π-acceptor (withdrawal of electron density from any group lowers the energies of both bonding and antibonding orbitals). The Lewis acid also has an additional effect beyond that of stabilizing the π* orbital - it results in the formation of a strong oxygen-acid bond. It has been argued that Lewis acid coordination should deactivate the molecule it coordinates to, since electron transfer from the metal to the carbonyl ligand will increase [167]. This was, however, an incorrect assumption since the formation of an acid-oxygen bond will result in an overall decrease in electron density at the carbonyl, *i.e.* the carbonyl is activated since the increase in metal to carbon π-donation will only partially compensate for the decrease in oxygen to carbon π-donation.

### 1.4.1.6 Orthometallation Reactions

Orthometallation reactions are reactions between a phenyl or benzyl organic compound bearing a substituent group capable of acting as a ligand, and an organometallic compound. Electron-withdrawing substituents on the phenyl ring will tend to activate it. $[Mn(CH_2Ph)(CO)_5]$ is the most reactive organomanganese compound towards orthometallation. The reaction is thought to occur *via* formation of an initial complex of the organic moiety through carbonyl displacement. Further dissociation of CO gives a sixteen electron intermediate that can undergo oxidative addition to an ortho C-H group of the aryl ring. Reductive elimination of methane then gives the final product. For example, the following reaction (Scheme 13) has been reported by Bennett *et al.* [168]

$$[Mn(CH_3)(CO)_5] + Me_2NCH_2Ph \longrightarrow \mathit{cis}\text{-}[Mn(CH_3)(CO)_4(Me_2NCH_2Ph)] \xrightarrow{-CO} \underset{16e}{[Mn(CH_3)(CO)_3(Me_2NCH_2Ph)]}$$



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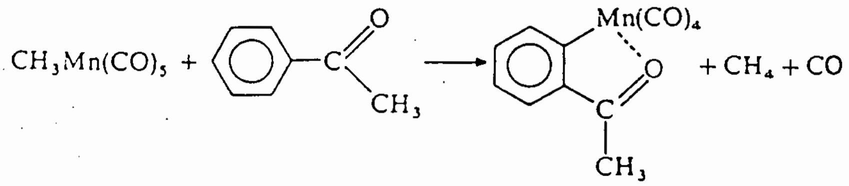
Scheme 13 Reaction of $[Mn(CH_3)(CO)_5]$ with $Me_2NCH_2Ph$

Most orthometallation studies have involved the reactions between $[Mn(R)(CO)_5]$ compounds and either nitrogen or phosphorus donor ligands, whereas relatively few have investigated the metallation with oxygen donor ligands. This has been investigated by McKinney and Crawford who describe the metallation of aromatic ketones by $[Mn(CH_3)(CO)_5]$ [169]. They describe the reaction of acetophenone with $[Mn(CH_3)(CO)_5]$ to give the expected product (equation 43):

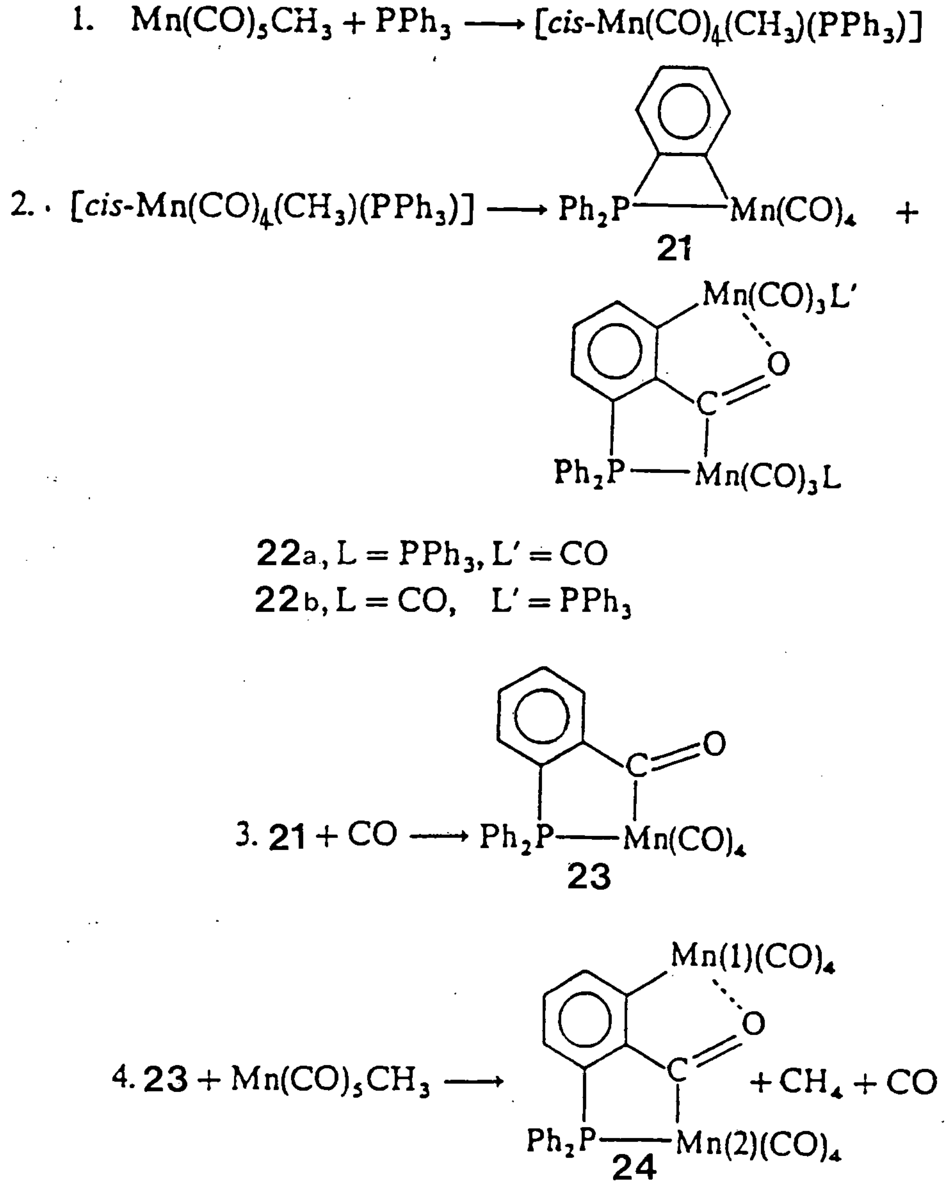


(43)

**20**

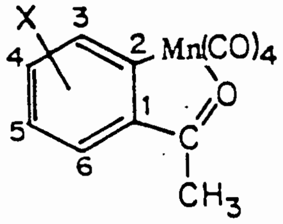
They also describe a rather unique metallation of an aromatic ketone derived from the cyclometallation of $PPh_3$.

The product of this reaction is of interest because it contains an extended planar π-system, including the two manganese atoms which are not bonded directly to each other (Scheme 14).



Scheme 14 Orthometallation of an Aromatic Ketone by $[Mn(CH_3)(CO)_5]$

The reaction of $[Mn(CH_3)(CO)_5]$ with substituted aromatic ketones [170] gave the cyclometallated derivatives, with elimination of $CH_4$.



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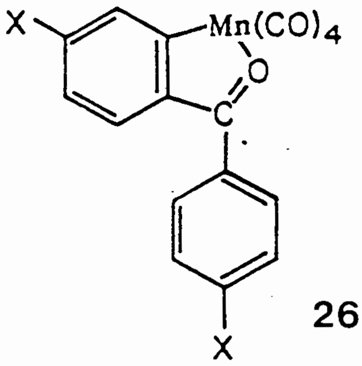
(X = 3-, 4- or 5-$CH_3$;
3-, 4- or 5-$OCH_3$;
4-Cl)

and



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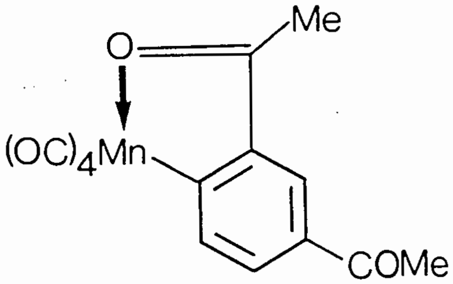
(X = H, $CH_3$, $OCH_3$,
F,Cl)

A very recent report [171] of an orthometallation reaction involves the reaction of 1,3-diacetylbenzene with $[Mn(CH_2Ph)(CO)_5]$ to give the mono- and dicyclomanganated complexes 23 and 24. The structure of 24 was confirmed by a crystal structure determination.



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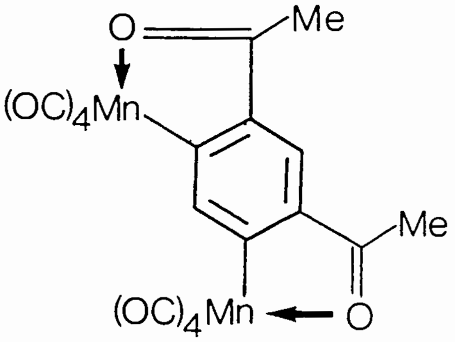

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Analogous cyclomanganated compounds were formed with 1,4-diacetylbenzene.

An extensive review of orthometallation reactions using $[Mn(R)(CO)_5]$ compounds prior to 1982 is given in reference 4, pages 78-85.

## 1.4.2 ACYL MANGANESEPENTACARBONYLS

Although $[Mn(COR)(CO)_5]$ compounds have not been subjected to as many reactivity studies as the corresponding $[Mn(R)(CO)_5]$ compounds, numerous reactions have in fact been reported, the most well known being the decarbonylation reaction to form alkyls. The reactions of $[Mn(COR)(CO)_5]$ can be divided into six categories, namely

(1) decarbonylation (thermal, photolytic or chemical),
(2) reaction with neutral nucleophiles, *e.g.* $PPh_3$,
(3) reaction with anionic nucleophiles, *e.g.* $I^-$
(4) reaction with cationic species, *e.g.* $H^+$
(5) hydrosilation, *e.g.* with $H_2SiPh_2$
(6) reaction with Lewis acids, *e.g.* $AlBr_3$

### 1.4.2.1 Decarbonylation of $[Mn(COR)(CO)_5]$

The facile decarbonylation of numerous manganesepentacarbonyl acyl, aroyl or perfluoroacyl derivatives is of particular interest as it permits the preparation of many alkyl, aryl and perfluoroalkyl derivatives of manganesepentacarbonyl not obtainable by the reaction of $[Mn(CO)_5]^-$ with alkyl or acyl halides. Decarbonylation may be accomplished thermally, photolytically or chemically (by using a metal complex such as $[Rh(Cl)(PPh_3)_3]$).

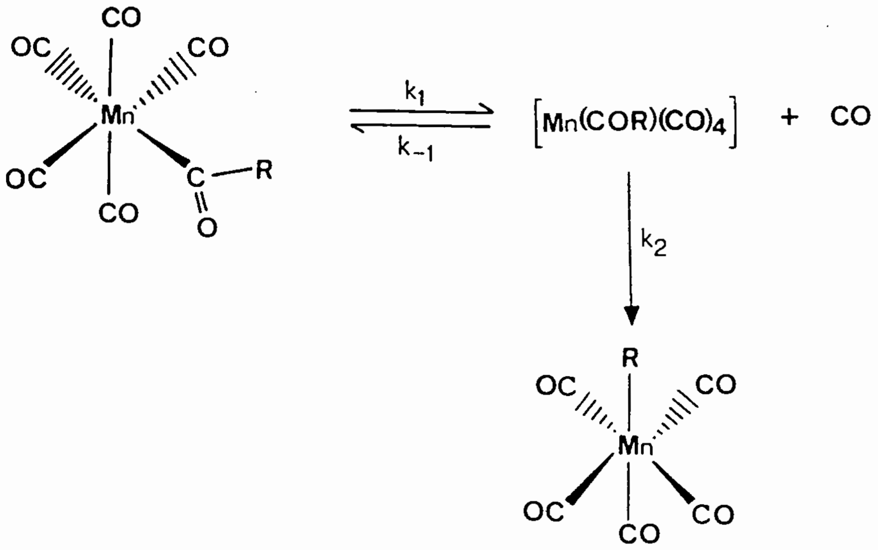
Although numerous decarbonylation reactions have been reported in the literature, most of them were not investigated in any great detail since the decarbonylation was merely used as a route to the alkyl compounds. Very few detailed and mechanistic studies have been made on this reaction. Because all the decarbonylation reactions of $[Mn(COR)(CO)_5]$ compounds reported in the literature are too numerous to be fully discussed within the scope of this thesis, this section will consider only general mechanistic studies which can apply to most decarbonylation reactions of $[Mn(COR)(CO)_5]$. Chemical decarbonylation reactions are likely to proceed by a somewhat different mechanism.

The first such decarbonylation reaction was reported by Coffield *et al.* in 1957 [16] who thermally decarbonylated acetyl and benzoyl manganesepentacarbonyl to form the corresponding methyl and phenyl derivatives (equation 44).

$$[Mn(COR)(CO)_5] \xrightarrow{\Delta} [Mn(R)(CO)_5] + CO \qquad (44)$$

$(R = CH_3, C_6H_5)$

Thermal decarbonylation is the most extensively, as well as intensively studied type of decarbonylation. The early studies of Calderazzo and Cotton [17,73], Booth *et al.* [172] and later Cause *et al.* [14] have provided most of the information on this subject. The following mechanistic scheme may apply:



Scheme 15 Decarbonylation of $[Mn(COR)(CO)_5]$

Thus, decarbonylation also occurs by alkyl migration. The coordinatively unsaturated intermediate, $[Mn(COR)(CO)_4]$, is the same as that for carbonyl insertion. Photolysis of $[Mn(COCH_3)(CO)_5]$ in an Ar matrix at 15K produces a trigonal bipyramidal [$Mn(COCH_3)(CO)_4$] species [173]. Studies with labelled CO [83] show that the molecule of CO which is lost does not come from the acyl carbonyl group, but rather from a terminal carbonyl group attached to manganese.

The reaction thus occurs by displacement of a terminal carbonyl group (the rate-determining step) followed by migration of the alkyl group from carbon to manganese. The ease of decarbonylation will therefore depend on the strength of the bond between the metal atom and one of the terminal carbonyl groups.

Calderazzo and Cotton performed kinetic studies on the decarbonylation of [$Mn(COR)(CO)_5$] in 2,2$'$-diethoxydiethylether at 30°C [17] and obtained results as shown in Table 4. Cawse *et al.* [14] repeated the reaction in benzene at 80°C (using a wider range of R groups) and obtained the results shown in Table 5.

Thus, the observed rate constants increase in the following order of R: $COCH_2Ph = COMe < CF_3 = CO_2Et < CH_2OMe << CH_2Ph < Me = CH_2C_6H_{11} < Et < n\text{-}Pr << Ph$, but the spread is only ~10. With the exception of R = Ph, the order parallels that for the carbonylation reaction. The fact that the rate constants span such a narrow range is not too surprising, since dissociation of a terminal carbonyl in the rate-determining step need not be greatly influenced by the nature of R in COR. It appears that electronegative substituents have a retarding effect on the decarbonylation reaction which is to be expected. If a substituent causes electron density to be removed from the metal atom, the loss of two electrons with the departing CO ligand will be unfavourable. The relative rates of decarbonylation (with varying R) have been correlated with the Taft $\sigma^*$ inductive parameter for the group [14].

| R | $10^5k_{OBS}$ ($sec^{-1}$) |
|---|---|
| Ph | 22.4 |
| n-Pr | 2.8 |
| Et | 3.7 |
| Me | 5.2 |
| $CH_2Ph$ | 2.3 |

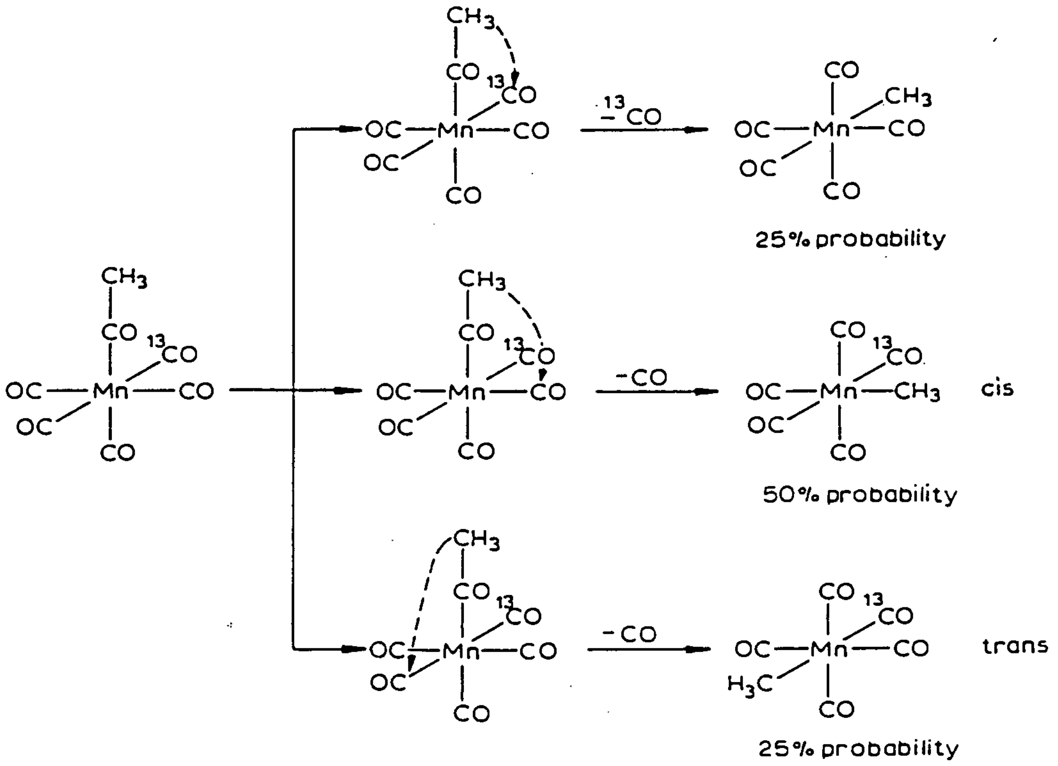
Table 4 Effect of R on Rate of Decarbonylation [17]

| R | $10^5k_{OBS}$ ($sec^{-1}$) |
|---|---|
| $CH_2C_6H_{11}$ | 250 |
| Me | 250 |
| $CH_2Ph$ | 159 |
| $CH_2OMe$ | 58 |
| $CO_2Et$ | 28 |
| COMe | 21 |
| $COCH_2Ph$ | 20 |
| $CF_3$ | 28 |

Table 5 Effect of R on Rate of Decarbonylation [14]

Solvent effects on the decarbonylation reaction are in general very small and no trends have been discerned [174].

As to the question of stereochemistry, Noack and Calderazzo [76] demonstrated that the decarbonylation of *cis*-$[Mn(COCH_3)(CO)_4(^{13}CO)]$ gave *cis*- and *trans*-$[Mn(CH_3)(CO)_4(^{13}CO)]$ in the ratio 2:1, consistent with the mechanism of methyl migration onto the site of dissociated CO (Scheme 16).



Scheme 16 CO Dissociation from *cis*-[Mn($COCH_3$)$(CO)_4$($^{13}CO$)]

Most photolytic decarbonylations have been of a synthetic rather than a mechanistic utility. However, one instance is known where photolysis of [Mn($COCH_3$)$(CO)_5$] produces a trigonal bipyramidal structure, [Mn($COCH_3$)$(CO)_4$], which may be representative of the coordinatively unsaturated intermediate in thermal decarbonylations [173]. Chemical decarbonylation can be accomplished by using a stoichiometric amount of a CO-abstracting metal complex, *e.g.* [Rh(Cl)$(PPh_3)_3$] [175] or [Ir$(dppe)_2$Cl][176]. However, a major side-reaction can be ligand substitution. Trimethylamine-N-oxide has also been used as a chemical decarbonylating agent [106] and the mechanistic route shown in Scheme 17 was proposed.

$$\begin{tikzcd}[Mn(COR)(CO)_5] \arrow[r, "Me_3NO"] & {[Mn(COR)(CO)_4(NMe_3)] + CO_2} \arrow[d] \\ & {[Mn(R)(CO)_5] + NMe_3}\end{tikzcd}$$

Scheme 17 Decarbonylation of $[Mn(COR)(CO)_5]$ by $Me_3NO$

### 1.4.2.2 The Reaction of $[Mn(COR)(CO)_5]$ with Neutral Nucleophiles

As for $[Mn(R)(CO)_5]$ species, this category involves mainly the reactions of $[Mn(COR)(CO)_5]$ with amines or tertiary phosphines. The earliest study was that of Keblys and Filbey [118], who reported the following reaction (equation 45)

$$[Mn(COCH_3)(CO)_5] + L \longrightarrow [Mn(COCH_3)(CO)_4(L)] + CO \qquad (45)$$

($L = NH_3$, aliphatic or aromatic amines)

Thus, the reaction gave the same products as the reaction of $[Mn(CH_3)(CO)_5]$ with amines. Calderazzo and Noack [84,102] subsequently reported the reaction of acetyl manganesepentacarbonyl with a variety of ligands to give the substituted products as shown in equation 45, with L = $PPh_3$, $C_6H_{11}NH_2$ and $C_4H_9NH_2$.

The reaction was found to be independant of [L] and to occur at the same rate as the decarbonylation reaction, indicating that the same mechanism operates for both reactions.

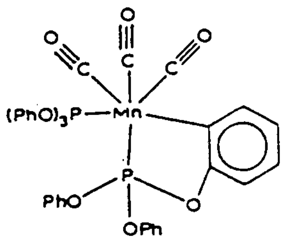
Kraihanzel and Maples [103] and Noack *et al.* [83] (using $^{13}C$ and $^{2}D$ labelling studies) investigated the stereochemistry of the reaction of $[Mn(COCH_3)(CO)_5]$ with $PPh_3$ and found that the initial product was *cis*-$[Mn(COCH_3)(CO)_4(PPh_3)]$ but that this product rapidly isomerized *via* a dissociative mechanism (*i.e.* dissociation of $PPh_3$) to a *cis/trans* mixture. A later study by Drew *et al.* [61] investigated the reaction of $[Mn(COCH_2Ph)(CO)_5]$ with $PPhMe_2$ (equation 46) and $P(OPh)_3$ (equation 47).

$$[Mn(COCH_2Ph)(CO)_5] + PPhMe_2 \rightarrow \textit{cis}\text{-}[Mn(COCH_2Ph)(CO)_4(PPhMe_2) \qquad (46)$$

$$[Mn(COCH_2Ph)(CO)_5] + P(OPh)_3 \rightarrow [Mn(COCH_2Ph)(CO)_4\{P(OPh)_3\}] \qquad (47)$$

After 10 days, *cis*-$[Mn(COCH_2Ph)(CO)_4(PPhMe_2)]$ had undergone further reaction to form *fac*-$[Mn(COCH_2Ph)(CO)_3(PPhMe_2)_2]$. The product of equation 47, $[Mn(COCH_2Ph)(CO)_4\{P(OPh)_3\}]$ initially adopted a *cis* geometry, but after 12 hours an isomeric mixture (77% *cis*/23% *trans*) had formed. At high temperatures $[Mn(COCH_2Ph)(CO)_4(P\{OPh\}_3)]$ decarbonylates, resulting in formation of the orthometallated product, 29 (equation 48) [177].

$$[Mn(COCH_2Ph)(CO)_5] + P(OPh)_3 \xrightarrow{55°C}$$



(48)

29

Darensbourg *et al.* [177] also reported the reaction of $[Mn(COCH_2Ph)(CO)_5]$ with 1,2-bis(diphenylphosphino)ethane (equation 49). The product of this reaction did not decarbonylate.

$$[Mn(COCH_2Ph)(CO)_5] + dppe \longrightarrow \textit{fac}\text{-}[Mn(COCH_2Ph)(CO)_3(dppe)] \quad (49)$$

Only one attempt to react $[Mn(COR)(CO)_5]$ species with carbon monoxide has been reported; Casey *et al.* [178] reacted $[Mn(COCH_3)(CO)_5]$ with CO (258 atm) at 80°C for 9 hours, but observed no reaction. They did, however, synthesize pyruvoyl manganesepentacarbonyl, $[Mn(COCOCH_3)(CO)_5]$, by reaction of $Na[Mn(CO)_5]$ with pyruvoyl chloride, and found it to be fairly stable. The rate of decarbonylation was 21 times lower than that for acetyl manganesepentacarbonyl.

Reactions of $[Mn(COR)(CO)_5]$ compounds with other neutral nucleophiles have been reported. These include:

(i) Reaction with a Transition Metal Hydride

Ruszczyk *et al.* have reported the following reaction (equation 50) [116].

$$[Mn(COCH_3)(CO)_5] + \textit{cis}\text{-}[Mn(H)(CO)_4(PBu_3)] \xrightarrow{CO} [Mn_2(CO)_9(PBu_3)] + CH_3CHO + CO \quad (50)$$

The above reaction is thought to occur by rate-determining methyl migration, followed by coordination to the hydride.

(ii) Reaction with Hydrogen

The reaction of $[Mn(COCH_3)(CO)_5]$ with $H_2$ is known [118] and is thought to occur *via* oxidative addition of $H_2$ (equation 51).

$$[Mn(COCH_3)(CO)_5] + H_2 \xrightarrow[\text{tetradecane}]{\text{313 atm}} [Mn_2(CO)_{10}] + CH_3CHO \quad (51)$$

A later study involved the reaction of $[Mn(COCH_2Ph)(CO)_5]$ with $H_2$ (equation 52) [127].

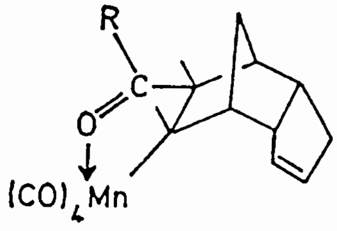
$$[Mn(COCH_2Ph)(CO)_5] + H_2 \xrightarrow[\text{sulfolane}]{\text{81 atm}} [Mn(CO)_{10}] + PhCH_2CHO \qquad (52)$$

Mapolie and Moss [25], however, reported that the reaction of the binuclear species, $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$, with $H_2$ gave the diol, not the aldehyde, as the organic product (equation 53).

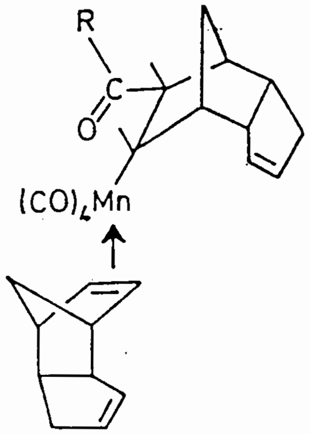
$$[(CO)_5MnCO(CH_2)_4COMn(CO)_5] + H_2 \xrightarrow[\text{THF}]{\text{40 atm}} [Mn_2(CO)_{10}] + HO\text{-}CH_2(CH_2)_4CH_2\text{-}OH \qquad (53)$$

(iii) Reaction with an Alkene

Booth *et al.* [179] have reported the reactions of acetyl- and benzoyl manganesepentacarbonyl with dicyclopentadiene to form a number of products (30-33), the proportions of which varied according to the solvents used.



**30**



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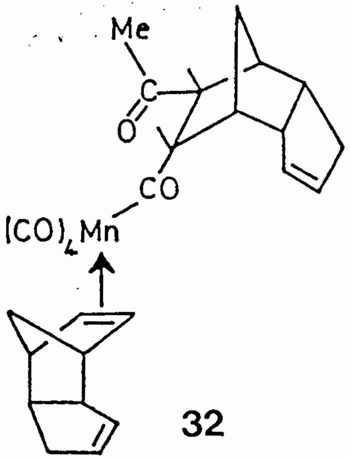
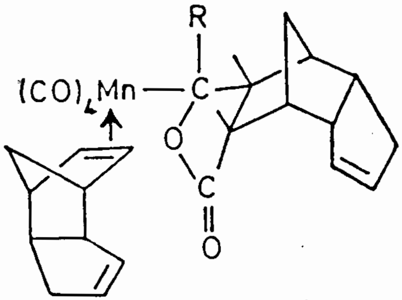


**32**

R = $CH_3, C_6H_5$



**33**

For compound **32** only the methyl-substituted derivative was isolated.

### (iv) Reaction with Boron Compounds

[Mn($COCH_3$)(CO)$_5$] was implicated as an intermediate in the reaction of $B_2H_6$ with [Mn($CH_3$)(CO)$_5$] to form hydrocarbons [141]. The reaction of [Mn(p-$CH_3C_6H_4CO$)(CO)$_5$] with $B_2S_3$ has been reported [180].

### (v) Reaction with Synthesis Gas

This topic has already been discussed in Section 1(b).

### 1.4.2.3 Reaction of [Mn(COR)(CO)$_5$] with Anionic Nucleophiles

The earliest report in this category came from Calderazzo and Noack [84] who reacted an optically active manganesepentacarbonyl species with lithium iodide and observed retention of configuration in the product (equation 54).

$$[Mn\{COCH(Me)CH_2Ph\}(CO)_5] + LiI \longrightarrow Li[Mn\{COCH(Me)CH_2Ph\}(CO)_4(I)] \quad (54)$$

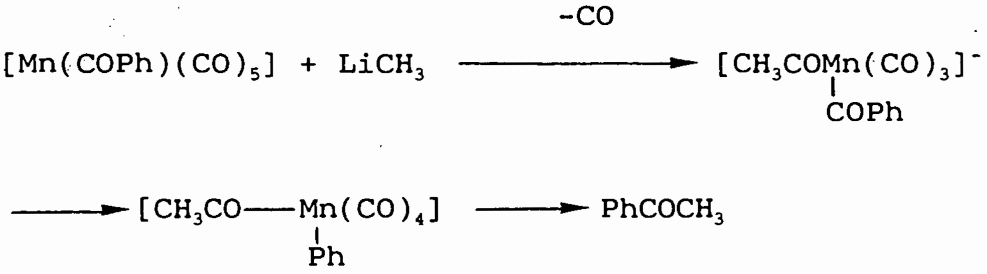
Johnson and Pearson [151] subsequently investigated the reaction of acetyl manganesepentacarbonyl with a variety of anionic species (equations 55,56).

$$[Mn(COCH_3)(CO)_5] + NaOCH_3 \longrightarrow Na[Mn(CO)_5] + CH_3CO_2CH_3 \quad (55)$$

$$[Mn(COCH_3)(CO)_5] + 2NaOH \longrightarrow Na[Mn(CO)_5] + CH_3CO_2Na + H_2O \quad (56)$$

Equations 55 and 56 involve the cleavage of an acyl group by an alkoxide to give an ester. Thus, equations 57-59 indicate that only the most reactive nucleophiles will attack at the acyl carbonyl.

Casey and Bunnell [181] reacted methyllithium with benzoyl manganesepentacarbonyl and isolated acetophenone as the final product. On the basis of separate labelling studies, they proposed the mechanism outlined in Scheme 18.



$$[Mn(COPh)(CO)_5] + LiCH_3 \xrightarrow{-CO} [CH_3CO\underset{\displaystyle COPh}{\underset{|}{Mn}}(CO)_3]^-$$

$$\longrightarrow [CH_3CO\text{—}\underset{\displaystyle Ph}{\underset{|}{Mn}}(CO)_4] \longrightarrow PhCOCH_3$$

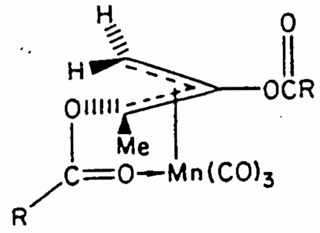
Scheme 18 Reaction of [Mn(COPh)(CO)$_5$] with LiCH$_3$

The acetophenone was formed by the migration of the phenyl group to manganese. The authors then repeated the experiment with acetyl manganesepentacarbonyl and phenyllithium and again isolated acetophenone as the product. Casey and Bunnell [18] also showed that the phenyl group migrates approximately twenty times faster than the methyl group *cf.* the preferential phenyl migration to electron deficient carbon centres of carbonium ions and free radicals . Casey and Bunnell's study was extremely valuable from a mechanistic point of view, since very little is known about the relative ease of migration of various groups from an acyl moiety to a metal, due to the fact that the rate of decarbonylation does not involve alkyl migration as the rate-determining step.

More recently, Lukehart and Srinivasan [182] reacted [Mn(COCH$_3$)(CO)$_5$] with methyllithium to give an $\eta^3$-allyl manganesepentacarbonyl complex, formed by manganese-induced interligand carbon-carbon bond formation. Diacylation with benzoyl- or acetyl chloride gives a neutral complex (equation 57).

$$[\mathrm{Mn(COCH_3)(CO)_5}] + \mathrm{LiCH_3} \xrightarrow{\mathrm{LiTMP}} [\mathrm{Mn}\{\eta^3\text{-}\mathrm{CH_2C(O^-)C(O^-)CH_3}\}(\mathrm{CO})_4] \qquad (57)$$

$$\xrightarrow{\mathrm{RCl}}$$



(LiTMP = lithium tetramethylpiperidide; R = $CH_3$,Ph)

### 1.4.2.4 Reaction of Mn(COR)(CO)$_5$] with Cationic Species

It was expected that since [Mn(R)(CO)$_5$] complexes underwent protonolysis to give RH species, that [Mn(COR)(CO)$_5$] complexes would give aldehydes upon similar protonolysis. However, this was found not to be the case by Motz *et al.* [12] who found that when treated with triflic acid, [Mn(COR)(CO)$_5$] compounds will reversibly form hydroxycarbene species and will also slowly decarbonylate to the corresponding [Mn(R)(CO)$_5$] species which then undergo proton cleavage reactions to give quantitative yields of RH. The same reactions were observed with $HBF_4$, but at a slower rate. However, although Motz *et al.* were unable to isolate the hydroxycarbene species, they did isolate the product of the reaction of [Mn(COCH$_3$)(CO)$_3$(dppp)] with triflic acid (equation 58).

$$[Mn(COCH_3)(CO)_3(dppp)] + CF_3SO_3H \longrightarrow [(CH_3)(OH)C{=}Mn(CO)_3(dppp)]^+CF_3SO_3^- \quad (58)$$

(dppp = bis(diphenylphosphino)propane

Johnson and Pearson [151] have reported the reaction of $[Mn(COCH_3)(CO)_5]$ with hydrochloric and p-toluenesulfonic acid. In both cases, the organic product was $CH_3CO_2CH_3$

### 1.4.2.5 Hydrosilation of $[Mn(COR)(CO)_5]$

The hydrosilation of manganesepentacarbonyl acyl compounds usually results in the formation of $\alpha$-siloxyalkyl species. A recent example of this is the report by Akita *et al.* [183] who reacted acetyl and benzoyl manganesepentacarbonyl with diphenylsilane to form a manganese siloxyalkyl comples (equation 59).

$$[Mn(COR)(CO)_5] + H_2SiPh_2 \xrightarrow{[Rh(Cl)(PPh_3)_3]} [Mn\{CH(OSiHPh_2)(R)\}(CO)_5] + [Mn(CH_2R)(CO)_5] \quad (59)$$

$(R = CH_3, Rh)$

However, the siloxyalkyl complexes proved to be very unstable and decomposed rapidly at room temperature to give a mixture of homologated hydrocarbons ($C_2$-$C_4$ olefins) by a repeating reduction-carbonylation sequence. This system was used, in conjunction with other metal-acyl species, to model the Pichler-Schultz mechanism for the Fischer-Tropsch synthesis.

Gregg *et al.* [184] have reported a similar reaction of $[Mn(COR)(CO)_5]$ complexes with various silanes (equation 60).

$$[Mn(COR)(CO)_5] + R'_2SiH_2 \longrightarrow [Mn\{CH(OSiHR'_2)(R)\}(CO)_5] \quad (60)$$

$(R = CH_3,\ Ph;\ R' = Et, Ph)$

The reaction of acetyl manganesepentacarbonyl with a monohydrosilane also gave a siloxyalkyl complex, as expected (equation 61)

$$[Mn(COCH_3)(CO)_5] + Me_2PhSiH \longrightarrow [Mn\{CH(OSiMe_2Ph)(CH_3)\}(CO)_5] \quad (61)$$

However, the reaction of benzoyl manganesepentacarbonyl with monohydrosilanes gave different products, *viz.* benzyl silyl ethers and manganese silyl complexes (equation 62)

$$[Mn(COPh)(CO)_5] + 2\ R_3SiH \longrightarrow [Mn(SiR_3)(CO)_5] + PhCH_2OSiR_3$$

$(R_3 = Me_2Ph$ or $Et_3)$

(62)

Hanna *et al.* [185] reported the use of $[Mn(COR)(CO)_5]$ complexes ($R = CH_3,Ph$) as catalysts for the hydrosilation of organoiron acyl compounds to iron $\alpha$-siloxyalkyl compounds (equation 63).

$$[Mn(COR)(CO)_5] + [CpFe(COR')(CO)_2] + R_3SiH \longrightarrow$$

$$[CpFe\{CH(OSiR_3)(R')\}(CO)_2] + [Mn(COR)(CO)_5] \quad (63)$$

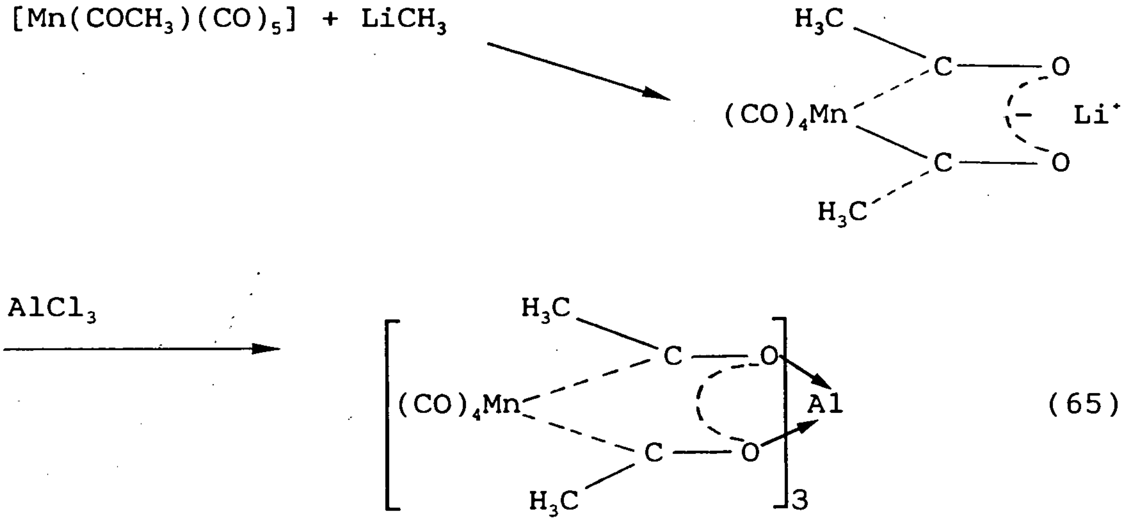
($R = CH_3C_6H_5$, $R' = CH_3,C_6H_5$; $R_3 = Et_3,Me_2Ph$; dihydro- and trihydrosilanes were also used)

The manganese catalyst endures (within NMR detection limits) until all the iron acyl substrate is consumed, and then undergoes rapid hydrosilation itself. The manganese acyls proved to be more active and general catalysts for the hydrosilation of iron acyls than $[Rh(Cl)(PPh_3)_3]$. These results, however, contrasted those of Wegman [186] which involved the reaction of $[Mn(COCH_3)(CO)_5]$ with a 10-fold excess of hydrosilanes ($R_3SiH$; $R_3 = Bu_3,Ph_3$) under an atmosphere of CO. Cleavage of the manganese-acyl carbon bond was observed, giving acetaldehyde and a manganese silyl complex (equation 64).

$$[Mn(COCH_3)(CO)_5] + R_3SiH \longrightarrow [Mn(SiR_3)(CO)_5] + CH_3CHO \qquad (64)$$

### 1.4.2.6 Reaction of $[Mn(COR)(CO)_5]$ with Lewis Acids

This type of reaction has not been widely reported in the literature; only two reports could be found [164,187]. The first was that of Lukehart *et al.* [187] who reacted acetyl manganesepentacarbonyl with methyllithium followed by $AlCl_3$ (equation 65).



(65)

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The second report (from Nolan *et al.* [164]) involved the reaction of acetyl manganesepentacarbonyl with 0.5 equivalents of $Al_2Br_6$ to form an $AlBr_3$ adduct (equation 66).

$$[Mn(COCH_3)(CO)_5] + \tfrac{1}{2}Al_2Br_6 \longrightarrow [Mn\{C(OAlBr_3)(CH_3)\}(CO)_5] \qquad (66)$$

This reaction formed part of a thermochemical study on the reactions of Lewis acids with organomanganese complexes .

### 1.4.3 ALKYL RHENIUMPENTACARBONYLS

Compared to manganese, relatively little work has been carried out on analogous alkyl complexes of rhenium, although that which has may be divided into the same categories, *viz.*

(1) reaction with neutral nucleophiles, *e.g.* $PPh_3$
(2) reaction with anionic nucleophiles, *e.g.* $BF_4^-$
(3) reaction with cationic species, *e.g.* $H^+$
(4) reaction with transition metal hydrides, *e.g.* $[CpW(H)(CO)_3]$
(5) reaction with Lewis acids, *e.g.* $AlCl_2Et$, and
(6) orthometallation reactions

### 1.4.3.1 Reaction of $[Re(R)(CO)_5]$ with neutral nucleophiles

Alkyl rheniumpentacarbonyl species are known to be reluctant to undergo alkyl migration reactions [4]; 5d metals are usually less inclined to undergo alkyl migration reactions than the 3d and 4d metals of the same subgroup [40]. This can be attributed to the higher strength of the metal-carbon bond for 5d metals [188]. The increase in bond strength going from 3d to 5d correlates with an increase in the bonding overlaps between the $2\sigma CH_3$ orbital and the (p,d)hybrid $\sigma ML_n$ orbital on the metal centre (in $[M(CH_3)(CO)_5]$), shown in Fig. 11.

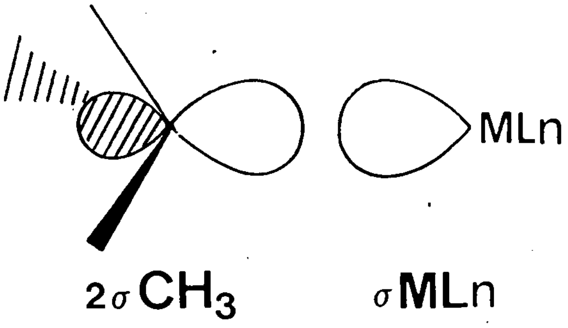


Fig. 11

The $M-CH_3$ bond dissociation energies in $[M(CH_3)(CO)_5]$ ($M =$ Mn,Re) were measured thermochemically and were found to be 117 kJ.mol$^{-1}$ for $M =$ Mn and 223 kJ.mol$^{-1}$ for $M =$ Re, indicating a much stronger $Re-CH_3$ bond [188]. More recent calculations have been reported by McQuillan *et al.* [44]; however, these results were discussed in section 1.3.

### (i) Reaction with CO

The reluctance of [Re($CH_3$)$(CO)_5$] to undergo alkyl migration was demonstrated by King *et al.* who reacted it with CO (320 atm at 200°C), but isolated only [$Re_2(CO)_{10}$] and unreacted [Re($CH_3$)$(CO)_5$] from the reaction mixture [117]. Ethyl rheniumpentacarbonyl is also very resistant to CO-induced alkyl migration; the reaction of [Re($C_2H_5$)$(CO)_5$] with CO was not complete after 1 hour at 100°C and 100 atm. of CO [32]. However, the reaction of the binuclear species [$(CO)_5$-Re$(CH_2)_4$Re$(CO)_5$] was partially successful; after reaction with CO (40 atm., 70°C) over 24h, 30% conversion to the acyl species [$(CO)_5$ReCO$(CH_2)_4$CORe$(CO)_5$] was observed [25].

### (ii) Reaction with tertiary phosphines

In contrast to the reactions of [Mn(R)$(CO)_5$] compound with tertiary phosphines, which yield acyl products, reactions of the analogous [Re(R)$(CO)_5$] compounds with phosphines gives only the phospine-substituted alkyl species, *i.e.* the rhenium compounds undergo CO substitution as opposed to alkyl migration. For example, the reaction of the binuclear compound [$(CO)_5$Re$(CH_2)_4$Re$(CO)_5$] with tertiary phosphines gives the binuclear phosphine-substituted alkyl compounds [25] (equation 67).

$$[(CO)_5Re(CH_2)_4Re(CO)_5] + 2PR_3 \xrightarrow[66°C]{THF}$$

$$cis,cis\text{-}[(PR_3)(CO)_4Re(CH_2)_4Re(CO)_4(PR_3)] + 2CO \qquad (67)$$

($PR_3$ = $PPh_3$, $PPh_2Me$, $PPhMe_2$)

For $PR_3$ = $PPhMe_2$, the acyl intermediate was isolated .

Anisimov *et al.* [189] reported the reaction of [Re(p-$ClC_6H_4$)$(CO)_5$] with $PPh_3$ to give the aryl product (equation 68).

$$[Re(p\text{-}ClC_6H_4)(CO)_5] + PPh_3 \xrightarrow{50\text{-}60°C} cis\text{-}[Re(p\text{-}Cl_6H_4)(CO)_4(PPh_3)] \quad (68)$$

Wang and Angelici [190] have reported the reaction of [Re($CH_3$)$(CO)_5$] with $PPh_3$ using [Pt$(PPh_3)_4$] as a catalyst (equation 69).

$$[Re(CH_3)(CO)_5] + PPh_3 \xrightarrow[\text{benzene}]{[Pt(PPh_3)_4]} cis\text{-}[Re(CH_3)(CO)_4(PPh_3)] \quad (69)$$

The phosphine-substituted product was obtained in 86% yield with almost quantitative recovery of the catalyst.

### (iii) Reaction with $SO_2$

$SO_2$ is known to insert into rhenium-alkyl bonds [131,134]; the kinetic products of $SO_2$ insertion are the O-bonded sulfinate derivatives [Re{OS(O)R}$(CO)_5$] [134]. The mechanism of this reaction is thought to be the same as for the analogous [Mn(R)$(CO)_5$] compounds [4].

For example, Hartman and Wojcicki [131] have isolated the species [Re{S$(O)_2$R}$(CO)_5$] (where R = $CH_3$ or $CH_2C_6H_5$) (equation 70).

$$[Re(R)(CO)_5] + SO_2 \longrightarrow [Re\{S(O)_2R\}(CO)_5] \quad (70)$$

Allyl rheniumpentacarbonyls can also insert $SO_2$ *e.g.* the following reaction has been reported [134] (equation 71).

$$[Re\{CH_2CH{=}C(Me)_2\}(CO)_5] + SO_2 \longrightarrow [Re\{S(O)_2C(Me)_2CH{=}CH_2\}(CO)_5] \quad (71)$$

### (iv) Miscellaneous Reactions

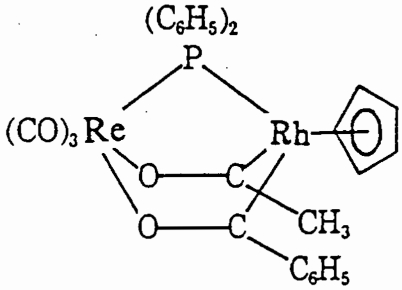
The reaction of methyl rheniumpentacarbonyl with tetrafluoroethylene has been reported [142] (equation 72).

$$[Re(CH_3)(CO)_5] + CF_2CF_2 \longrightarrow [Re(CF_2CF_2CH_3)(CO)_5] \qquad (72)$$

Thus, the fluorocarbon-inserted product is formed.

The reaction of methyl rheniumpentacarbonyl with other organometallic compounds is known. For example, reaction with $\eta^5$-(cyclopentadienyl)carbonyltriphenylphosphine-rhodium resulted in the formation of a bridged diphenylphosphidoheterodinuclear complex [136] (equation 73).

$$[Re(CH_3)(CO)_5] + [CpRh(CO)(PPh_3)] \longrightarrow$$



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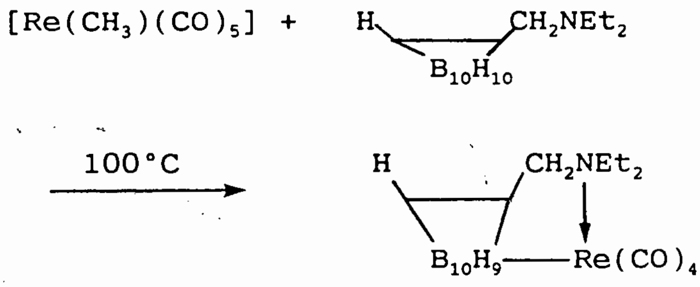
The reaction of $[Re(CH_3)(CO)_5]$ with amino- and phenylazocarboranes has been reported [191] (equation 74).



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The reaction of the binuclear complex $[(\mathrm{CO})_5\mathrm{Re(CH_2)_4Re(CO)_5}]$ with synthesis gas (40 atm. 70°C) was carried out, but was not very successful, giving unreacted starting material as the major product, with minor amounts of $[(\mathrm{CO})_5\mathrm{ReCO(CH_2)_4CORe(CO)_5}]$, 1,6-hexanediol and the corresponding aldehyde, $\mathrm{OHC(CH_2)_4CHO}$, also being formed [128].

### 1.4.3.2 Reaction of $[\mathrm{Re(R)(CO)_5}]$ with Anionic Nucleophiles

Methyl rheniumpentacarbonyl has been subjected to three tetrafluoroboranation studies, all by Beck and co-workers [23,192,193]. The first tetrafluoroboranation reaction was used as a route to binuclear rhenium compounds [23] (equation 75).

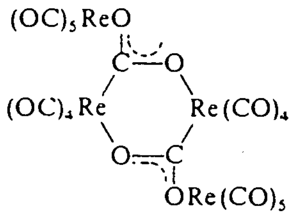
$$[\mathrm{Re(CH_3)(CO)_5}] + \mathrm{Ph_3CBF_4} \longrightarrow [\mathrm{Re(FBF_3)(CO)_5}] + \mathrm{H_3CCPh_3}$$

$$\xrightarrow{\mathrm{CH_2CHR}} [\mathrm{Re(CH_2CHR)(CO)_5}]^+\mathrm{BF_4}^- \xrightarrow{[\mathrm{Re(CO)_5}]^-} [(\mathrm{CO})_5\mathrm{Re\{CH_2CH(R)\}Re(CO)_5}]\ (\mathrm{R} = \mathrm{H}, \mathrm{CH_3}) \qquad (75)$$

The second study used the tetrafluoroboranation reactions a route to a polynuclear rhenium compound [191] (equation 76).

$$[\mathrm{Re(CH_3)(CO)_5}] + \mathrm{Ph_3CBF_4} \longrightarrow [\mathrm{Re(FBF_3)(CO)_5}] + \mathrm{H_3CCPh_3}$$

$$\xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-}} [\mathrm{Re(CO)_4(COOH)}]_n \xrightarrow[-\mathrm{H_2O}]{\text{acetone}} \qquad (76)$$



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A third study [193] involved treating the tetrafluoroborate derivative with a variety of σ- and π-donors, L, forming the salts $[Re(L)(CO)_5]^+BF_4^-$ (equation 77).

$$[Re(FBF_3)(CO)_5] + L \longrightarrow [Re(L)(CO)_5]^+BF_4^- \qquad (77)$$

($L = Me_2CO, CH_3CN, CO$, ethylene, propylene and pentene)

Reaction with germyllithium reagents can yield CO inserted products [146] (equation 78).

$$\begin{tikzcd}[Re(CH_3)(CO)_5] + R_3GeLi \arrow[r] & {[Re(COCH_3)(R_3Ge)(CO)_4]Li} \arrow[dl, "Et_4NCl"'] \arrow[dr, "Et_3CBF_4"] & (78) \\ {[Re(COCH_3)(R_3Ge)(CO)_4]Et_4N} & & {[Re\{C(OEt)CH_3\}(R_3Ge)(CO)_4]}\end{tikzcd}$$

($R_3 = Ph_3$ or MePh-1-naphthyl)

Thus, methyl rheniumpentacarbonyl reacts with germyllithium compounds to give anionic acyl complexes, which can be isolated as tetraethyl ammonium salts or alkylated to give carbene complexes.

### 1.4.3.3 Reaction of $[Re(R)(CO)_5]$ with Cationic Species

The gas phase reaction of $[Re(CH_3)(CO)_5]$ with proton donors was reported [154] (equations 79a and 79b).

$$\begin{tikzcd} & {[Re(CO)_5]^+ + CH_4 + B} & (79a) \\ {[Re(CH_3)(CO)_5] + BH^+} \arrow[ur] \arrow[dr] & & \\ & {[Re(H)(CH_3)(CO)_5]^+ + B} & (79b)\end{tikzcd}$$

The products of the reaction depend on the nature of B ($B = NH_3$, 2-MeTHF, $Et_2O$, THF, $Me_2CO$, $Me_2CCH_2$, $Me_2O$, MeCHO, MeOH, $MeCHCH_2$, $F_2CHCH_2OH$, HCN, $H_2S$, $H_2O$).

### 1.4.3.4 Reaction of $[Re(R)(CO)_5]$ with Transition Metal Hydrides

Ethyl rheniumpentacarbonyl was reacted with various metal hydrides in acetonitrile. The observed products were the heterobimetallic species, although a solvated rheniumtetracarbonyl acyl complex was detected [194] (equation 80).

$$[\mathrm{Re(Et)(CO)_5}] \xrightarrow{\mathrm{CH_3CN}} [\mathrm{Re(COEt)(CO)_4(CH_3CN)}]$$

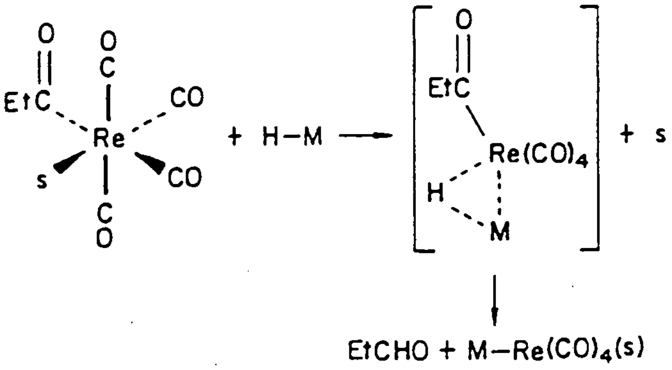
$$\xrightarrow{\mathrm{M{-}H}} [\mathrm{Re(M)(CO)_4(CH_3CN)}] + \mathrm{EtCHO}$$

$$\xrightarrow{\mathrm{CO}} [\mathrm{Re(M)(CO)_5}] + \mathrm{CH_3CN} \qquad (80)$$

(M-H = $[Re(H)(CO)_5]$, $[Mn(H)(CO)_5]$, $[CpW(H)(CO)_3]$ and $[Os(H)_2(CO)_4]$

When the metal hydride was in excess, the rate-determining step was formation of the propionyl complex. The reaction was subsequently found to be first order in the propionyl complex, and first order in the metal hydride. The second order rate constants were measured and found to be the reverse of the order of acidities of these hydrides, which implies that the hydrides react as nucleophiles with the propionyl complex. The rate of dissociation of $CH_3CN$ from $[Re(COEt)(CO)_4(CH_3CN)]$ was measured and the results indicate a dissociative mechanism for the reaction of the propionyl complex involving a three-centre two-electron bond as shown in Scheme 19.

In a separate experiment, $[Re(COEt)(CO)_5]$ was found to only react with $[Re(H)(CO)_5]$ after carbonyl dissociation, implying that the metal and not the acyl carbonyl is the site of nucleophilic attack by transition metal hydrides on acyl complexes.



(s = solvent)

Scheme 19 Formation of the Three-Centred Two-Electron Bond

Another study by the same group reported the above reaction in benzene instead of acetonitrile [33]. In this case, the solvated species were not observed and the reaction went straight to the binuclear compounds.

### 1.4.3.5 Reaction of $[Re(R)(CO)_5]$ with Lewis acids

McKinney and Stone have isolated a rhenium hydroxycarbene species from the reaction of $[Re(R)(CO)_5]$ with a Lewis acid [195] (equation 81).

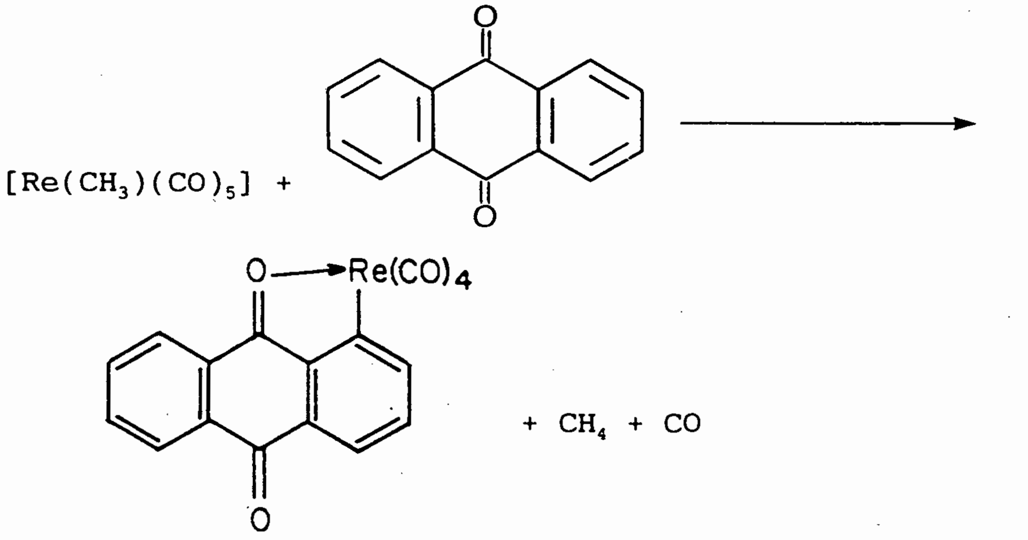
$$[Re(R)(CO)_5] + 2AlCl_2Et \longrightarrow \textit{cis}\text{-}[Re(Cl)\{C(R)(OH)\}(CO)_4] + \text{other products}$$

$(R = CH_3, C_6H_5)$ (81)

This hydroxycarbene compound can act as a catalyst for olefin metathesis.

### 1.4.3.6 Orthometallation reactions

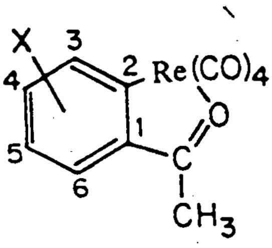
Methyl rheniumpentacarbonyl reacts with anthraquinone to give an orthometallated product [170] (equation 82).



(82)

38

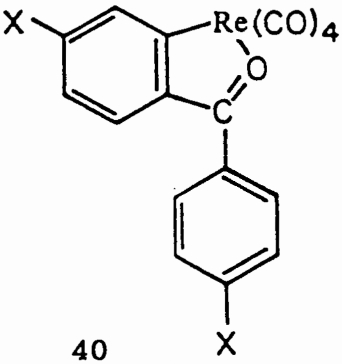
Methyl rheniumpentacarbonyl has also been reacted with substituted aceto- and benzophenones to give orthometallated products **39** and **40** [170].



39

($X$ = 3-,4- or 5-$CH_3$;
3-,4- or 5-$OCH_3$;
4-Cl)

and



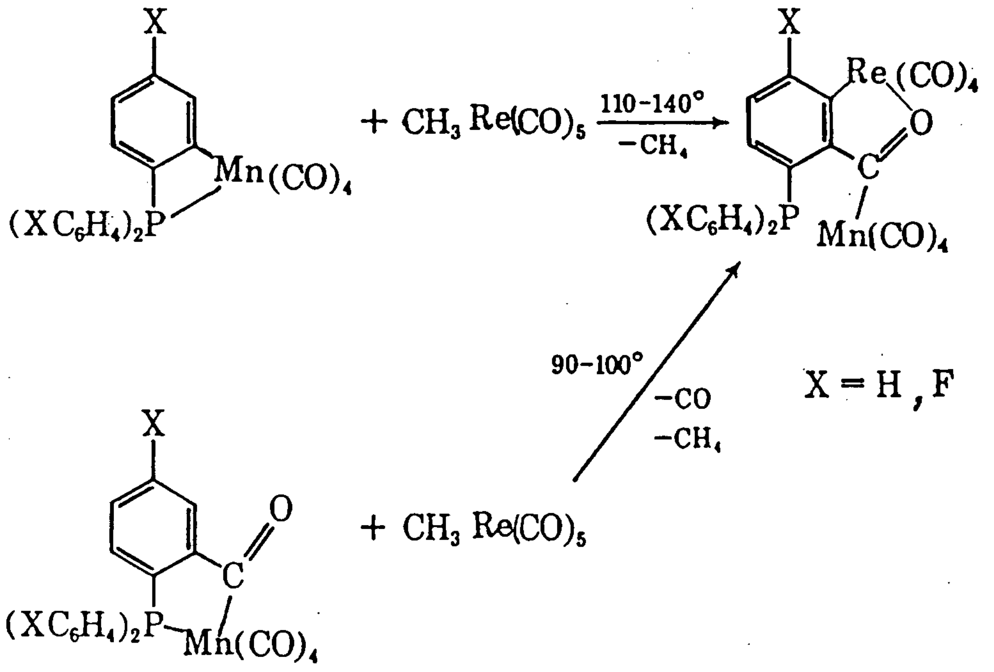
40

($X$ = H, $CH_3$, $OCH_3$,
F, Cl)

McKinney and Kaesz have reacted methyl rheniumpentacarbonyl with orthometallation products of alkyl manganesepentacarbonyls to yield bis(tetracarbonylmetal) secondary metallation products [196] (see Scheme 20).

## 1.4.4 ACYL RHENIUMPENTACARBONYLS

Very few reactions are in fact known for $[Re(COR)(CO)_5]$ compounds, and they may be divided into four categories, *viz*.



Scheme 20 Reaction of [Re(CH$_3$)(CO)$_5$] with Orthometallation Products of [Mn(R)(CO)$_5$]

(1) decarbonylation reactions
(2) reaction with neutral nucleophiles
(3) reaction with anionic nucleophiles, and
(4) reaction with transition metal hydrides

### 1.4.4.1 Decarbonylation of [Re(COR)(CO)$_5$]

This is by far the most well-documented category of reactions. Acyl rheniumpentacarbonyls lose CO on heating, but generally at temperatures 30-70°C higher than those required for the analogous [Mn(COR)(CO)$_5$] compounds [174]. In decarbonylation reactions, the metal-terminal carbonyl bond cleavage is the rate-determining step. The Re-CO (terminal) bond dissociation energy in [Re(CH$_3$)(CO)$_5$] has been measured as 181 kJ.mol$^{-1}$ [188] and if this value is compared to the Mn-CO (terminal) bond dissociation energy in $[Mn(CH_3)(CO)_5]$ of 95 $kJ.mol^{-1}$, one would expect decarbonylation reactions of rheniumpentacarbonyl acyls to be far less facile than those of the analogous manganesepentacarbonyl acyl compounds.

By means of the reaction

$$[Re(COR)(CO)_5] \xrightarrow{ca\ 100°C} [Re(R)(CO)_5] + CO \qquad (82)$$

the following acyl compounds have been decarbonylated: R = $CH_3$, $C_6H_5$ [198], o-$R'CB_{10}H_{10}C$ (R' = $CH_3$, $C_6H_5$)[198], m- and p-$CH_3C_6H_4$ [36], p-$XC_6H_4$ (X = Cl,Br,I)[34] and o- and m-$ClC_6H_4$ [35]. Elimination of CO was reported to proceed more rapidly from ortho or meta halogen-substituted aroyl derivatives than from the para substituted homologues [35]. The bimetallic complexes $[(CO)_5ReCO(R)CORe(CO)_5]$ (R = m- and p-$C_6H_4$) thermally decarbonylate to yield the corresponding aryl complexes [38] and $[(CO)_5ReCO(CH_2)_4$-$CORe(CO)_5]$ decarbonylates at 110°C to give the alkyl species [25]. However, not all aroyl or acyl derivatives undergo decarbonylation to the corresponding aryls or alkyls. $[Re(o\text{-}CH_3C_6H_4CO)(CO)_5]$ gives $[Re_2(CO)_{10}]$ upon heating rather than $[Re(o\text{-}CH_3C_6H_4)(CO)_5]$ [35], while attempts to obtain $[Re(cyclo\text{-}C_3H_5)(CO)_5]$ from $[Re\{(cyclo\text{-}C_3H_5)CO\}(CO)_5]$ either by thermal or chemical means (using $[Rh(Cl)(PPh_3)_3]$) were unsuccessful [199]. However, the cyclopropenoyl derivatives $[Re\{(CHCR{=}CR)CO\}(CO)_5]$ (R = $C_2H_5$, $C_6H_5$) undergo relatively facile decarbonylation, proceeding *via* an allylic rearrangement, to give the 1-$\eta^1$-cyclopropenyl derivatives $[Re(CRCR{=}CH)(CO)_5]$ [200].

Thermal decarbonylations of the acyl derivatives $[Re(COR)(CO)_5]$ (R = $CH_3$ to $C_9H_{19}$; $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$) to give the corresponding alkyl derivatives are reported in Chapter 4 of this thesis.

### 1.4.4.2 Reaction of [Re(COR)(CO)$_5$] with Neutral Nucleophiles

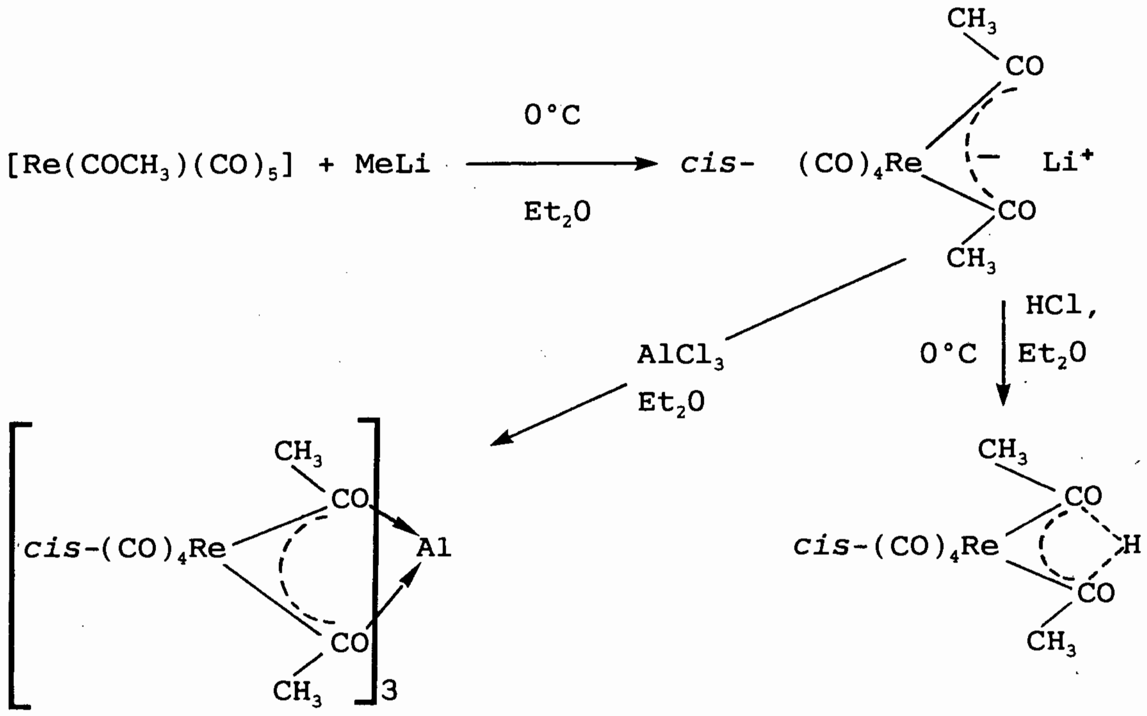
[Re(p-ClC$_6$H$_4$CO)(CO)$_5$] has been reacted with triphenylphosphine to give the phosphine-substituted aryl species [189] (equation 83)

$$[\mathrm{Re(p\text{-}ClC_6H_4CO(CO)_5]} + \mathrm{PPh_3} \longrightarrow \textit{cis}\text{-}[\mathrm{Re(p\text{-}ClC_6H_4)(CO)_4(PPh_3)}] + \mathrm{CO} \qquad (83)$$

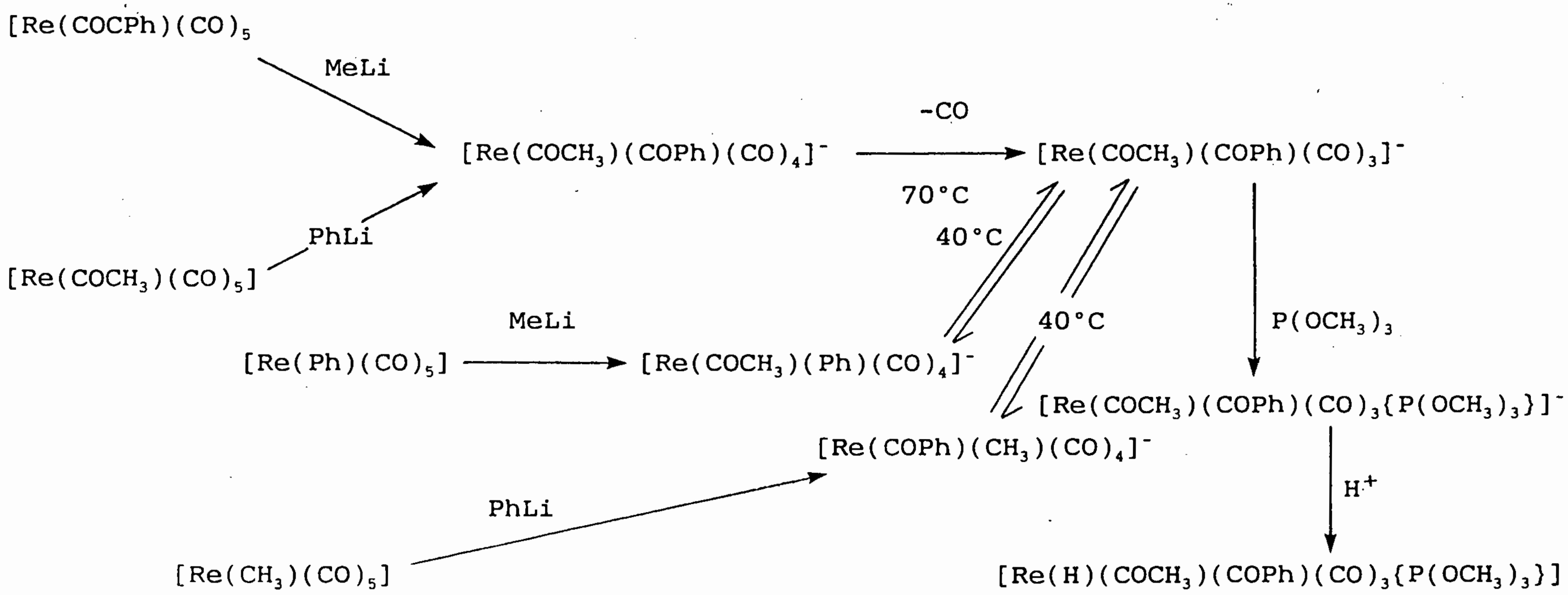
The reaction of [Re(m-ClC$_6$H$_4$CO(CO)$_5$] with PPh$_3$ proceeds similarly [189].

### 1.4.4.3 Reaction of [Re(COR)(CO)$_5$] with Anionic Nucleophiles

Two reactions of this type will be discussed. The first was reported by Lukehart *et al.* [201] who reacted acetyl rheniumpentacarbonyl with methyllithium followed by AlCl$_3$. They observed that the lithium reagent attacked a co-ordinated CO (equation 84).



**41** **42** (84)



Scheme 21 Reaction of [Re(COR)(CO)$_5$] (R = $CH_3$, $C_6H_5$) with lithium reagents [202]

Casey and Sheck subsequently reacted acetyl and benzoyl rheniumpentacarbonyl with lithium reagents [202] (see Scheme 21).

### 1.4.4.4 Reaction of $[\mathrm{Re(COR)(CO)_5}]$ with Transition Metal Hydrides

Martin *et al* showed that $[\mathrm{Re(COEt)(CO)_5}]$ will only react with $[\mathrm{Re(H)(CO)_5}]$ after carbonyl ligand dissociation [194] (equation 85). This implies that the metal and not the acyl carbonyl is the site of nucleophilic attack by transition metal hydrides on acyl complexes.

$$[\mathrm{Re(COEt)(CO)_5}] \xrightarrow{\mathrm{CH_3CN}} [\mathrm{Re(COEt)(CO)_4(CH_3CN)}]$$

$$\xrightarrow{[\mathrm{Re(H)(CO)_5}]} [\mathrm{Re\{Re(CO)_5\}(CO)_4(CH_3CN)}] \xrightarrow{\mathrm{CO}} \mathrm{CH_3CN} + [\mathrm{Re_2(CO)_{10}}] \qquad (85)$$

## 1.5 CONCLUSIONS

It has been shown that while a wide variety of alkyl (and acyl) derivatives of manganese- and rheniumpentacarbonyl have been prepared, very few simple n-alkyl derivatives are known. For manganese, only methyl, ethyl, n-propyl and i-propyl manganesepentacarbonyl have been reported and the list is even shorter for rhenium - only methyl, ethyl and i-butyl rheniumpentacarbonyl are known. This is in part due to the remarkably high instability of $[\mathrm{Mn(C_2H_5)(CO)_5}]$ and $[\mathrm{Mn(n\text{-}C_3H_7)(CO)_5}]$, which may have deterred researchers from investigating this field any further. The synthetic routes to these alkyl and acyl derivatives vary, but the most widely used pathway involves treating $\mathrm{Na[M(CO)_5]}$ (M = Mn,Re) with the appropriate alkyl halide or acyl chloride.

Thermal decarbonylation has proved to be useful in cases where the manganese- or rheniumpentacarbonyl anion will not react with the alkyl halide in question.

Reactions of these alkyl derivatives are extensive, the most common being reaction with a neutral nucleophile in order to induce alkyl migration. The alkyl migration reaction has important implications in the field of catalysis, thus, reactions with synthesis gas ($CO/H_2$) yield some novel products. Because of the weaker Mn-C(alkyl) bond cf. the Re-C(alkyl) bond, manganesepentacarbonyl alkyl derivatives have been more widely studied in terms of reactivity.

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# CHAPTER 2

# THE SYNTHESIS AND CHARACTERIZATION OF LONG CHAIN ACYL AND ALKYL COMPOUNDS OF THE TYPES $[Mn(COR)(CO)_5]$, $[Mn(R)(CO)_5]$, $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ and $[(CO)_5Mn(CH_2)_nMn(CO)_5]$

## 2.1 INTRODUCTION

The first reported synthesis of the simplest manganesepentacarbonyl alkyl species, methyl manganesepentacarbonyl, was by Closson *et al.* in 1957 [1]. Reaction of $Na[Mn(CO)_5]$ with $CH_3I$ gave the required $[Mn(CH_3)(CO)_5]$. In 1958, Hieber and Wagner followed suit with the synthesis of ethyl and n-propyl manganesepentacarbonyl [2]. However, these latter two complexes were subsequently found to be extremely unstable [3], decomposing in the dark under vacuum at -15°C. The n-propyl derivative was found to be even more unstable than the ethyl derivative and it may therefore have been assumed that the n-butyl derivative would be even more unstable, followed by the n-pentyl etc. This assumption may have deterred even the most determined researcher from further investigation into manganesepentacarbonyl alkyl species. However, some discrepency exists in the literature as to the nature of the decomposition products and reasons for the instability of ethyl manganesepentacarbonyl. One school of thought seems to hold with the idea that $[Mn(C_2H_5)(CO)_5]$ may decompose *via* ß-hydride alkene elimination to give $[Mn(H)(CO)_5]$ and ethylene [4-6]. However, the more popular opinion now seems to be that $[Mn(C_2H_5)(CO)_5]$ decomposes *via* carbonyl insertion to give the propionyl compound, $[Mn(COC_2H_5)(CO)_5]$ [7,8,9]. This is supported by the large rate constant for the carbonylation reaction measured for $[Mn(C_2H_5)(CO)_5]$ [10]. Indeed, Gismondi and Rausch [7] have thermally degraded $[Mn(C_2H_5)(CO)_5]$ and isolated $[Mn(COC_2H_5)(CO)_5]$ as the product. They also synthesized and characterized a pure sample of $[Mn(COC_2H_5)(CO)_5]$ and found it to be identical in all respects to the "$[Mn(C_2H_5)(CO)_5]$" reported by Hieber and Wagner. The first actual synthesis of $[Mn(C_2H_5)(CO)_5]$ was in fact therefore reported by Calderazzo and Cotton in 1962 [10]. In order to resolve this discrepancy we synthesized $[Mn(C_2H_5)(CO)_5]$ and followed its decomposition by $^1H$ NMR spectroscopy. The observed product was indeed $[Mn(COC_2H_5)(CO)_5]$ (and not $[Mn(H)(CO)_5]$ and $C_2H_4$) and this prompted us to successfully attempt the synthesis of long chain alkyl (LCA) manganesepentacarbonyl species with the idea that a LCA complex may in fact undergo the carbonylation process slower than the corresponding short chain alkyl (SCA) complexes, and thus be more stable.

In fact, the majority of studies on transition metal alkyl complexes ($L_nMR$) as models for catalytic intermediates have involved SCA groups ($R = CH_3$, $C_2H_5$, $C_3H_7$) whereas there have been relatively few studies on the longer chain homologues. Studies on the SCA complexes can provide information on chain growth processes, whereas studies on the LCA complexes may provide information about the chain termination steps which are important in catalytic reactions such as Ziegler-Natta polymerizations [11] and the Fischer-Tropsch process [12], where the preferential formation of a product of a particular carbon chain number is desirable. It has been shown that many reactions of transition metal alkyl complexes relevant to catalysis depend on the length of the alkyl chain [13-16]. Berke and Hoffmann [17] have also reported that activation parameters for alkyl migration in metal alkyl complexes depend on the number of carbon atoms in the alkyl chain.

Numerous investigations into the rate of migratory carbonyl insertion (and the reverse reaction, decarbonylation) for $[Mn(R)(CO)_5]$ (R = SCA) have been carried out [9,14,18-24] and all reports seem to be in agreement with the fact that the rates of both carbonylation and decarbonylation follow the order R = n-Pr>Et>Me, and that the reactions proceed by migration of the alkyl group onto an adjacent carbonyl ligand rather than by direct CO insertion.

The particular question we wished to address was whether or not the LCA groups would migrate even faster than the SCA groups, perhaps resulting in even greater instability, or whether the rate of migratory insertion would reach a peak at a particular chain length and then, due to steric factors, slow down.

Binuclear transition metal alkyls, which may be a closer approximation to a catalyst surface, have also been proposed as models for catalytic intermediates. Besides their importance in catalysis, binuclear transition metal alkyls are interesting in their own right. They may be expected to show different reactivity patterns to their mononuclear analogues, *e.g.* bridging hydrocarbyl ligands could be involved in rearrangements which are not a viable process for the mononuclear alkyls and, therefore, studies on these compounds may result in a wealth of new chemical knowledge.

We now report our results on the synthesis and characterization of $[Mn\{(CH_2)_nCH_3\}(CO)_5]$(n = 0 to 8, 10 to 17), $[(CO)_5Mn(CH_2)_nMn(CO)_5]$(n = 4 to 8; 10), $[Mn\{CO(CH_2)_nCH_3\}(CO)_5]$(n = 0 to 8; 10; 12; 14; 16) and $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$(n = 4 to 8;10). Reactivity studies are reported in Chapter 3 of this thesis.

## 2.2 SYNTHESIS AND CHARACTERIZATION

### 2.2.1 MONONUCLEAR ACYL COMPOUNDS $[Mn(COR)(CO)_5]$ (R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

Acetyl, 1 (R = $CH_3$)[25], propionyl, 2 (R = $C_2H_5$)[25], butanoyl, **3** (R = n-$C_3H_7$)[9] and hexanoyl, **5** (R = $C_5H_{11}$)[26] manganesepentacarbonyl have been reported previously. They were all prepared in good yield by the reaction of the manganesepentacarbonyl anion with the appropriate acyl chloride (equation 1).

$$\mathrm{Na[Mn(CO)_5] + RCOCl \xrightarrow[25^\circ C]{THF} [Mn(COR)(CO)_5] + NaCl} \qquad (1)$$

(R = $CH_3$, $C_2H_5$, n-$C_3H_7$, n-$C_5H_{11}$)

The syntheses of the new acyl compounds, $[Mn(COR)(CO)_5]$ (R = n-$C_4H_9$, **4**; n-$C_6H_{13}$, **6**; n-$C_7H_{15}$, **7**; n-$C_8H_{17}$, **8**; n-$C_9H_{19}$, **9**; n-$C_{11}H_{23}$, **10**; n-$C_{13}H_{27}$, **11**; n-$C_{15}H_{31}$, **12**; n-$C_{17}H_{35}$, **13**) are now reported. These new compounds were all prepared as shown in equation 1. Compounds **1**, **2**, **3** and **5** were also prepared by us in this manner.

All the compounds (**1-13**) were isolated as pale yellow solids which are relatively stable, both thermally and to air. They are also fairly stable in solution when kept under nitrogen. They have been fully characterized by IR, $^1H$ and $^{13}C$ NMR, elemental analysis and mass spectroscopy. The data are presented in Tables 2.1 - 2.4.

## IR

The IR spectra in the $\nu$(CO) region (see Table 2.1) are in good agreement with the values reported for other $[Mn(COR)(CO)_5]$ species [26,27] and show the expected number of peaks for $[M(COR)(CO)_5]$ species, [28] *viz.*. $A_1$ (2112cm$^{-1}$), B (2048cm$^{-1}$), E (2006cm$^{-1}$), $A_1$ (2000cm$^{-1}$) and acyl (1658$^{-1}$). There is no significant variation in $\nu$(CO) upon changing the length of the alkyl chain.

Table 2.1

Data for $[Mn(COR)(CO)_5]$

| R | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) (cm$^{-1}$)$^a$ | Elemental Analysis C;found(calcd) | H;found(calcd) |
|---|---|---|---|---|---|---|
| $CH_3$ | 1 | 61 | 54–55 | 2113w, 2050w, 2010brs, 1660w | 35.1(35.2) | 1.4(1.3) |
| $C_2H_5$ | 2 | 37 | 55–57 | 2112w, 2048w, 2008s, 2001s, 1658w | 38.1(38.1) | 1.9(2.0) |
| n-$C_3H_7$ | 3 | 38 | 45–47 | 2112w, 2048w, 2007s, 2000s, 1661w | 41.1(40.6) | 2.8(2.7) |
| n-$C_4H_9$ | 4 | 42 | 35–37 | 2112w, 2048w, 2006s, 2000s, 1658w | 43.1(42.9) | 3.1(3.2) |
| n-$C_5H_{11}$ | 5 | 43 | 33–35 | 2112w, 2048w, 2006s, 2000s, 1658w | 44.7(44.9) | 3.9(3.8) |
| n-$C_6H_{13}$ | 6 | 40 | 28–30 | 2111w, 2048w, 2006s, 2000s, 1652w | 47.3(46.8) | 4.3(4.3) |
| n-$C_7H_{15}$ | 7 | 38 | 29–31 | 2112w, 2048w, 2006s, 2000s, 1658w | 48.6(48.5) | 4.9(4.7) |
| n-$C_8H_{17}$ | 8 | 42 | 27–29 | 2112w, 2048w, 2006s, 2000s, 1652w | 50.8(50.0) | 5.3(5.1) |
| n-$C_9H_{19}$ | 9 | 46 | 28–29 | 2112w, 2048w, 2006s, 2000s, 1658w | 53.2(53.7) | 5.2(5.7) |
| n-$C_{11}H_{23}$ | 10 | 38 | 27–30 | 2112w, 2048w, 2006s, 2000s, 1653w | 54.2(54.0) | 6.2(6.1) |
| n-$C_{13}H_{27}$ | 11 | 29 | 36–39 | 2111w, 2048w, 2006s, 2000s, 1658w | 56.0(56.2) | 6.3(6.7) |
| n-$C_{15}H_{31}$ | 12 | 32 | 44–46 | 2112w, 2048w, 2006s, 2000s, 1658w | 57.3(58.1) | 7.1(7.2) |
| n-$C_{17}H_{35}$ | 13 | 38 | 48–50 | 2112w, 2048w, 2006s, 2000s, 1658w | 59.5(59.7) | 7.5(7.6) |

a: in hexane, w = weak, s = strong, brs = broad strong

## Table 2.2

$^1H$ NMR Data for $[Mn(COR)(CO)_5]^a$

| R | Cmpd No | $MnCOC\underline{H_2}$ | $MnCOCH_2C\underline{H_2}$ | $MnCOCH_2CH_2(C\underline{H_2})_x$ | $C\underline{H_3}$ |
|---|---|---|---|---|---|
| $CH_3$ | 1 | | | | 2.58s |
| $C_2H_5$ | 2 | 2.93q(2H) | | | 0.95tr |
| n-$C_3H_7$ | 3 | 2.90tr(2H) | 1.50c(2H) | | 0.86tr |
| n-$C_4H_9$ | 4 | 2.86tr(2H) | 1.42c(2H) | 1.22tr(2H) | 0.84tr |
| n-$C_5H_{11}$ | 5 | 2.88tr(2H) | 1.46c(2H) | 1.28bs(4H) | 0.89tr |
| n-$C_6H_{13}$ | 6 | 2.89tr(2H) | 1.45c(2H) | 1.22bs(6H) | 0.84tr |
| n-$C_7H_{15}$ | 7 | 2.91tr(2H) | 1.49c(2H) | 1.30bs(8H) | 0.86tr |
| n-$C_8H_{17}$ | 8 | 2.92tr(2H) | 1.48c(2H) | 1.24bs(10H) | 0.87tr |
| n-$C_9H_{19}$ | 9 | 2.90tr(2H) | 1.44c(2H) | 1.22bs(12H) | 0.85tr |
| n-$C_{11}H_{23}$ | 10 | 2.93tr(2H) | 1.50c(2H) | 1.26bs(16H) | 0.87tr |
| n-$C_{13}H_{27}$ | 11 | 2.92tr(2H) | 1.48c(2H) | 1.25bs(20H) | 0.87tr |
| n-$C_{15}H_{31}$ | 12 | 2.91tr(2H) | 1.48c(2H) | 1.24bs(24H) | 0.87tr |
| n-$C_{17}H_{35}$ | 13 | 2.90tr(2H) | 1.48c(2H) | 1.24bs(28H) | 0.87tr |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm), s = singlet,
bs = broad singlet, tr = triplet, q = quartet,
c = complex signal

### $^1H$ and $^{13}C$ NMR

Assignments of the $^1H$ and $^{13}C$ NMR spectra were made by comparison of all of the NMR data for these compounds, and by comparison of this data with the NMR data reported for $[Mn(COCH_3)(CO)_5]$ [29], $[Mn(COC_2H_5)(CO)_5]$ [3] and $[Mn\{CO(CH_2)_4CH_3\}(CO)_5]$ [26]. As an example of the results obtained the $^1H$ and $^{13}C$ NMR spectra of $[Mn(CO\{CH_2\}_8CH_3)(CO)_5]$ are shown in Figures 1 and 2, respectively.

### $^1H$ NMR

From the $^1H$ NMR data (Table 2.2) it can be seen that

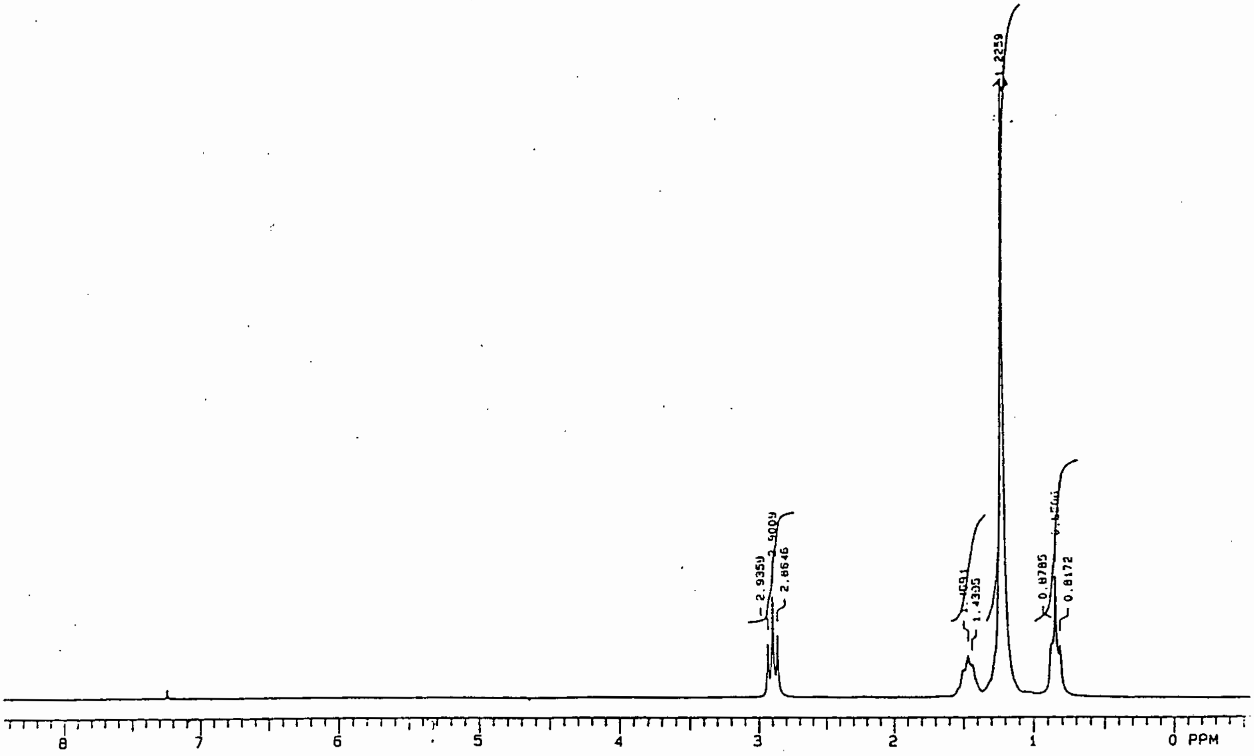


Figure 1 $^{1}H$ NMR Spectrum of $[Mn\{CO(CH_2)_8CH_3\}(CO)_5]$ (in $CDCl_3$)

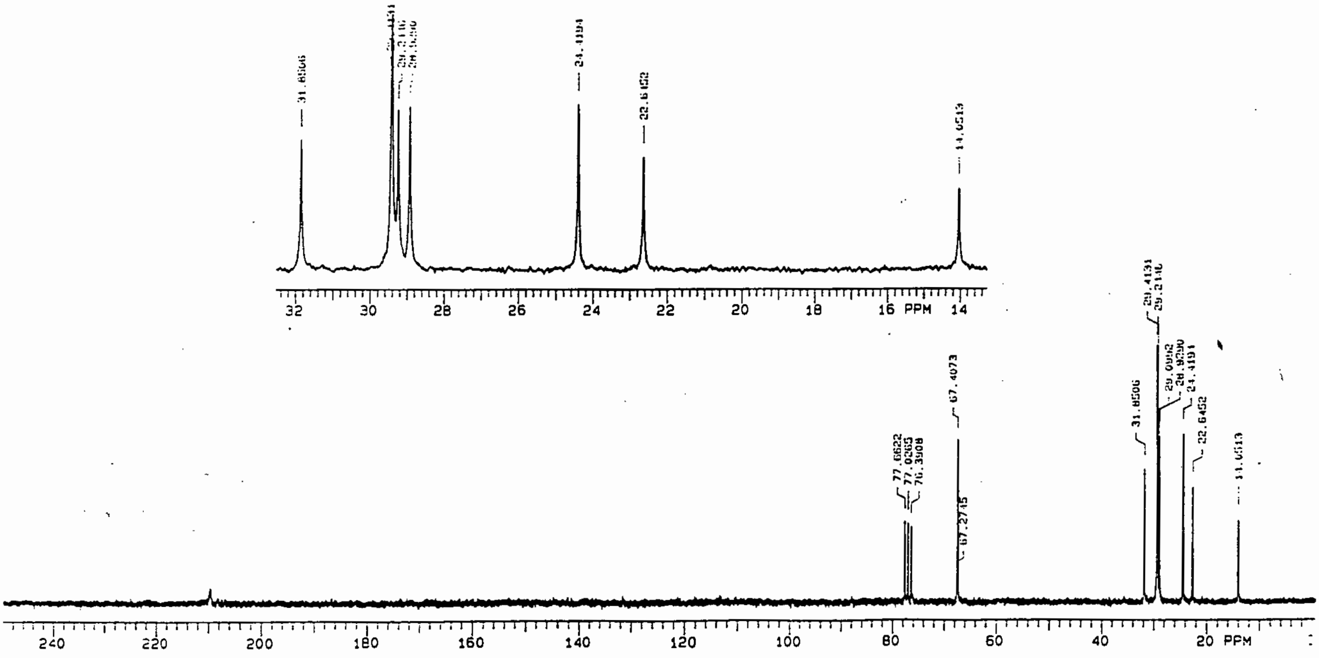


Figure 2 $^{13}C$ NMR Spectrum of $[Mn\{CO(CH_2)_8CH_3\}(CO)_5]$
(X = Solvent ($CDCl_3$))

separate resonances are observed for the methyl protons of the alkyl chain and the α and β protons in these acyl complexes. The remaining methylene protons appear as a broad singlet. It can be seen that there is no significant variation in chemical shift with variation in the length of the alkyl chain, and integration is thus the only way to distinguish between these compounds using $^1H$ NMR spectroscopy. The same was found for analogous rhenium compounds [31] and for related LCA iron and ruthenium compounds [32].

## $^{13}C$ NMR

The $^{13}C$ NMR data are presented in Table 2.3. The $^{13}C$ NMR spectra of $[Mn(COCH_3)(CO)_5]$ [29] and $[Mn(COC_2H_5)(CO)_5]$ [30] have previously been reported. The spectra obtained by us showed the terminal carbonyl resonances to be at the usual positions [33] and not resolved. They did not show any variation in chemical shift with increase in the length of the alkyl chain (with the exception of $[Mn(COCH_3)(CO)_5]$). For compounds 1-8, all the carbon atoms of the alkyl chain were assigned, whereas for compounds 9-13 the peaks due to the central methylene carbon atoms were not resolved. This was also observed for substituted n-alkanes, $CH_3(CH_2)_nX$ [32]. When compared to the $^{13}C$ NMR spectra of the starting acyl chlorides [34], it is apparent that the manganese atom only exerts an influence on the first two carbon atoms of the alkyl chain. Thus, as was also found for the analogous series of rhenium acyl compounds [31], the influence that the metal has on the chemical shifts of carbon atoms in the methylene chain diminishes along the chain and is only really apparent in the α and β methylene positions.

## MASS SPECTRA

The mass spectra of 1-13 are reported in Table 2.4 and are all similar and relatively simple. Most of them show

**Table 2.3**

$^{13}C$ NMR Data for $[Mn(COR)(CO)_5]^a$

| R | Cmpd No | CO$^b$ | MnCO-$\underline{C}H_2$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{17}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | 1 | 256 | 53.40 | | | | | | | | | | | | | | | | |
| $C_2H_5$ | 2 | 210 | 61.42 | 10.04 | | | | | | | | | | | | | | | |
| n-$C_3H_7$ | 3 | 211 | 69.21 | 30.09 | 14.30 | | | | | | | | | | | | | | |
| n-$C_4H_9$ | 4 | 209 | 67.00 | 26.47 | 22.03 | 13.78 | | | | | | | | | | | | | |
| n-$C_5H_{11}$ | 5 | 212 | 69.15 | 32.89 | 25.90 | 24.27 | 15.67 | | | | | | | | | | | | |
| n-$C_6H_{13}$ | 6 | 210 | 67.30 | 31.53 | 28.50 | 24.28 | 22.38 | 13.86 | | | | | | | | | | | |
| n-$C_7H_{15}$ | 7 | 211 | 68.10 | 32.37 | 29.79 | 25.67 | 25.13 | 23.30 | 14.72 | | | | | | | | | | |
| n-$C_8H_{17}$ | 8 | 211 | 68.69 | 33.14 | 30.71 | 30.46 | 30.28 | 25.75 | 23.95 | 15.34 | | | | | | | | | |
| n-$C_9H_{19}$ | 9 | 210 | 67.40 | 31.85 | {29.41 → | | | → 28.93}$^c$ | 24.42 | 22.65 | 14.05 | | | | | | | | |
| n-$C_{11}H_{23}$ | 10 | 212 | 68.79 | 33.28 | {30.97 → | | | | | → 30.31}$^c$ | 25.81 | 24.05 | 15.46 | | | | | | |
| n-$C_{13}H_{27}$ | 11 | 211 | 68.46 | 32.97 | {30.69 → | | | | | | | → 29.99}$^c$ | 25.48 | 23.73 | 15.13 | | | | |
| n-$C_{15}H_{31}$ | 12 | 211 | 68.00 | 34.91 | {30.24 → | | | | | | | → 29.52}$^c$ | 26.71 | 25.57 | 25.01 | 23.27 | 14.68 | | |
| n-$C_{17}H_{35}$ | 13 | 212 | 68.80 | 35.72 | {31.08 → | | | | | | | | | | → 30.33}$^c$ | 26.38 | 25.81 | 24.08 | 15.49 |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm)
b:broad, weak signal
c:peaks for these carbon atoms were not resolved or assigned

## Table 2.4

## Mass Spectral Data for [Mn(COR)(CO)$_5$]

| Possible Assignments[a] | Cmpd No | | | | | Relative Peak Intensities[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| Parent, M | 18 | 0 | 0 | 4 | 5 | 8 | 3 | 5 | 4 | 5 | 0 | 0 | 0 |
| M-CO | 47 | 2 | 0 | 6 | 7 | 6 | 5 | 10 | 6 | 8 | 0 | 0 | 0 |
| M-2CO | 19 | 0 | 0 | 11 | 8 | 4 | 6 | 9 | 4 | 6 | 0 | 0 | 0 |
| M-3CO | 9 | 0 | 0 | 8 | 8 | 12 | 5 | 8 | 3 | 5 | 0 | 0 | 0 |
| M-4CO | 20 | 0 | 0 | 13 | 17 | 20 | 20 | 21 | 10 | 8 | 0 | 2 | 0 |
| M-5CO | 68 | 4 | 17 | 20 | 23 | 24 | 36 | 54 | 50 | 70 | 40 | 43 | 38 |
| M-6CO | 18 | 0 | 10 | 31 | 40 | 52 | 60 | 100 | 72 | 100 | 92 | 100 | 100 |
| Mn(CO)$_5$ | 17 | 0 | 0 | 38 | 100 | 100 | 100 | 100 | 100 | 100 | 18 | 100 | 0 |
| M-4CO-CH$_3$ | 23 | 0 | 0 | 6 | 10 | 0 | 0 | 0 | 8 | 0 | 0 | 0 | 0 |
| M-5CO-CH$_3$ | 32 | 0 | 11 | 0 | 10 | 0 | 10 | 0 | 30 | 18 | 0 | 0 | 10 |
| M-5CO-C$_2$H$_5$ | | 0 | 22 | 12 | 4 | 4 | 7 | 14 | 8 | 4 | 0 | 0 | 0 |
| M-5CO-C$_3$H$_7$ | | | 32 | 6 | 10 | 0 | 10 | 4 | 9 | 10 | 0 | 0 | 0 |
| M-5CO-C$_4$H$_9$ | | | | 43 | 12 | 10 | 24 | 10 | 10 | 13 | 0 | 10 | 0 |
| M-5CO-C$_5$H$_{11}$ | | | | | 0 | 0 | 10 | 6 | 10 | 13 | 10 | 22 | 1 |
| M-5CO-C$_6$H$_{13}$ | | | | | | 10 | 0 | 16 | 11 | 13 | 38 | 10 | 11 |
| M-5CO-C$_7$H$_{15}$ | | | | | | | 0 | 17 | 8 | 12 | 9 | 10 | 0 |
| M-5CO-C$_8$H$_{17}$ | | | | | | | | 7 | 6 | 11 | 10 | 0 | 0 |
| M-5CO-C$_9$H$_{19}$ | | | | | | | | | 10 | 12 | 9 | 11 | 0 |
| M-5CO-C$_{10}$H$_{21}$ | | | | | | | | | | 10 | 12 | 0 | 0 |
| M-5CO-C$_{11}$H$_{23}$ | | | | | | | | | | 12 | 20 | 0 | 12 |
| M-5CO-C$_{12}$H$_{25}$ | | | | | | | | | | | 50 | 9 | 0 |
| M-5CO-C$_{13}$H$_{27}$ | | | | | | | | | | | 0 | 13 | 9 |
| M-5CO-C$_{14}$H$_{29}$ | | | | | | | | | | | | 8 | 9 |
| M-5CO-C$_{15}$H$_{31}$ | | | | | | | | | | | | 48 | 13 |
| M-5CO-C$_{16}$H$_{33}$ | | | | | | | | | | | | | 18 |
| M-5CO-C$_{17}$H$_{35}$ | | | | | | | | | | | | | 21 |
| M-5CO-H/M-4CO-C$_2$H$_5$ | 0 | 0 | 0 | 10 | 0 | 10 | 2 | 0 | 0 | 3 | 0 | 10 | 0 |

a:all ions have a single positive charge

b:peak intensities relative to base peaks for [Mn(CO)$_5$]$^+$, [M-6CO]$^+$ or [CO]$^+$

parent molecular ions and the major fragmentation pathway is sequential loss of carbonyl groups, followed by sequential loss of methylene fragments.

All spectra exhibit most of the peaks characteristic of $[Mn(COR)(CO)_5]$ species, *viz.*. the ions $[Mn(CO)_5]^+$ ($^m/_e$ 195); $[Mn(CO)_2]^+$ ($^m/_e$ 111); $[Mn(CO))]^+$ ($^m/_e$ 83); [MnH] ($^m/_e$ 56); $[Mn]^+$ ($^m/_e$ 55) and $[CO]^+$ ($^m/_e$ 28).

## 2.2.2 BINUCLEAR ACYL COMPOUNDS $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5(n = 4-8;10)$

The binuclear acyl compounds $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$ [35,36], $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5](n = 5,6)$[37] and $[(CO)_5MnCO(CH_2)_8COMn(CO)_5]$ [26] have previously been reported. We now report some further characterization data for these compounds, and the synthesis of the new compounds $[(CO)_5COMn(CH_2)_nCOMn(CO)_5]$ (n = 7,10) and $[(CO)_5MnCOCH_2$-$CH(CH_3)CH_2CH_2COMn(CO)_5]$. These compounds were all prepared by the reaction of $Na[Mn(CO)_5]$ with the appropriate diacyl chloride, as shown in equations 2 and 3

$$2Na[Mn(CO)_5] + ClCO(CH_2)_nCOCl \xrightarrow[25°C]{THF} 2NaCl + [(CO)_5MnCO(CH_2)_nCOMn(CO)_5)] \quad (2)$$

(n = 4-8;10)

and

$$2Na[Mn(CO)_5] + ClCOCH_2CH(CH_3)CH_2CH_2COCl \xrightarrow[25°C]{THF} [(CO)_5MnCOCH_2CH(CH_3)CH_2CH_2COMn(CO)_5] + 2NaCl \quad (3)$$

All the compounds (14-20; see Table 2.5) were isolated as cream/off-white microcrystalline solids, which, like their mononuclear analogues, are stable both thermally and to air and in solution when kept under nitrogen. They have been fully characterized by IR, $^1H$ and $^{13}C$ NMR, elemental analysis and mass spectroscopy. The results are presented in Tables 2.5 - 2.8.

### IR

The IR spectra in the $\nu(CO)$ region (see Table 2.5) are in good agreement with the values reported for $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ (n = 4-6,8) species [26, 35-37] and, like their mononuclear analogues, show the expected number of peaks for $[M(COR)(CO)_5]$ species [28] (where $R = (CH_2)_nCOMn(CO)_5$), *viz.* $A_1$ (2114cm$^{-1}$), B (2050cm$^{-1}$), E and $A_1$ (2013cm$^{-1}$, broad) and acyl (1638cm$^{-1}$). There was no significant variation in $\nu(CO)$ upon changing the length of the bridging hydrocarbyl chain, or upon substituting one of the ß-hydrogens in the hydrocarbyl chain for a methyl group.

### $^1H$ and $^{13}C$ NMR

Assignments of the $^1H$ and $^{13}C$ NMR spectra were made by comparison of all of the NMR data for these compounds, and by comparison of this data with the $^1H$ NMR data reported for $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ (n = 4-6;8) [26,37]. As an example of the results obtained, the $^1H$ and $^{13}C$ NMR spectra of $[(CO)_5MnCO(CH_2)_7COMn(CO)_5]$ are shown in Figures 3 and 4, respectively.

### $^1H$ NMR

From the $^1H$ NMR data (Table 2.6), it can be seen that, as was noted for the mononuclear acyl compounds, separate resonances are observed only for the $\alpha$ and ß protons of the bridging alkyl chain. The remaining (central) methylene

Table 2.5

Data for $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$

| n | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) ($cm^{-1}$)[a] | Elemental Analysis | |
|---|---|---|---|---|---|---|
| | | | | | C;found(calcd) | H;found(calcd) |
| 4 | 14 | 86 | 119-224[b] | 2114w, 2050sh, 2014s, 1636w | 38.5(38.3) | 1.6(1.6) |
| 5 | 15 | 82 | 129–132 | 2114w, 2050sh, 2015s, 1638w | 39.1(39.6) | 2.0(1.9) |
| 6 | 16 | 78 | 97–99 | 2115w, 2052sh, 2014s, 1636w | 40.6(40.9) | 2.3(2.3) |
| 7 | 17 | 60 | 100–104[b] | 2116w, 2050sh, 2013s, 1638w | 41.7(41.9) | 2.3(2.6) |
| 8 | 18 | 62 | 96–97 | 2114w, 2052sh, 2014s, 1640w | 43.0(43.0) | 3.0(2.9) |
| 10 | 19 | 49 | 85–87 | 2112w, 2050sh, 2012s, 1638w | 45.3(45.1) | 3.2(3.4) |
| $CH_2CH(CH_3)CH_2CH_2$ | 20 | 33 | 100–103 | 2114w, 2049sh, 2012s, 1640w | 39.4(39.6) | 2.2(1.9) |

a:in $CHCl_3$, w = weak, sh = shoulder, s = strong
b:decomposed

**Table 2.6**
**$^1$H NMR Data for $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]^a$**

| n | Cmpd No | $MnCO\underline{CH_2}$ | $MnCOCH_2\underline{CH_2}$ | $MnCOCH_2CH_2(\underline{CH_2})_x$ |
|---|---|---|---|---|
| 4 | 14 | 2.91tr(4H) | 1.44tr(4H) | |
| 5 | 15 | 2.86tr(4H) | 1.41bs(4H) | 1.18bs(2H) |
| 6 | 16 | 2.88bs(4H) | 1.42bs(4H) | 1.20bs(4H) |
| 7 | 17 | 2.91bs(4H) | 1.47bs(4H) | 1.23bs(6H) |
| 8 | 18 | 2.90tr(4H) | 1.47bs(4H) | 1.22bs(8H) |
| 10 | 19 | 2.82bs(4H) | | 1.18bs(16H) |
| $CH_2CH(CH_3)CH_2CH_2$ | 20 | 2.84bs(4H) | 2.15bs(2H) | 1.38c(1H);0.81bs(3H)($CH_3$) |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm), bs = broad singlet
tr = triplet, c = complex signal

protons appear as a broad singlet. The only exception to this is compound **20**, $[(CO)_5MnCOCH_2CH(CH_3)CH_2CH_2COMn(CO)_5]$, where the methyl group renders the central protons inequivalent and they thus resonate as separate signals. A separate signal is also seen for the methyl group. The *α* protons on both sides of this hydrocarbyl chain do, however, resonate as one signal, as is the case for the unsubstituted hydrocarbyl chains.

### $^{13}$C NMR

The $^{13}$C NMR data are presented in Table 2.7. No $^{13}$C NMR data has previously been reported for any of these compounds. The terminal carbonyl resonances are at the expected positions and were not resolved. They showed no variation in chemical shift with variation in the length of the alkyl chain. For compounds **14-18** and **20**, separate resonances were observed for all of the different carbon atoms in the alkyl chain (carbon atoms at opposite ends of the

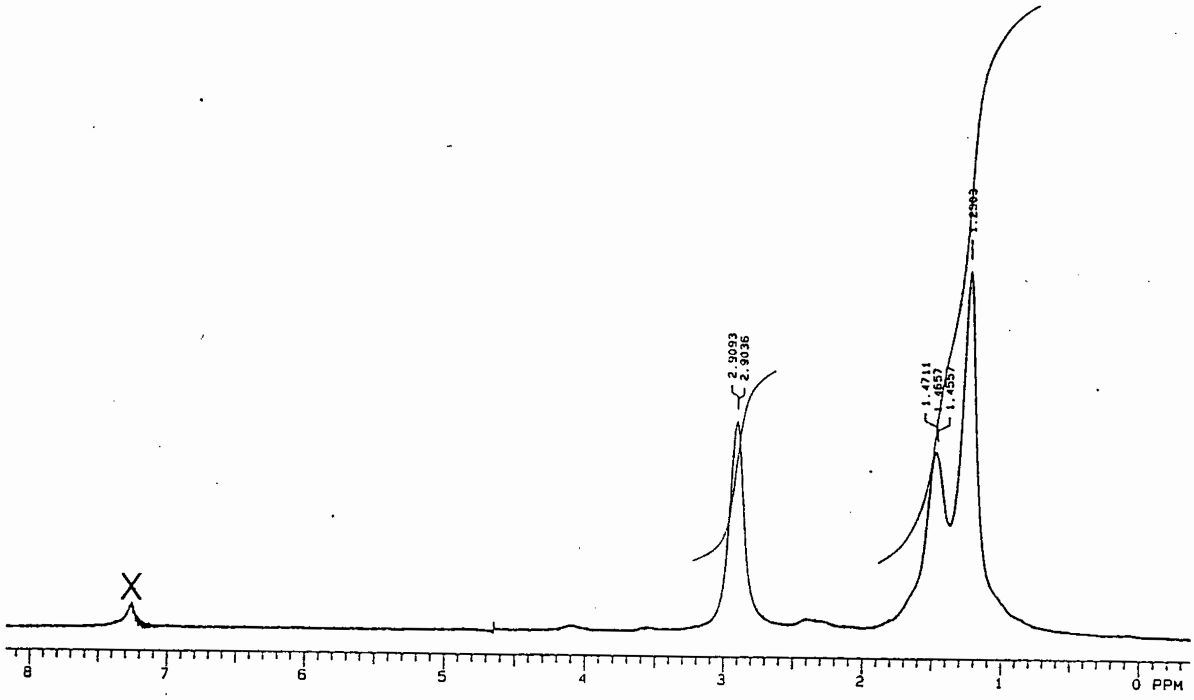


**Figure 3** $^{1}H$ NMR Spectrum of $[(CO)_5MnCO(CH_2)_7COMn(CO)_5]$
(X = solvent($CDCl_3$) impurity)

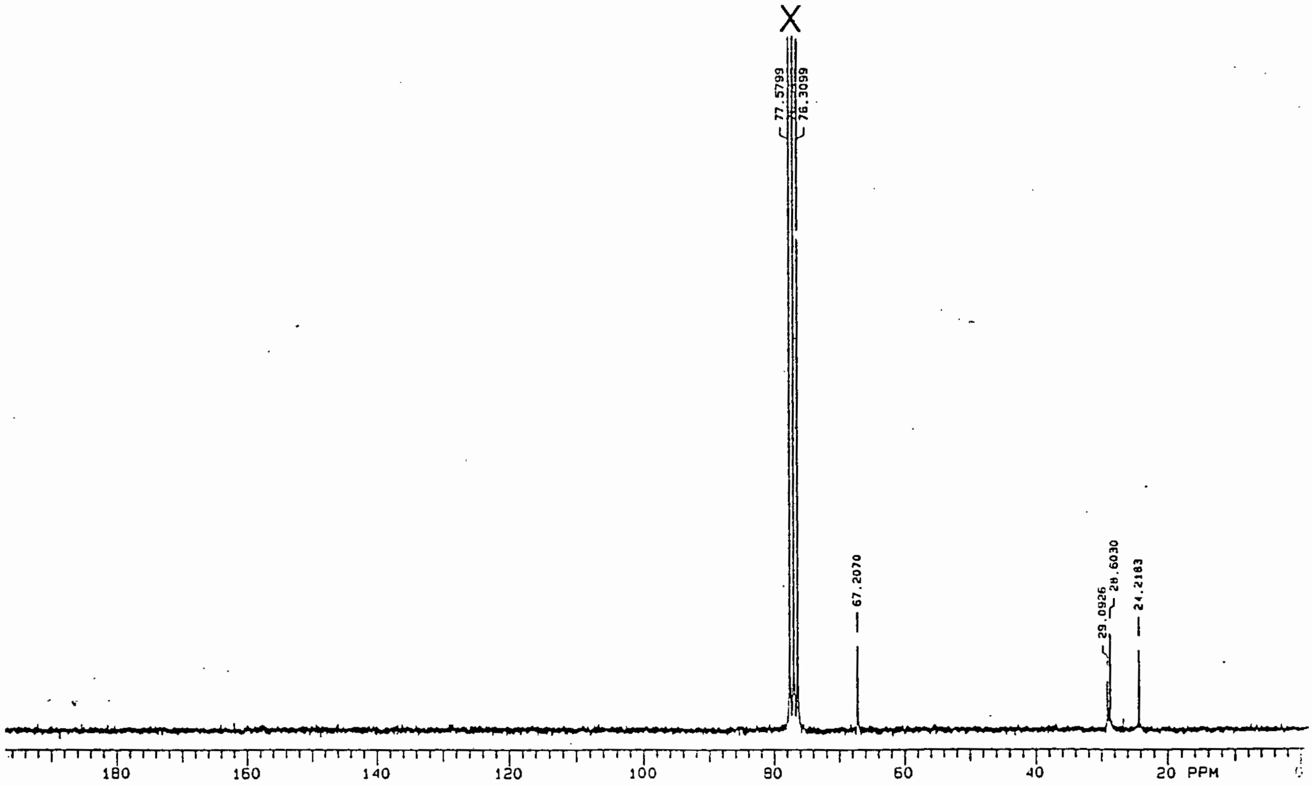


**Figure 4** $^{13}C$ NMR Spectrum of $[(CO)_5MnCO(CH_2)_7COMn(CO)_5]$
(X = solvent($CDCl_3$))

Table 2.7

$^{13}C$ NMR Data for $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]^a$

| n | Cmpd No | $CO^b$ (terminal) | $MnCO\underline{C}H_2$ ($\alpha$) | $C_2$ ($\beta$) | $C_3$ ($\gamma$) | $C_4$ ($\delta$) | $C_5$ ($\epsilon$) | $CH_3$ |
|---|---|---|---|---|---|---|---|---|
| 4 | 14 | 213 | 66.83 | 23.61 | | | | |
| 5 | 15 | 209 | 66.94 | 24.10 | 28.10 | | | |
| 6 | 16 | 209 | 67.13 | 24.15 | 28.64 | | | |
| 7 | 17 | 210 | 67.21 | 24.22 | 28.60 | 29.10 | | |
| 8 | 18 | 209 | 67.25 | 24.27 | 28.73 | 29.11 | | |
| 10 | 19 | 209 | 67.24 | 24.27 | {28.54 | → | 29.25}$^c$ | |
| $CH_2CH(CH_3)CH_2CH_2$ | 20 | 209 | 74.83<br>64.12 | 30.87 | 28.94<br>($CH_3\underline{C}H$) | | | 19.72 |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm)
b:broad, weak signal
c:peaks for these carbon atoms were not resolved or assigned

symmetrical alkyl chain are equivalent and will resonate as a single peak). For compound **19**, *i.e.* [$(CO)_5MnCO(CH_2)_{10}$-$COMn(CO)_5$], the peaks due to the central methylene carbon atoms were not resolved. The methyl substituent in compound **20** rendered the two $MnCOCH_2$ carbon atoms inequivalent and they thus gave rise to two separate signals. Compound **20** has a chiral centre, and, since the starting diacyl chloride was a mixture of optical isomers, compound **20** is itself a mixture of optical isomers. The protons attached to these two carbon atoms, however, did not appear as separate signals as they were one bond further away from the methyl group, which was too far away for the effect to be felt.

## MASS SPECTRA

The mass spectra of **14-20** are reported in Table 2.8. They are all similar and relatively simple. None of the compounds show parent molecular ions; the parent ion in all cases is $[M-Mn(CO)_5]^+$ ( = $M'$). The predominant fragmentation pathway is sequential loss of carbonyl groups (from $M'$), followed by sequential loss of methylene fragments. No mass spectral data for any of these compounds has previously been reported.

All spectra exhibit most of the peaks characteristic of $[Mn(COR)(CO)_5]$ species, *viz*.. the ions $[Mn(CO)_5]^+$ ($^m/_e$ 195); $[Mn(CO)_2]^+$ ($^m/_e$ 111); $[Mn(CO)^+$ ($^m/_e$ 83); $[MnH]^+]$ ($^m/_e$ 56); $[Mn]^+$ ($^m/_e$ 55) and $[CO]^+$ ($^m/_e$ 28).

### 2.2.3 MONONUCLEAR ALKYL COMPOUNDS OF THE TYPE $[Mn(R)(CO)_5](R = CH_3$ to $n-C_9H_{19}$, $n-C_{11}H_{23}$ to $n-C_{18}H_{37})$

Relatively few n-alkyl derivatives of manganese-pentacarbonyl have been prepared until now. The only examples in the literature are the methyl [1], ethyl [2,3,10] and n-propyl [10] derivatives. Other substituted

## Table 2.8

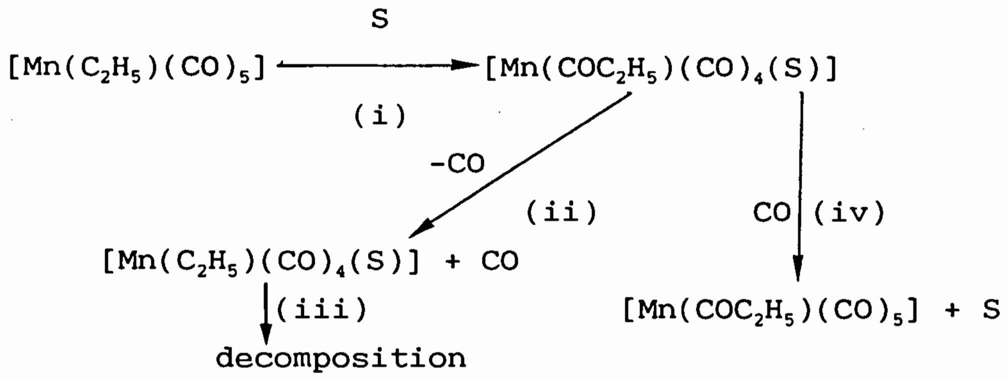
## Mass Spectral Data for $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$

| Possible Assignments[a] | Cmpd No | | | Relative Peak Intensities[b] | | | |
|---|---|---|---|---|---|---|---|
| | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Parent, M | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| M-Mn(CO)$_5$( = M$'$) | 15 | 5 | 5 | 12 | 4 | 11 | 6 |
| M$'$-CO | 11 | 6 | 0 | 0 | 0 | 0 | 0 |
| M$'$-2CO | 70 | 10 | 10 | 22 | 10 | 7 | 8 |
| M$'$-3CO | 70 | 12 | 32 | 12 | 7 | 10 | 15 |
| M$'$-4CO | 54[c] | 30 | 51 | 31 | 21 | 8 | 24 |
| M$'$-5CO | 32 | 17 | 37[c] | 52 | 92 | 13 | 10 |
| M$'$-6CO | 57 | 36 | 36 | 41 | 58[c] | 44 | 32 |
| M$'$-7CO | 30[c] | 22 | 20 | 38 | 60 | 75[c] | 41 |
| M$'$-7CO-Mn | 100 | 16 | 22[c] | 11 | 7 | 4 | 5 |
| M$'$-2CO-CH$_2$ | 0 | 55 | 0 | 0 | 0 | 0 | 0 |
| M$'$-3CO-CH$_2$ | 0 | 58 | 0 | 0 | 0 | 0 | 0 |
| M$'$-4CO-CH$_2$ | 0 | 66[c] | 0 | 0 | 0 | 0 | 0 |
| M$'$-5CO-CH$_2$ | 0 | 24 | 0 | 0 | 0 | 0 | 0 |
| M$'$-6CO-CH$_2$ | 0 | 17 | 12 | 0 | 0 | 0 | 0 |
| M$'$-7CO-CH$_2$ | 6 | 23[c] | 8 | 6 | 0 | 0 | 0 |
| M$'$-7CO-$C_2H_4$ | 23[c] | 27 | 18[c] | 9 | 34 | 12 | 16 |
| M$'$-7CO-$C_3H_6$ | 18 | 21[c] | 10 | 18[c] | 0 | 9 | 0 |
| M$'$-7CO-$C_4H_8$ | 100 | 6 | 8[c] | 28 | 36[c] | 13 | 14 |
| M$'$-7CO-$C_5H_{10}$ | - | 100 | 100 | 18[c] | 13[c] | 7 | 3 |
| M$'$-7CO-$C_6H_{12}$ | - | - | 78 | 22 | 7 | 12[c] | 3 |
| M$'$-7CO-$C_7H_{14}$ | - | - | - | 61 | 23 | 7 | |
| M$'$-7CO-$C_8H_{16}$ | - | - | - | - | 100 | 18[c] | |
| M$'$-7CO-$C_9H_{18}$ | - | - | - | - | - | 8 | |
| M$'$-7CO-$C_{10}H_{20}$ | - | - | - | - | - | 64 | |

a:all ions have a single positive charge
b:peak intensities relative to base peak at $^m/_e$ 28 ($[CO]^+$)
c:these assignments may be ambiguous

alkyl derivatives have, however, been reported, *e.g.* alkyl = $CH_2Ph$ [1], $CH_2CH(Ph)(CH_3)$ [21], $CH_2CH_2Ph$ [38] and $CH_2CH_2CH=C(Ph)(CH_3)$ [39]. The reason for this scarcity of $[Mn(R)(CO)_5]$ compounds is presumably a result of the extremely high instability of $[Mn(C_2H_5)(CO)_5]$, as reported by Green and Nagy [3]. It has thus been suggested that higher n-alkyl derivatives of manganesepentacarbonyl may be subject to the same instability [40]. As a result, we could find no reports of attempts to synthesize them, nor any investigations into their reactivity.

The reasons behind the instability of the ethyl (and n-propyl) derivatives have never been fully explained, although there are, two general schools of thought, as mentioned earlier. The first is that ethyl manganesepentacarbonyl can and does undergo the well-known ß-hydride alkene-elimination reaction, resulting in decomposition to (presumably) $[Mn(H)(CO)_5]$ and $C_2H_4$ [4]. The use of the trimethylsilyl group has been reported to result in more stable alkyl complexes because the ß-elimination reaction is effectively blocked. Thus the observation that $[Mn(CH_2SiMe_3)(CO)_5]$ is more stable than $[Mn(C_2H_5)(CO)_5]$ was attributed to the lack of ß-hydrogens in the former complex [4]. Since this time, however, other substituted alkyl manganesepentacarbonyl derivatives have been reported, *e.g.* $[Mn(CH_2CH_2Ph)(CO)_5]$ [38] and $[Mn\{CH_2CH_2CH=C(Ph)(CH_3)\}(CO)_5]$ [39]. These compounds also contain ß-hydrogens, but are relatively stable. The second proposal is that ethyl manganesepentacarbonyl decomposes *via* a very rapid carbonylation reaction to form propionyl manganesepentacarbonyl [8,9,30,41]. Thus, the carbonylation process for $[Mn(C_2H_5)(CO)_5]$ is so rapid [10] that some of the carbon monoxide liberated during the decomposition of this compound will react with the remaining $[Mn(C_2H_5)(CO)_5]$ to form the propionyl derivative, $[Mn(COC_2H_5)(CO)_5]$. We have in fact found the second proposal to be correct. We have followed the decomposition of $[Mn(C_2H_5)(CO)_5]$ by $^1H$ NMR and observed $[Mn(COC_2H_5)(CO)_5]$ as the major product, not $[Mn(H)(CO)_5]$ and ethylene. We propose the following scheme for the decomposition of $[Mn(C_2H_5)(CO)_5]$ in solution:



(S = a molecule of solvent, *e.g.* THF)

Scheme 1 Decomposition of Ethyl Manganesepentacarbonyl

Thus, the instability of ethyl (and n-propyl) manganesepentacarbonyl is probably due to the fact that the carbonylation process is so facile. This being the case, we decided that it may be quite possible that higher n-alkyl derivatives of manganesepentacarbonyl could very well be stable if the carbonylation process is somewhat slower for them. Indeed, for very large alkyl groups, such as n-heptadecyl (R = $(CH_2)_{16}CH_3$) this seemed very likely due to the alkyl group being so much larger than ethyl or n-propyl. Steric factors have been shown to be very important in carbonylation reactions of $[Mn(CH_2C_6H_4X)(CO)_5]$ systems [40]. We in fact find this to be the case for an extensive series of n-alkyl derivatives of manganesepentacarbonyl and we now report the synthesis of and characterization data for the compounds $[Mn(R)(CO)_5]$ where R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$ to n-$C_{18}H_{37}$. With the exception of the methyl, ethyl and n-propyl derivatives, all of these compounds are new. The majority of the compounds were stable both thermally, and to air for short periods of time.

The compounds with R = $C_2H_5$ to n-$C_9H_{19}$, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-

$C_{15}H_{31}$ and n-$C_{17}H_{35}$ were synthesized by thermal decarbonylation (in refluxing hexane) of the acyl precursors, as shown in equation 4

$$[Mn(COR)(CO)_5] \longrightarrow [Mn(R)(CO)_5] + CO \qquad (4)$$

For R = n-$C_{12}H_{25}$, n-$C_{14}H_{29}$, n-$C_{16}H_{33}$, n-$C_{18}H_{37}$, the compounds were synthesized by reaction of Na[Mn(CO)$_5$] with the appropriate n-alkyl bromide, as shown in equation 5.

$$Na[Mn(CO)_5] + RBr \xrightarrow[25^\circ C]{THF} [Mn(R)(CO)_5] + NaBr \qquad (5)$$

This latter synthetic pathway was previously thought to be inaccessible as it was assumed that a coordinating solvent such as THF would induce decomposition of the metal-alkyl species, as shown in steps (i) to (iii) of Scheme 1. However, since the alkyl migration process in these long chain alkyl (LCA) derivatives of manganese has been shown to be much slower than for the shorter chain analogues (see Chapter Three of this thesis), this mode of decomposition is not easily accessible for LCA species.

Owing to its high volatility, [Mn(CH$_3$)(CO)$_5$] was synthesized by a separate procedure, which has been outlined in Chapter Seven.

This now represents, to our knowledge, the most extensive series of n-alkyl complexes of a transition metal. Reactivity studies on this series could have important bearings on catalytic reactions where the migration of an alkyl group of a particular chain length plays a crucial role in determining product distribution. Berke and Hoffmann, on the basis of a molecular orbital study [17], predicted that the alkyl migration process should depend on the chain length of the alkyl group; our experimental results support this proposal (see Chapter Three). There have been several reports of rate studies on alkyl migration reactions of [Mn(R)$(CO)_5$] but these studies were limited to n-alkyl groups having no more than three carbon atoms [10,14].

The majority of the compounds synthesized in this study were fully characterized by IR, $^1$H and $^{13}$C NMR, elemental analysis and mass spectroscopy. The results are reported in Tables 2.9 - 2.12. The ethyl, n-propyl, n-butyl and n-pentyl derivatives proved too unstable to obtain reliable results for elemental analysis, mass spectroscopy and $^{13}$C NMR spectroscopy.

**IR**

As was found for the mononuclear acyl compounds, [Mn(COR)$(CO)_5$], the IR data in the $\nu$(CO) region for [Mn(R)$(CO)_5$] (see Table 2.9) shows no significant variation upon changing the length of the alkyl chain. This data is also in good agreement with that predicted for [M(R)$(CO)_5$] species [28], *viz.* peaks due to the $A_1$ (2105cm$^{-1}$), E (2008cm$^{-1}$) and $A_1$ (1988cm$^{-1}$) vibrations are observed.

**$^1$H and $^{13}$C NMR**

Assignments of the $^1$H and $^{13}$C NMR spectra were made by comparison of all of the NMR spectra for these compounds and also by comparison of this data with those for the analogous acyl species, [Mn(COR)$(CO)_5$], and the data reported for [Mn$(CH_3)(CO)_5$] and [Mn$(C_2H_5)(CO)_5$] [30,33]. As an example of the results obtained, the $^1$H and $^{13}$C NMR spectra of compound 37, [Mn$\{(CH_2)_{17}CH_3\}(CO)_5$], are shown in Figures 5 and 6 respectively.

Table 2.9

Data for $[Mn(R)(CO)_5]$

| R | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) ($cm^{-1}$)$^a$ | Elemental Analysis C;found(calcd) | Elemental Analysis H;found(calcd) |
|---|---|---|---|---|---|---|
| $CH_3$ | 21 | 64 | 93-95 | 2105(w), 2007(s), 1987(m) | 34.2(34.3) | 1.3(1.4) |
| $C_2H_5$ | 22 | 28 | oil | 2105(w), 2006(s), 1987(m) | b | |
| n-$C_3H_7$ | 23 | 32 | oil | 2104(w), 2006(s), 1989(m) | b | |
| n-$C_4H_9$ | 24 | 31 | oil | 2104(w), 2008(s), 1988(m) | b | |
| n-$C_5H_{11}$ | 25 | 52 | oil | 2105(w), 2007(s), 1988(m) | 44.8(45.1) | 4.0(4.2) |
| n-$C_6H_{13}$ | 26 | 63 | oil | 2104(w), 2007(s), 1988(m) | 47.3(47.2) | 4.6(4.7) |
| n-$C_7H_{15}$ | 27 | 64 | oil | 2104(w), 2008(s), 1987(m) | 49.0(49.0) | 4.8(5.1) |
| n-$C_8H_{17}$ | 28 | 80 | oil | 2105(w), 2008(s), 1988(m) | 50.5(50.7) | 5.5(5.6) |
| n-$C_9H_{19}$ | 29 | 92 | oil | 2104(w), 2008(s), 1988(m) | 52.6(52.2) | 5.8(5.9) |
| n-$C_{11}H_{23}$ | 30 | 88 | oil | 2103(w), 2007(s), 1987(m) | 54.8(54.9) | 6.7(6.6) |
| n-$C_{12}H_{25}$ | 31 | 50 | 36-40 | 2104(w), 2006(s), 1987(m) | 56.2(56.0) | 6.8(6.9) |
| n-$C_{13}H_{27}$ | 32 | 84 | 30-32 | 2104(w), 2008(s), 1988(m) | 57.2(57.1) | 7.1(7.2) |
| n-$C_{14}H_{29}$ | 33 | 56 | 37-41 | 2105(w), 2008(s), 1988(m) | 58.2(58.2) | 7.3(7.4) |
| n-$C_{15}H_{31}$ | 34 | 78 | 31-33 | 2105(w), 2007(s), 1988(m) | 58.7(59.1) | 7.6(7.7) |
| n-$C_{16}H_{33}$ | 35 | 48 | 42-45 | 2104(w), 2008(s), 1987(m) | 60.2(60.0) | 7.8(7.9) |
| n-$C_{17}H_{35}$ | 36 | 89 | 35-37 | 2104(w), 2006(s), 1988(m) | 60.5(60.8) | 7.9(8.1) |
| n-$C_{18}H_{37}$ | 37 | 51 | 41-44 | 2104(w), 2006(s), 1988(m) | 61.5(61.6) | 8.2(8.3) |

a:in hexane; w = weak, s = strong, m = medium

b:elemental analyses were not obtained for these compounds, owing to their instability

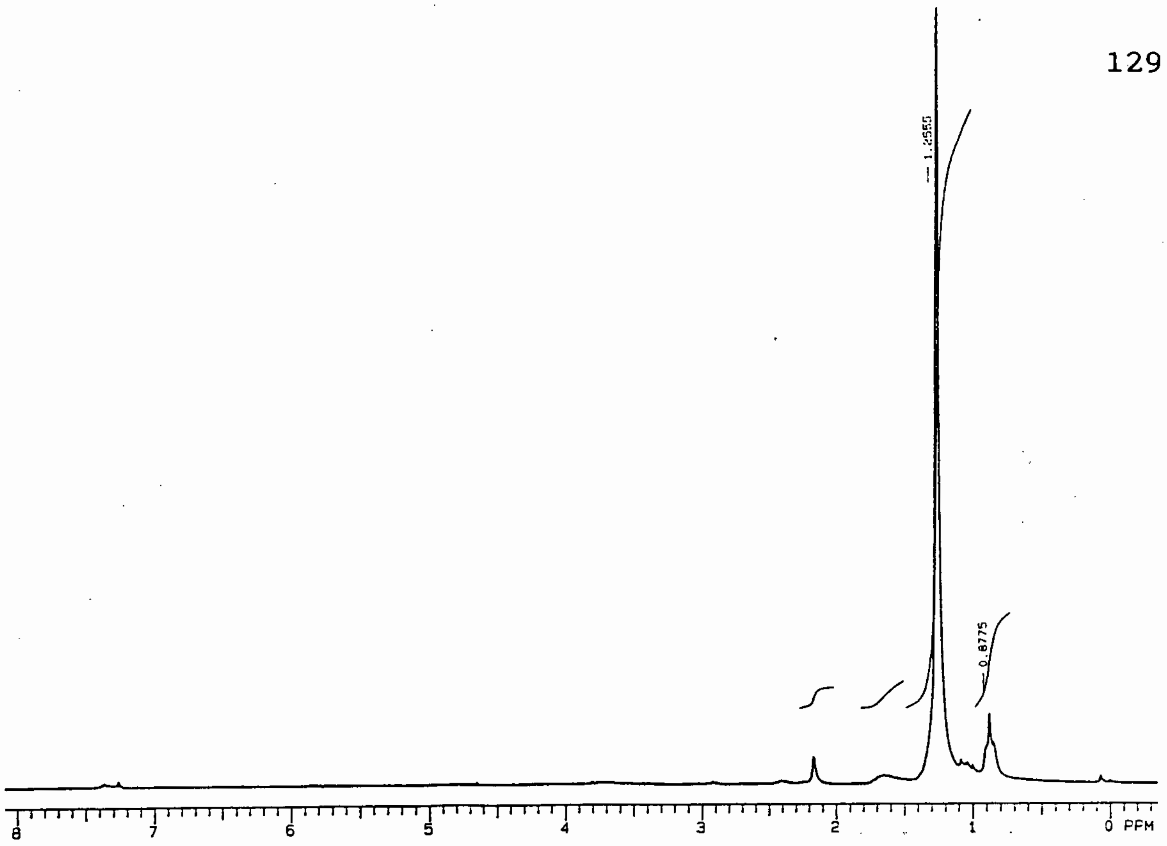


Figure 5 $^{1}H$ NMR Spectrum of $[Mn\{(CH_2)_{17}CH_3\}(CO)_5]$

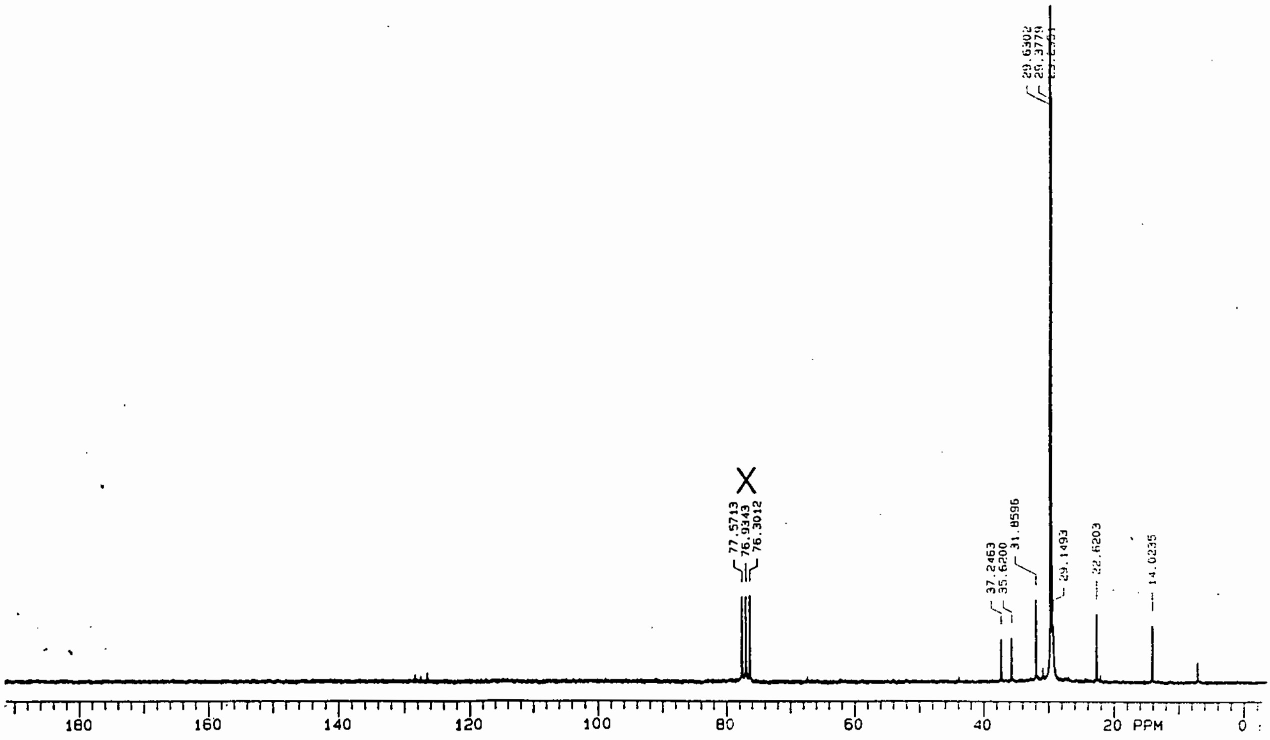


Figure 6 $^{13}C$ NMR Spectrum of $[Mn\{(CH_2)_{17}CH_3\}(CO)_5]$
(X = solvent $(CDCl_3)$)

**Table 2.10**

**$^1$H NMR Data for $[Mn(R)(CO)_5]^a$**

| R | Cmpd No | $MnC\underline{H_2}$ | $MnCH_2C\underline{H_2}$ | $MnCH_2CH_2(C\underline{H_2})_x$ | $CH_3^b$ |
|---|---|---|---|---|---|
| $CH_3$ | 21 | - | - | | -0.12s |
| $C_2H_5$ | 22 | 1.02(br,2H) | - | | 1.42 |
| n-$C_3H_7$ | 23 | 1.20(br,2H) | 1.53(br,2H) | | 0.90 |
| n-$C_4H_9$ | 24 | 1.06(tr,2H) | 1.60(br,2H) | 1.22(br,2H) | 0.90 |
| n-$C_5H_{11}$ | 25 | 1.03(tr,2H) | 1.62(br,2H) | 1.28(br,4H) | 0.89 |
| n-$C_6H_{13}$ | 26 | 1.05(tr,2H) | 1.70(br,2H) | 1.32(br,6H) | 0.89 |
| n-$C_7H_{15}$ | 27 | 1.04(tr,2H) | 1.68(br,2H) | 1.28(br,8H) | 0.88 |
| n-$C_8H_{17}$ | 28 | 1.06(tr,2H) | 1.68(br,2H) | 1.26(br,10H) | 0.89 |
| n-$C_9H_{19}$ | 29 | 1.05(tr,2H) | 1.66(br,2H) | 1.27(br,12H) | 0.89 |
| n-$C_{11}H_{23}$ | 30 | 1.02(tr,2H) | 1.67(br,2H) | 1.27(br,16H) | 0.88 |
| n-$C_{12}H_{25}$ | 31 | 1.03(tr,2H) | 1.65(br,2H) | 1.26(br,18H) | 0.88 |
| n-$C_{13}H_{27}$ | 32 | 1.04(tr,2H) | 1.66(br,2H) | 1.28(br,20H) | 0.89 |
| n-$C_{14}H_{29}$ | 33 | 1.03(tr,2H) | 1.65(br,2H) | 1.27(br,22H) | 0.89 |
| n-$C_{15}H_{31}$ | 34 | 1.02(tr,2H) | 1.68(br,2H) | 1.26(br,24H) | 0.88 |
| n-$C_{16}H_{33}$ | 35 | 1.02(tr,2H) | 1.68(br,2H) | 1.28(br,26H) | 0.88 |
| n-$C_{17}H_{35}$ | 36 | 1.03(tr,2H) | 1.64(br,2H) | 1.26(br,28H) | 0.88 |
| n-$C_{18}H_{37}$ | 37 | 1.03(tr,2H) | 1.66(br,2H) | 1.26(br,30H) | 0.88 |

a:in $CDCl_3$, relative to TMS ($\delta$ = 0.00ppm);
s = singlet, br = broad signal, tr = triplet
b:the methyl resonances were triplets unless otherwise stated

### $^1$H NMR

From the $^1$H NMR data (Table 2.10) one can see that separate resonances are seen for the methyl protons and the *α* and ß protons of the alkyl chain. This was also the case with the acyl compounds, $[Mn(COR)(CO)_5]$. The *α* protons of the alkyl chain are shielded by the metal atom resulting in a signal at *ca.* 1.02 ppm. The remaining methylene protons appear as one broad signal. As with the acyl compounds, there is no significant variation in chemical shift of any of the peaks when changing the length of the alkyl chain. Thus, integration is the only method of distinguishing between these compounds using $^1H$ NMR measurements.

## $^{13}C$ NMR

The $^{13}C$ NMR data are given in Table 2.11. Only the $^{13}C$ NMR spectrum of $[Mn(CH_3)(CO)_5]$ has been reported previously [33]; the $^{13}C$ NMR spectra of the ethyl and n-propyl derivatives could not be found in the literature. This is presumably due to their extreme instability in solution. We also found this to be the case, and thus could not obtain any reliable $^{13}C$ NMR data for these two compounds. The n-butyl derivative also proved too unstable for analysis by $^{13}C$ NMR spectroscopy. For the rest of the series (compounds **21** and **25** to **37**), the carbonyl resonances were at the expected positions [33] but were not resolved; they also showed no variation in chemical shift when the chain length of the alkyl group was altered. For compounds **25** to **28** (*i.e.* R = n-pentyl to n-octyl) all of the carbon atoms of the alkyl chain gave rise to separate resonances. This was also the case for the acyl homologues. However, for compound 29 onwards (*i.e.* R = n-nonyl to n-octadecyl), the peaks due to the central methylene carbon atoms were not resolved. Separate resonances were observed only for the methyl carbon atom, the adjacent methylene carbon atom (*i.e.* $CH_2CH_3$) and the $\alpha$, $\beta$, $\gamma$ and $\delta$ carbon atoms (*i.e.* $C_1$ to $C_4$) of the alkyl chain. Beyond $C_3$, the $^{13}C$ NMR spectra of corresponding acyl and alkyl compounds are very similar, although this is hardly surprising.

## MASS SPECTRA

The mass spectral data are reported in Table 2.12. All the mass spectra that were obtained were similar and relatively simple. They all showed weak parent molecular ions with

## Table 2.11

## $^{13}C$ NMR Data for $[Mn(R)(CO)_5]^a$

| R | Cmpd No | CO$^b$ | MnCO-$\underline{C}H_2$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{17}$ | $C_{18}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | 21 | 214 | −19.22 | | | | | | | | | | | | | | | | | |
| $C_2H_5$$^c$ | 22 | | | | | | | | | | | | | | | | | | | |
| n-$C_3H_7$$^c$ | 23 | | | | | | | | | | | | | | | | | | | |
| n-$C_4H_9$$^c$ | 24 | | | | | | | | | | | | | | | | | | | |
| n-$C_5H_{11}$ | 25 | 214 | 7.02 | 37.10 | 36.11 | 32.18 | 15.02 | | | | | | | | | | | | | |
| n-$C_6H_{13}$ | 26 | 215 | 6.80 | 37.16 | 36.10 | 31.02 | 24.52 | 15.77 | | | | | | | | | | | | |
| n-$C_7H_{15}$ | 27 | 212 | 6.98 | 37.22 | 35.62 | 31.80 | 29.70 | 23.18 | 15.21 | | | | | | | | | | | |
| n-$C_8H_{17}$ | 28 | 213 | 7.00 | 37.24 | 35.61 | 31.83 | 29.71 | 29.16 | 23.12 | 14.61 | | | | | | | | | | |
| n-$C_9H_{19}$ | 29 | 210 | 6.93 | 37.21 | 35.58 | 31.79 | {29.55 → | → | 29.12}$^d$ | 22.56 | 13.89 | | | | | | | | | |
| n-$C_{11}H_{23}$ | 30 | 214 | 7.02 | 37.25 | 35.60 | 31.85 | {29.60 → | → | → | → | 29.12}$^d$ | 22.60 | 14.21 | | | | | | | |
| n-$C_{12}H_{25}$ | 31 | 212 | 7.01 | 37.24 | 35.61 | 31.85 | {29.58 → | → | → | → | → | 29.14}$^d$ | 22.61 | 14.01 | | | | | | |
| n-$C_{13}H_{27}$ | 32 | 210 | 7.03 | 37.25 | 35.62 | 31.86 | {29.65 → | → | → | → | → | → | 29.10}$^d$ | 22.62 | 14.02 | | | | | |
| n-$C_{14}H_{29}$ | 33 | 212 | 7.01 | 37.24 | 35.62 | 31.85 | {29.61 → | → | → | → | → | → | → | 29.15}$^d$ | 22.60 | 14.03 | | | | |
| n-$C_{15}H_{31}$ | 34 | 214 | 7.02 | 37.25 | 35.62 | 31.86 | {29.62 → | → | → | → | → | → | → | → | 29.14}$^d$ | 22.62 | 14.02 | | | |
| n-$C_{16}H_{33}$ | 35 | 214 | 7.02 | 37.25 | 35.61 | 31.87 | {29.62 → | → | → | → | → | → | → | → | → | 29.12}$^d$ | 22.61 | 14.02 | | |
| n-$C_{17}H_{35}$ | 36 | 213 | 7.03 | 37.24 | 35.01 | 31.85 | {29.62 → | → | → | → | → | → | → | → | → | → | 29.10}$^d$ | 22.62 | 14.03 | |
| n-$C_{18}H_{37}$ | 37 | 214 | 7.01 | 37.25 | 35.62 | 31.86 | {29.63 → | → | → | → | → | → | → | → | → | → | → | 29.15}$^d$ | 22.62 | 14.02 |

a:in $CDCl_3$, relative to TMS ($\delta$ = 0.00ppm)
b:broad, weak signal
c:spectra were not obtained for these compounds owing to their instability in solution
d:signals were not resolved or assigned

Table 2.12

Mass Spectral Data for [Mn(R)(CO)$_5$]

| Possible Assignments$^a$ | Cmpd No | Relative Peak Intensities$^b$ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 21 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 |
| M | 2 | 8 | 6 | 8 | 10 | 8 | 7 | 10 | 5 | 4 | 7 | 8 | 3 | 6 |
| M-CO | 0 | 0 | 8 | 6 | 7 | 6 | 4 | 7 | 5 | 6 | 5 | 5 | 4 | 6 |
| M-2CO | 0 | 3 | 0 | 3 | 0 | 5 | 0 | 0 | 1 | 6 | 0 | 0 | 3 | 2 |
| M-3CO | 4 | 0 | 0 | 3 | 2 | 6 | 0 | 3 | 0 | 0 | 2 | 0 | 0 | 2 |
| M-4CO | 16 | 12 | 18 | 21 | 24 | 32 | 42 | 30 | 48 | 56 | 68 | 31 | 60 | 64 |
| M-5CO | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| M-3CO-CH$_3$ | 8 | 0 | 0 | 0 | 0 | 14 | 12 | 0 | 6 | 0 | 0 | 0 | 0 | 0 |
| M-5CO-H | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 5 | 0 | 2 | 0 | 0 | 0 | 0 |
| M-5CO-CH$_3$ | 48 | 7 | 0 | 0 | 0 | 10 | 9 | 8 | 0 | 0 | 0 | 0 | 0 | 0 |
| M-5CO-C$_2$H$_5$ | - | 4 | 8 | 12 | 6 | 18 | 10 | 12 | 9 | 10 | 8 | 7 | 9 | 9 |
| M-5CO-C$_3$H$_7$ | - | 6 | 6 | 6 | 4 | 9 | 8 | 4 | 3 | 4 | 3 | 4 | 2 | 3 |
| M-5CO-C$_4$H$_9$ | - | 3 | 12 | 10 | 14 | 13 | 12 | 8 | 10 | 11 | 6 | 5 | 4 | 6 |
| M-5CO-C$_5$H$_{11}$ | - | 21 | 6 | 11 | 4 | 10 | 8 | 3 | 10 | 9 | 10 | 6 | 3 | 4 |
| M-5CO-C$_7$H$_{15}$ | - | - | - | 52 | 12 | 12 | 12 | 11 | 10 | 12 | 11 | 11 | 10 | 12 |
| M-5CO-C$_8$H$_{17}$ | - | - | - | - | 48 | 9 | 3 | 4 | 8 | 3 | 3 | 2 | 1 | 2 |
| M-5CO-C$_9$H$_{19}$ | - | - | - | - | - | 50 | 10 | 7 | 6 | 4 | 8 | 3 | 12 | 5 |

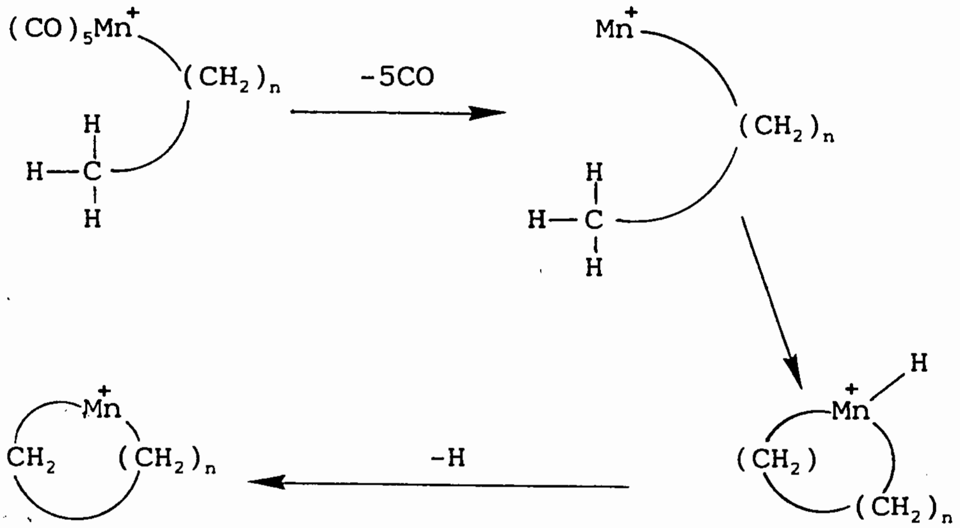
Table 2.12 (..... continued)

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M-5CO-$C_{10}H_{21}$ | - | - | - | - | - | - | 10 | 7 | 4 | 3 | 4 | 6 | 3 | 2 |
| M-5CO-$C_{11}H_{23}$ | - | - | - | - | - | - | 32 | 11 | 4 | 5 | | 7 | 7 | 6 |
| M-5CO-$C_{12}H_{25}$ | - | - | - | - | - | - | - | 48 | 4 | 5 | 5 | 5 | 2 | 4 |
| M-5CO-$C_{13}H_{27}$ | - | - | - | - | - | - | - | - | 43 | 7 | 8 | 8 | 6 | 6 |
| M-5CO-$C_{14}H_{29}$ | - | - | - | - | - | - | - | - | - | 39 | 9 | 10 | 6 | 10 |
| M-5CO-$C_{15}H_{31}$ | - | - | - | - | - | - | - | - | - | - | 37 | 11 | 7 | 8 |
| M-5CO-$C_{16}H_{33}$ | - | - | - | - | - | - | - | - | - | - | - | 51 | 11 | 8 |
| M-5CO-$C_{17}H_{35}$ | - | - | - | - | - | - | - | - | - | - | - | - | 36 | 10 |
| M-5CO-$C_{18}H_{37}$ | - | - | - | - | - | - | - | - | - | - | - | - | - | 37 |
| [$Mn(CO)_5$] | 16 | 21 | 6 | 10 | 8 | 12 | 9 | 12 | 9 | 10 | 8 | 7 | 9 | 9 |
| [Mn] | 48 | 29 | 38 | 52 | 48 | 50 | 32 | 48 | 43 | 39 | 37 | 51 | 36 | 37 |
| [CO] | 22 | 14 | 12 | 21 | 18 | 11 | 28 | 21 | 18 | 14 | 23 | 18 | 9 | 12 |

a:all ions have a single positive charge
b:peak intensities relative to base peak for $[M-5CO]^+$
c:mass spectra were not obtained for compounds **22-24** owing to their high thermal lability

the major fragmentation pathway being sequential loss of carbonyl groups followed by sequential loss of methylene fragments. This fragmentation pattern is in good agreement with that proposed by Mays and Simpson [42] for the compounds $[Mn(R)(CO)_5]$ where R = $CH_3$, $C_6H_5$, $CF_3$ and $SO_2CH_3$.

All the spectra reported in Table 2.12 are, however, low resolution mass spectra. We did obtain a high resolution mass spectrum of compound **37**, $[Mn\{(CH_2)_{17}CH_3\}(CO)_5]$, which proved to be interesting. Weak peaks at $^m/_e$ values corresponding to $[M-5CO-H]^+$ and $[M-5CO-2H]^+$ were observed. Very weak peaks corresponding to $[M-5CO-H]^+$ were also seen in the low resolution mass spectra of compounds **29**, **31** and **33**. A similar phenomenon has been observed for related iron alkyl complexes [32,43]. The reason for this fragmentation pattern may be a type of "remote functionalization" whereby the C-H bond of the methyl group of the alkyl chain can be activated by the now coordinatively unsaturated metal atom to give a metallacyclic species [44], as shown in Scheme 2.



Scheme 2

Further loss of hydride could occur by ß-hydride elminiation without cleavage of the remaining alkyl residue. This phenomenon demonstrates that selective C-H activation can be achieved at positions remote from the functional group. It is important to note that the five terminal carbonyl groups must be eliminated from the fragment before the remote functionalization can take place, as this phenomenon will only occur with a <u>bare</u> transition metal atom [44]. All spectra also exhibited most of the peaks characteristic of $[Mn(COR)(CO)_5]$ species, *viz.* $[Mn(CO)_4]^+$, $[Mn(CO)_3]^+$, $[Mn(CO)_2]^+$, $[Mn(CO)]^+$ and $[Mn(H)]^+$.

## 2.2.4 BINUCLEAR ALKYL COMPOUNDS OF THE TYPE $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ (n = 4 to 8;10)

While mononuclear manganesepentacarbonyl alkyl compounds, $[Mn(R)(CO)_5]$, have been known since 1957 [1], the study of their binuclear analogues, $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ is a relatively new field. The first reported synthesis of such a compound came from Raab *et al.* in 1983 [45] who reacted $[Mn(CH_3)(CO)_5]$ with $Ph_3CBF_4$, followed by ethylene ($C_2H_4$) and $Na[Mn(CO)_5]$ to give $[(CO)_5MnCH_2CH_2Mn(CO)_5]$. In 1985, Mapolie *et al.* [46] followed suit with the synthesis of $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$, formed by thermal decarbonylation of the acyl precursor $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$. Five years later, this same group reported the synthesis of the pentanediyl and hexanediyl derivatives $[(CO)_5Mn(CH_2)_5Mn(CO)_5]$ and $[(CO)_5Mn(CH_2)_6Mn(CO)_5]$ [47], also by thermal decarbonylation of the relevant acyl precursors. The most recent reports have come from the research group of E. Lindner [48,49] who have synthesized $[(CO)_5MnCH_2CH_2CH_2Mn(CO)_5]$ [48] and $[(CO)_5Mn(CH_2)_{10}Mn(CO)_5]$ [49] from $K[Mn(CO)_5]$ and the bistriflates, $Y(CH_2)_nY$ ($Y = F_3CSO_3$; n = 3,10). (The report on the synthesis of $[(CO)_5Mn(CH_2)_{10}Mn(CO)_5]$ appeared while this thesis was being written.

Thus, we can no longer lay claim to the first synthesis of $[(CO)_5Mn(CH_2)_{10}Mn(CO)_5]$, which was our original intention.

These binuclear compounds appear to be much more stable than their mononuclear analogues, especially the $[(CO)_5MnCH_2CH_2Mn(CO)_5]$ and $[(CO)_5MnCH_2CH_2CH_2Mn(CO)_5]$ species (even though they contain ß-hydrogen atoms). This must then be due to the second manganesepentacarbonyl moiety exerting a stabilizing effect. This supports the premise that ethyl and n-propyl manganesepentacarbonyl are unstable due to a reason other than ß-elimination *i.e.* a very rapid alkyl migration (carbonylation) reaction. The $(CH_2)_nMn(CO)_5$ moiety will not undergo alkyl migration nearly as easily as a $-(CH_2)_nH$ group.

We now report the synthesis and characterization of the compounds $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ where n = 4-8 and 10. The compounds with n = 7 and 8 are new. All of these compounds have been fully characterized by us by IR, $^1H$ and $^{13}C$ NMR, elemental analysis and mass spectroscopy. The data are presented in Tables 2.13 to 2.16.

**IR**

The infrared spectra in the $\nu(CO)$ region (as shown in Table 2.13) agree well with those reported for $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ (n = 3,4,5,6,10) [46-49]. They show the expected [28] number of peaks for $[M(R)(CO)_5)$ species where R = $(CH_2)_nMn(CO)_5$ , *viz.* $A_1$ (2104cm$^{-1}$) and E and $A_1$ (2007cm$^{-1}$; broad). There was no detectable variation in $\nu(CO)$ upon changing the length of the bridging hydrocarbyl chain.

**$^1H$ and $^{13}C$ NMR**

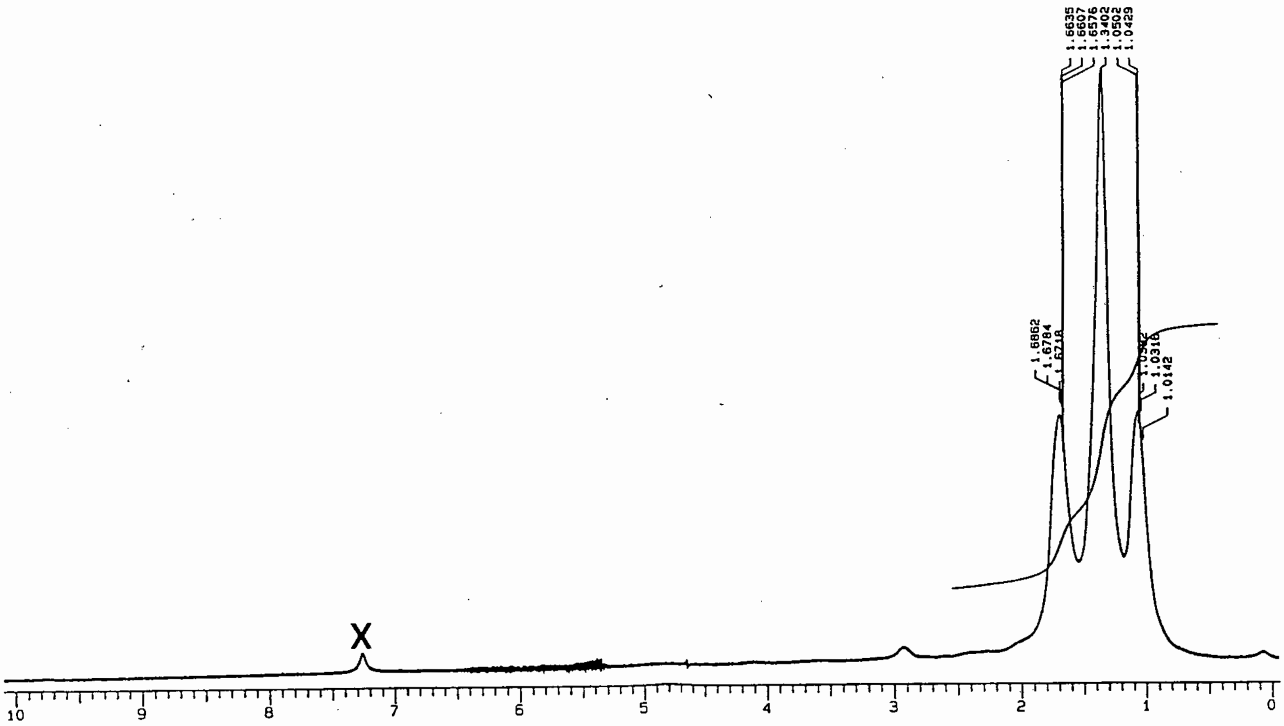
Assignments of the $^1H$ and $^{13}C$ NMR spectra were made by comparison of all of the NMR data for these compounds and

Table 2.13

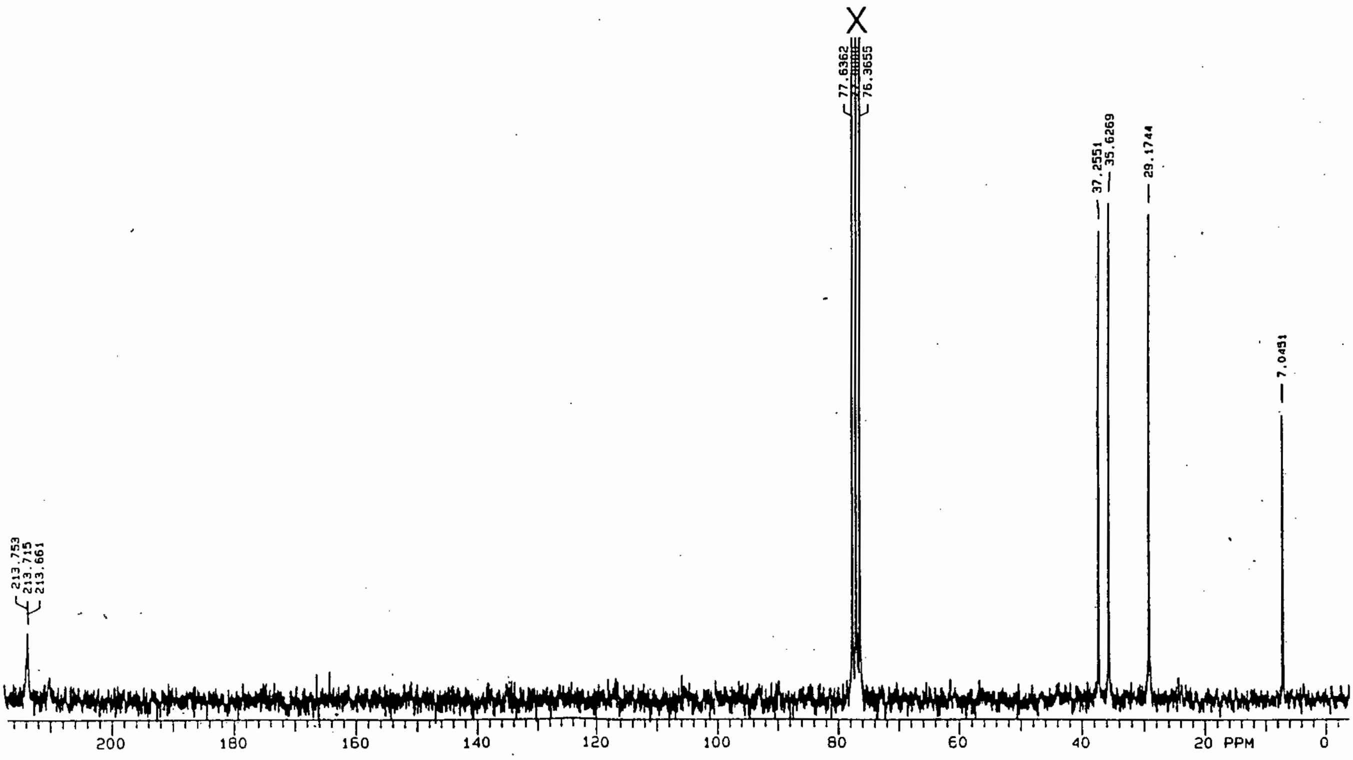
Data for $[(CO)_5Mn(CH_2)_nMn(CO)_5]$

| n | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) ($cm^{-1}$)[a] | Elemental Analysis C;found(calcd) | H;found(calcd) |
|---|---|---|---|---|---|---|
| 4 | 38 | 86 | 136-139 (decomp) | 2104(w),2007(vs) | 37.6(37.7) | 1.8(1.8) |
| 5 | 39 | 80 | 123-126 | 2104(w),2007(vs) | 39.0(39.2) | 2.3(2.2) |
| 6 | 40 | 74 | 120-128 | 2105(w),2007(vs) | 40.8(40.5) | 2.7(2.6) |
| 7 | 41 | 51 | 69-72 | 2105(w),2007(vs) | 41.12(41.8) | 2.6(2.9) |
| 8 | 42 | 78 | 71-74 | 2104(w),2007(vs) | 43.1(43.0) | 3.2(3.2) |
| 10 | 43 | 69 | 66-69 | 2104(w),2007(vs) | 45.1(45.3) | 3.7(3.8) |

a:in $CHCl_3$; w = weak, vs = very strong



<u>Figure 7</u> $^1$H NMR Spectrum for $[(CO)_5Mn(CH_2)_8Mn(CO)_5]$
($X$ = solvent ($CDCl_3$) impurity)



<u>Figure 8</u> $^{13}$C NMR Spectrum for $[(CO)_5Mn(CH_2)_8Mn(CO)_5]$
($X$ = solvent ($CDCl_3$))

by comparison of this data with the NMR data reported for $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ where n = 4-6 [50] and 10 [49]. As an example of the results obtained, the $^1H$ and $^{13}C$ NMR spectra of $[(CO)_5Mn(CH_2)_8Mn(CO)_5]$ are shown in Figures 7 and 8, respectively.

### $^1$H NMR

The $^1H$ NMR data are reported in Table 2.14 and show that for compounds **38** and **41-43** (n = 4 and 7,8,10), as with the analogous binuclear acyl compounds, separate resonances are seen for the *α* and ß protons of the bridging hydrocarbyl chain. The central methylene protons of the n = 7,8 and 10 compounds resonate as a separate, broad signal at *ca.* 1.35 ppm. However, for the n = 5 and 6 compounds, these central $CH_2$ groups resonate together with the *β* hydrogens as one broad signal. The signal for the ß hydrogens in these two compounds is at slightly higher field *viz.* 1.66ppm and 1.45ppm than that for the other compounds (*ca.* 1.69ppm). This is presumably due to the signals for the ß protons and

**Table 2.14**

$^1H$ NMR Data for $[(CO)_5Mn(CH_2)_nMn(CO)_5]^a$

| n | Cmpd No | $MnC\underline{H_2}$ | $MnCH_2C\underline{H_2}$ | Central $(CH_2)_x$ |
|---|---|---|---|---|
| 4 | 38 | 1.08(br,4H) | 1.72(br,4H) | |
| 5 | 39 | 1.09(br,4H) | 1.66(br,6H) | |
| 6 | 40 | 1.12(br,4H) | 1.45(br,8H) | |
| 7 | 41 | 1.06(br,4H) | 1.68(br,4H) | 1.35(br,6H) |
| 8 | 42 | 1.05(br,4H) | 1.68(br,4H) | 1.34(br,8H) |
| 10 | 43 | 1.05(br,4H) | 1.69(br,4H) | 1.37(br,12H) |

a: in $CDCl_3$, relative to TMS (δ = 0.00ppm), br = broad signal

Table 2.15

$^{13}C$ NMR Data for $[(CO)_5Mn(CH_2)_nMn(CO)_5]^a$

| n | Cmpd No | $CO^b$ | $MnCH_2$ (α) | $C_2$ | $C_3$ | $C_4$ | $C_5$ |
|---|---|---|---|---|---|---|---|
| 4 | 38 | 214 | 6.2 | 43.3 | | | |
| 5 | 39 | 215 | 6.6 | 36.7 | 41.2 | | |
| 6 | 40 | 213 | 6.9 | 35.1 | 37.4 | | |
| 7 | 41 | 213 | 7.0 | 37.7 | 35.5 | 29.3 | |
| 8 | 42 | 214 | 7.1 | 37.3 | 35.6 | 29.2 | |
| 10 | 43 | 214 | 7.1 | 37.3 | 35.7 | 29.7 | 29.2 |

a:in $CDCl_3$, relative to TMS (δ = 0.00ppm)
b:broad, weak signal

Table 2.16

Mass Spectral Data for $[(CO)_5Mn(CH_2)_nMn(CO)_5]^a$

| Possible Assignments$^b$ | Cmpd No | Relative Peak Intensities$^c$ | | | | |
|---|---|---|---|---|---|---|
| | 38 | 39 | 40 | 41 | 42 | 43 |
| M | 3 | 0 | 2 | 0 | 0 | 0 |
| M-CO | 2 | 2 | 0 | 0 | 0 | 0 |
| M-2CO | 4 | 0 | 0 | 0 | 0 | 0 |
| M-3CO | 0 | 3 | 1 | 6 | 12 | 0 |
| M-4CO | 6 | 0 | 10 | 18 | 18 | 35 |
| M-5CO | 10 | 7 | 6 | 22 | 26 | 19 |
| M-6CO | 5 | 4 | 0 | 6 | 9 | 7 |
| M-7CO | 4 | 4 | 8 | 11 | 10 | 6 |
| M-8CO | 11 | 8 | 6 | 10 | 13 | 13 |
| M-9CO | 28 | 19 | 21 | 44 | 43 | 20 |
| M-10CO | 21 | 10 | 18 | 16 | 20 | 28 |
| M-10CO-Mn | 0 | 12 | 10 | 20 | 22 | 39 |
| M-Mn(CO)$_5$ | 8 | 0 | 10 | 5 | 11 | 16 |
| M-CO-(CH$_2$)$_n$ | 0 | 0 | 10 | 0 | 26 | 7 |
| M-2CO-(CH$_2$)$_n$ | 6 | 2 | 6 | 0 | 9 | 6 |
| M-3CO-(CH$_2$)$_n$ | 10 | 1 | 0 | 2 | 10 | 13 |
| M-4CO-(CH$_2$)$_n$ | 5 | 0 | 8 | 3 | 13 | 20 |
| M-5CO-(CH$_2$)$_n$ | 4 | 20 | 6 | 2 | 43 | 28 |
| M-6CO-(CH$_2$)$_n$ | 11 | 18 | 21 | 5 | 20 | 36 |
| M-7CO-(CH$_2$)$_n$ | 28 | 12 | 18 | 10 | 0 | 60 |
| M-8CO-(CH$_2$)$_n$ | 21 | 4 | 8 | 6 | 23 | 6 |
| M-9CO-(CH$_2$)$_n$ | 6 | 10 | 22 | 14 | 5 | 11 |
| M-10CO-(CH$_2$)$_n$ | 27 | 14 | 41 | 8 | 36 | 22 |
| M-10CO-(CH$_2$)$_n$-Mn | 100 | 100 | 100 | 100 | 100 | 100 |

a: all spectra exhibited most of the peaks characteristic of $[Mn(R)(CO)_5]$ species, *viz.* $[Mn(CO)_5]^+$ $[Mn(CO)_4]^+$, $[Mn(CO)_3]^+$, $[Mn(CO)]^+$, $[Mn(H)]^+$, $[Mn]^+$ and $[CO]^+$

b: all ions have a single positive charge

c: peak intensities relative to base peak at $^m/_e$ 55 ([Mn]) central protons not being resolved; the central methylene protons thus cause the overall signal to be shifted slightly upfield. There was no observable variation in chemical shift with variation in length of the bridging hydrocarbyl chain. These data are in excellent agreement with that reported in the literature [47,49].

### $^{13}C$ NMR

The $^{13}C$ NMR data are presented in Table 2.15. All the $^{13}C$ NMR spectra were relatively simple and similar to each other. They showed no significant variation in chemical shift upon alteration of the chain length of the bridging alkyl group. This was also observed for the binuclear acyl complexes, $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$, as was the fact that the carbonyl resonances were at the expected positions and were not resolved.

The signals at *ca.* 7ppm can be assigned to the carbon atom of the methylene groups which are directly bonded to the manganese atoms. This is because the *α* carbon atom is strongly shielded by the nearby metal centre.

### MASS SPECTRA

The mass spectra of **38-43** are reported in Table 2.16. They are all similar to each other and are relatively simple; two fragmentation patterns are observed. The first is the usual successive loss of carbonyl groups. The second pathway involves the loss of the $[Mn(CO)_5]$ moiety to form $[Mn(C_nH_{2n})(CO)_5]^+$. The observation of this species is indicative of the absence of a metal-metal bond in these μ-(1,n)-alkanediyl complexes.

## 2.3 CONCLUSIONS

We have synthesized and fully characterized an extensive series of acyl and n-alkyl derivatives of manganese-pentacarbonyl. We have shown that the higher n-alkyl derivatives are relatively stable. The stability of the shorter chain binuclear species is remarkable compared to their mononuclear counterparts. This refutes assumptions that the short chain alkyl species are unstable due to ß-hydride elimination. We suggest the reason for the instability of these SCA compounds is an extremely facile carbonylation process.

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# CHAPTER THREE

# LONG CHAIN ACYL AND ALKYL MANGANESEPENTACARBONYL COMPOUNDS - SOME REACTIVITY STUDIES

## 3.1 DECARBONYLATION OF ACYL MANGANESEPENTACARBONYL COMPOUNDS - KINETIC STUDIES

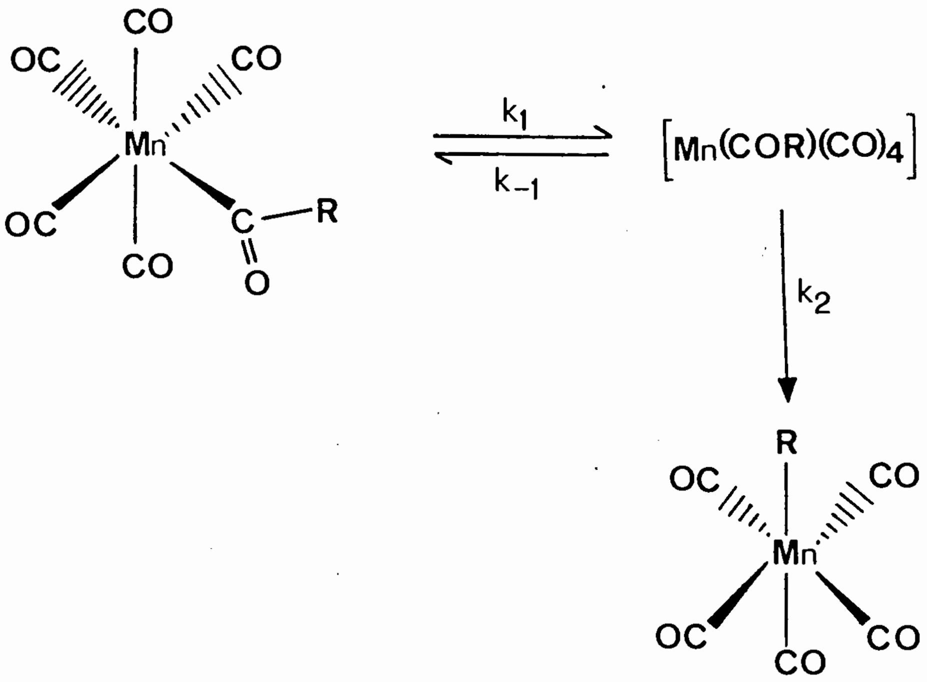
### 3.1.1 INTRODUCTION

The first reported decarbonylation of a compound of the type $[Mn(COR)(CO)_5]$ was in 1957 by Coffield *et al.*, [1] who thermally decarbonylated benzoyl and acetyl manganesepentacarbonyl to form phenyl and methyl manganesepentacarbonyl, respectively. Since then numerous reports on this reaction, as shown in equation 1, have appeared in the literature and it is now one of the most general routes to hydrocarbyl and perfluoroalkyl derivatives of manganesepentacarbonyl.

$$[Mn(COR)(CO)_5] \longrightarrow [Mn(R)(CO)_5] + CO \qquad (1)$$

Based on the initial studies of Calderazzo and Cotton [2,3], Booth *et al.* [4] and later studies of Cawse *et al.* [5], the mechanistic scheme as outlined in Scheme 1 was proposed.

Labelling studies using $[Mn(^{13}COCH_3)(CO)_5]$ [6] have shown that the molecule of CO which is lost is a terminal carbonyl group and does not derive from the acyl carbonyl group. The rate-determining step is displacement of this terminal carbonyl group and the ease of decarbonylation will therefore depend on the strength of the manganese to terminal carbonyl bond, which will, of course, be influenced to some degree by the nature of R.



Scheme 1

If one assumes a steady-state concentration of $[Mn(COR)(CO)_4]$ in Scheme 1, then one obtains the following:

$$\frac{d[[Mn(R)(CO)_5]]}{dt} = \frac{k_1k_2[[Mn(COR)(CO)_5]]}{k_{-1}[CO] + k_2} \qquad (2)$$

Since the term $k_{-1}[CO]$ is usually very small, equation 2 can simplify to

$$\frac{d[[Mn(R)(CO)_5]]}{dt} = k_1[[Mn(COR)(CO)_5]] \qquad (3)$$

Experimentally observed rate laws conform to the above equation [5]. Kinetic studies [2,5] gave the following reactivity order for the decarbonylation of $[Mn(COR)(CO)_5]$: R = $CO_2Ph$ = COMe < $CF_3$ = $CO_2Et$ < $CH_2OMe$ << $CH_2Ph$ < Me = $CH_2Cy$ < Et < n-Pr << Ph, but the spread is only ~10. This is not surprising though since the dissociation of a terminal carbonyl group as the rate-determining step is not necessarily greatly influenced by R in -COR. It has been shown that electronegative substituents have a general retarding effect on the decarbonylation process, sometimes even preventing it completely [7]. The relative rates of decarbonylation for various R groups have been correlated with the Taft $\sigma^*$ inductive parameter of R [5]. However, no kinetic studies have been performed on the decarbonylation reactions of $[Mn(COR)(CO)_5]$ compounds where R is greater than $C_3$, or an extensive, homologous series of R groups where R = n-alkyl. We now report the first study of this type where R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$.

## 3.1.2 RESULTS AND DISCUSSION

In our studies, typically, a 0.04M hexane solution of the acyl complex was thermally decarbonylated at 55.5°C. The reaction was monitored by IR spectroscopy, by following the disappearance of the highest energy ($A_1$) carbonyl vibration at *ca.* 2112cm$^{-1}$. A plot of ln(I∞-It) versus time gave $k_1$, the rate constant for the decarbonylation reaction (I∞ = intensity at time = ∞, It = intensity at time = t). An example is given in Appendix 2. Hexane was used as it is a non-coordinating solvent and thus is not expected to interfere with the mechanism of the reaction. The results are given in Table 3.1 and a plot of n in $[Mn\{CO(CH_2)_nCH_3\}(CO)_5]$ versus log k is shown in Figure 1.

From Figure 1, one can see that the rate of decarbonylation initially increases from n = o to n = 3 (*i.e.* R = methyl to R = n-butyl) but then decreases steadily and fairly rapidly through the series from n = 4 to n = 16, *i.e.* R = n-pentyl to n-heptadecyl. This can be explained by a combination of steric and electronic effects as follows: up until n = 3, electronic effects predominate with the electon-donating ability of R following the order R = n-butyl > n-propyl > ethyl > methyl.

Electron-donating groups would be expected to facilitate the decarbonylation process somewhat since they will stabilize the electron-deficient metal atom in the transition state, which is short of electrons due to two electrons being lost with the departing CO. Thus, our results agree well with those of Calderazzo and Cotton [2,3] and Cawse *et al.* [5] *i.e.* electron-donating substituents tend to facilitate the decarbonylation process. However when n>3, the electronic effect exerted by the alkyl group becomes more or less constant and steric effects start to take over. The larger alkyl groups can (a) exert more steric hindrance to the departing CO molecule in the rate-determining step, and (b) will encounter greater steric hindrance in the alkyl migration step of the reaction, and thus the overall rate will be slower. Thus, the alkyl migration step may become significant and the rate equation may change somewhat for larger R groups, since, if the migration of R to the metal atom becomes slower, the intermediate $[Mn(COR)(CO)_4]$ may have time to recombine with CO and revert to $[Mn(COR)(CO)_5]$. Thus, the $k_{-1}[CO]$ term may no longer be negligible. Another possibility is that a concerted process could be in operation.

**Table 3.1**

**Kinetic Data for the Decarbonylation of $[Mn(COR)(CO)_5]$ at 55.5°C in Hexane**

| R | $k_1$ $(x10^4 sec^{-1})$ | $\log k_1$ | $t_{½}$ (min) |
|---|---|---|---|
| $CH_3$ | 1.40 | -3.85 | 82.5 |
| $C_2H_5$ | 2.00 | -3.70 | 57.8 |
| $n-C_3H_7$ | 2.59 | -3.59 | 44.6 |
| $n-C_4H_9$ | 3.09 | -3.51 | 37.4 |
| $n-C_5H_{11}$ | 3.02 | -3.52 | 38.3 |
| $n-C_6H_{13}$ | 2.95 | -3.53 | 39.2 |
| $n-C_7H_{15}$ | 2.57 | -3.58 | 45.0 |
| $n-C_8H_{17}$ | 2.38 | -3.62 | 48.5 |
| $n-C_9H_{19}$ | 2.26 | -3.65 | 51.2 |
| $n-C_{11}H_{23}$ | 1.97 | -3.71 | 58.6 |
| $n-C_{13}H_{27}$ | 1.38 | -3.86 | 83.7 |
| $n-C_{15}H_{31}$ | 0.94 | -4.03 | 122.9 |
| $n-C_{17}H_{35}$ | 0.70 | -4.15 | 165.0 |

It is interesting to note that the shape of our curve follows the same trend as that obtained by Beckhaus [8] for a plot of n versus $\zeta_f$, a steric parameter. The constants calculated by Beckhaus reflect the steric repulsion of R groups by the (symmetrical) core of a molecule. $\zeta_f$ values were calculated as a measure of the "F-strain", which is the steric repulsion of the leaving group of a reaction. In several organic reactions [9-11], F-strain has been regarded as the principal factor determining reactivity.

The decarbonylation reactions of two of the binuclear compounds, *viz.* $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ (n = 7 and 10) were also followed kinetically by the same method as was used for the mononuclear species. Binuclear acyl compounds

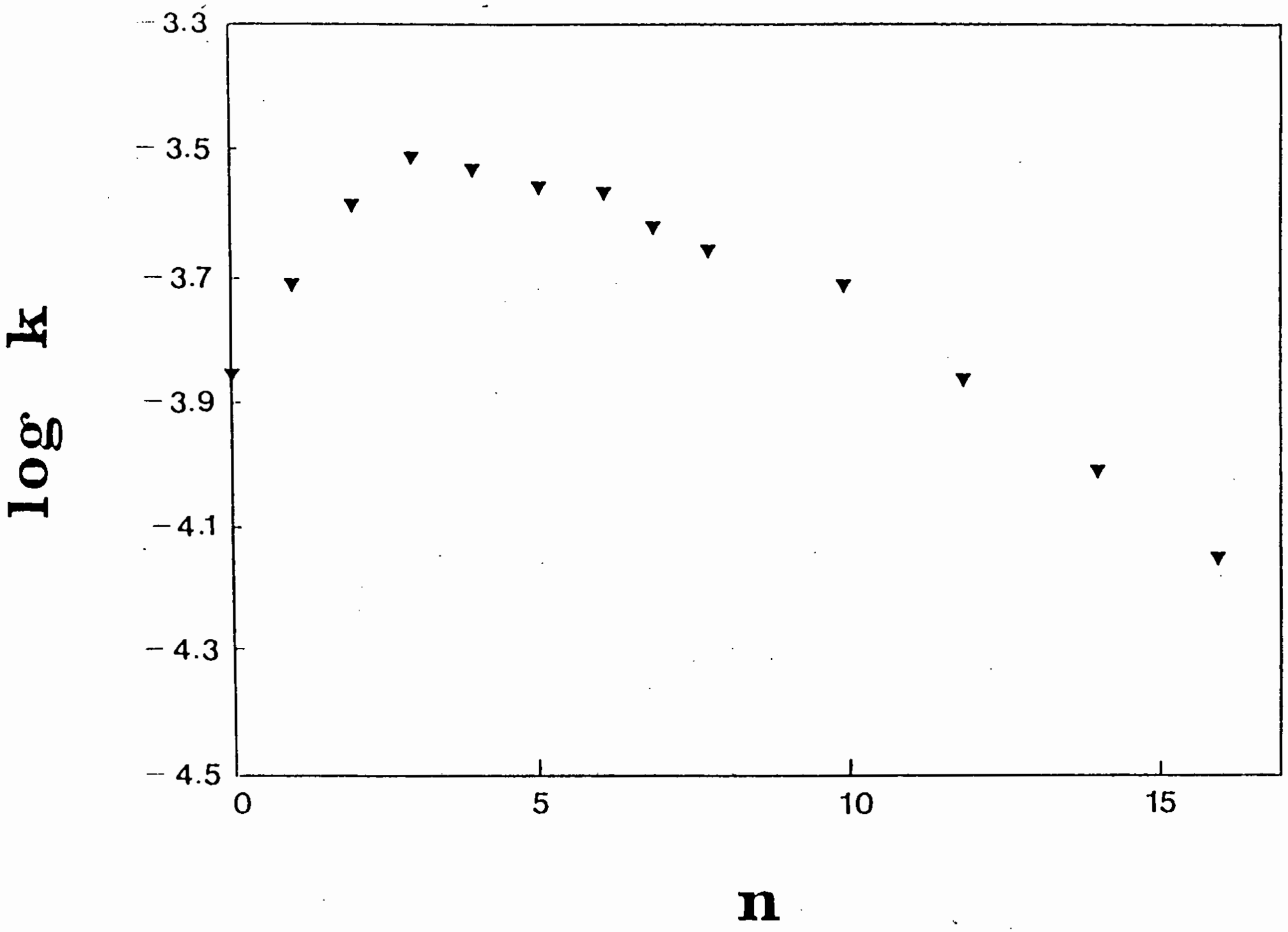


Figure 1 Plot of n in $[Mn\{CO(CH_2)_nCH_3\}(CO)_5]$ versus log k for the Reaction $[Mn(COR)(CO)_5] \longrightarrow [Mn(R)(CO)_5] + CO$

$[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ (n = 4-6, 10) [12,13] are known, but the decarbonylation rate has only been investigated for $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$[14]. The results are given in Table 3.2 and show that both compounds (where n = 7 and 10) decarbonylate in two stages due to one end of the molecule decarbonylating slower than the other. This may be a result of the increased steric hindrance that is encountered when the two ends of the molecule move closer together. This assumption is supported by the fact that the n = 10 binuclear compound decarbonylates (in both stages) approximately twice as fast as the n = 7 analogue. The first decarbonylation reaction for these binuclear species is faster than the rates observed for the mononuclear species while the second stage is considerably slower. The n = 4 compound, $[(CO)_5MnCO(CH_2)_4COMn(CO)_5]$, was found to decarbonylate in only one stage [14]. This may be a function of the shorter alkyl chain.

Thus, the decarbonylation of $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ (n = 7,10) may follow the general scheme outlined in Scheme 2 (with $k_1 >> k_3$):

$$\begin{tikzcd}
{[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]} \arrow[d, shift left, "k_1"] \\
{[(CO)_4MnCO(CH_2)_nCOMn(CO)_5] + CO} \arrow[u, shift left, "k_{-1}"] \arrow[d, "k_2"] \\
{[(CO)_5Mn(CH_2)_nCOMn(CO)_5]} \arrow[d, shift left, "k_3"] \\
{[(CO)_5Mn(CH_2)_nCOMn(CO)_4] + CO} \arrow[u, shift left, "k_{-3}"] \arrow[d, "k_4"] \\
{[(CO)_5Mn(CH_2)_nMn(CO)_5]}
\end{tikzcd}$$

**Scheme 2** **Decarbonylation of $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ (n = 7,10)**

**Table 3.2**

**Kinetic Data for the Decarbonylation of $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ in Hexane**

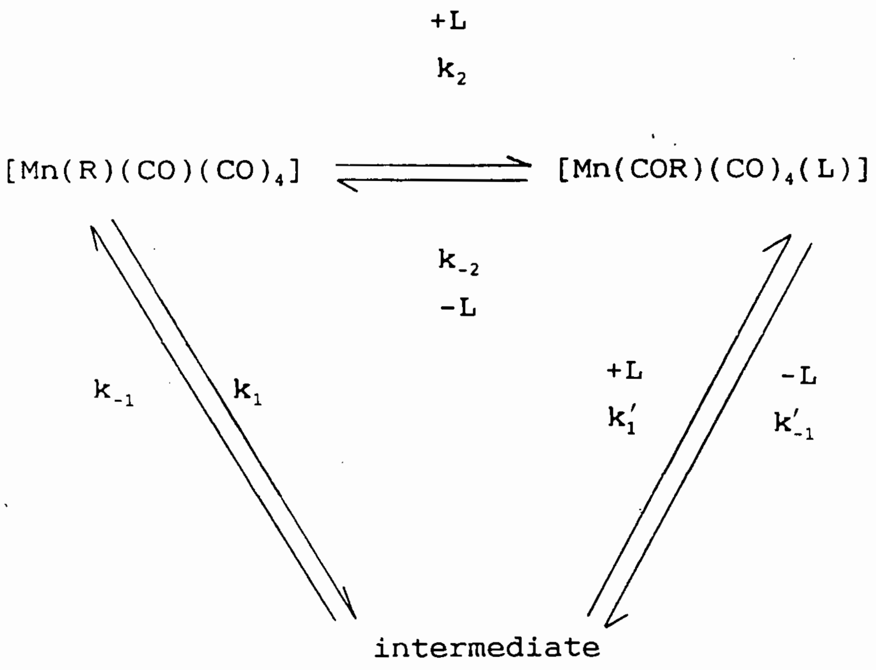
| n | $k_1$ ($x10^4 sec^{-1}$) | $k_3$ ($x10^4 sec^{-1}$) | log $k_1$ | log $k_3$ | $t1_{1/2}$ (min) | $t3_{1/2}$ (min) |
|---|---|---|---|---|---|---|
| 7 | 2.45 | 0.72 | -3.61 | -4.14 | 47.2 | 160.5 |
| 10 | 5.17 | 1.44 | -3.29 | -3.84 | 22.4 | 80.2 |
| 10[a] | 5.28 | 1.56 | -3.28 | -3.81 | 21.9 | 73.9 |
| 4[b] | 1.1 | - | -3.96 | - | 105.0 | - |

[a] reaction in $CDCl_3$ at 55.5°C, followed by $^1H$ NMR
[b] data from reference 14 (reaction in $CDCl_3$ at 55.0°C)

## 3.2 CARBONYL INSERTION IN ALKYL MANGANESEPENTACARBONYL COMPOUNDS - KINETIC STUDIES

### 3.2.1 **INTRODUCTION**

Over the years this has been one of the most widely studied reactions in the field of organometallic chemistry [15]. The first report, that of the formation of acetyl manganesepentacarbonyl from the methyl derivative and carbon monoxide, was published in 1957 by Coffield *et al.* [1]. Early studies by Calderazzo and co-workers [2,3,16,17] Mawby *et al.* [16] and later by Cawse *et al.* [5] have provided most of the mechanistic information on this process and the following scheme (as outlined in Chapter One) is now generally accepted.



Scheme 3

The intermediate is generally thought to be of the type $[Mn(COR)(CO)_4]$, although in coordinating/polar solvents it probably exists as a solvated hexacoordinate species, $[Mn(COR)(CO)_4(S)]$. By applying the steady-state approximation for the concentration of the intermediate, one can arrive at the following expression:

$$\frac{d[[Mn(COR)(CO)_4(L)]]}{dt} = k_1[[Mn(R)(CO)_5)]] \quad -$$

$$k_{-1} \frac{k_1[Mn(R)(CO)_5] + k'_{-1} [Mn(COR)(CO)_4(L)]}{k_{-1} + k_1 [L]} \quad +$$

$$k_2[[Mn(R)(CO)_5]][L] - k_{-2} [[Mn(COR)(CO)_4(L)]] \qquad (4)$$

If one assumes that the reaction goes to completion, $k_{-1}$ and $k_{-2}$ can be ignored, which simplifies equation 4 to:

$$\frac{d[[Mn(COR)(CO)_4(L)]]}{dt} = \frac{k_1k_1'[[Mn(R)(CO)_5]][L]}{k_1 + k_1' [L]}$$

$$+ k_2[[Mn(R)(CO)_5]][L] (5)$$

The two terms in equation 5 are referred to as the $k_1$ path and the $k_2$ path, respectively. The above rate equation can be simplified further by one or more of the following considerations:

(a) only the $k_1$ path is operative *i.e.* $[Mn(R)(CO)_5]$ does not interact directly with L. This is the usual situation in reactions of $[Mn(R)(CO)_5]$ compounds. In this case, three possibilities exist, *viz.*

(i) If $k_{-1} << k_1[L]$ *i.e.* if the intermediate reacts with L more effectively than it reverts to the alkyl, the rate expression simplifies to:

$$\frac{d[[Mn(COR)(CO)_4(L)]]}{dt} = k_1[[Mn(R)(CO)_5]] \quad (6)$$

and first-order kinetics are observed

(ii) If $k_{-1}$ is appreciable and $k_1[L]$ is small, one obtains the expression

$$\frac{d[[Mn(COR)(CO)_4(L)]]}{dt} = \frac{k_1k_1'}{k_{-1}}[[Mn(R)(CO)_5][L]] \quad (7)$$

This expression reflects second-order kinetics, first-order in both $[Mn(R)(CO)_5]$ and [L], which may occur when the concentration of L is low, *e.g.* if L = CO.

(iii) If $k_{-1}$ is comparable to $k_1[L]$, then $k_{OBS}$, the observed rate constant, is given by the expression

$$k_{OBS} = \frac{k_1k_1'[L]}{k_{-1}+k_1'[L]} \quad (8)$$

$k_{OBS}$ will then increase with increasing [L]. However, if one is using a concentration of L in excess of $[Mn(R)(CO)_5]$ and if one assumes $k_{-1}$ to be negligible (which indeed, for $[Mn(R)(CO)_5]$ systems with ligands of high nucleophilicity *e.g.* $PPh_3$, it is) then the reaction is pseudo-first-order and $k_{OBS}$ approximates $k_1$. This is the rate expression most commonly used in kinetic studies on $[Mn(R)(CO)_5]$ species [5,19,20].

(b) the $k_2$ path is followed, either alone or in tandem with the $k_1$ path. If [L] is relatively large, equation 5 reduces to

$$\frac{d[[Mn(COR)(CO)_4(L)]]}{dt} = k_{OBS}[[Mn(R)(CO)_5]] \qquad (9)$$

(where $k_{OBS} = k_1 + k_2[L]$)

The rates of carbonylation for $[Mn(R)(CO)_5]$ species are greatly dependent on R, with electron-withdrawing R groups severely retarding the reaction, or in some cases *e.g.* R = $CH_2I$[21], even preventing the reaction from taking place at all. The following reactivity orders for various R groups have been observed:

R = $n\text{-}Pr>Et>Ph>CH_3>CH_2F>>CF_3$ [2] and

R = $n\text{-}Pr>Et>CH_2Cy>CH_3>CH_2OCH_3>CH_2Ph>CH_2CO_2H$ [5]

However, an extensive study of the alkyl migration reaction in $[Mn(R)(CO)_5]$ with R = a homologous series of n-alkyl groups has never been reported, partly due to the fact that n-alkyl derivatives were expected to be unstable [19]. However, we have been able to prepare an extensive series of n-alkyl derivatives [22] and we now report our results on the reactivity of $[Mn(R)(CO)_5]$ compounds with respect to the carbonyl insertion reaction (R = $CH_3$ to $n\text{-}C_9H_{19}$; $n\text{-}C_{11}H_{23}$; $n\text{-}C_{13}H_{27}$; $n\text{-}C_{15}H_{31}$; $n\text{-}C_{17}H_{35}$; $n\text{-}C_{18}H_{37}$). Such a study is important since the alkyl migration reaction is a key step in many catalytic processes.

## 3.2.2 RESULTS AND DISCUSSION

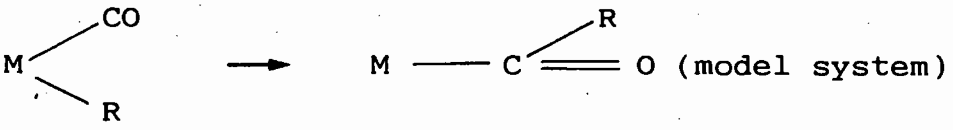
Typically, a 0.07M hexane solution of the alkyl complex, $[Mn(R)(CO)_5]$, was reacted with a *ca.* 9-molar excess of triphenylphosphine at 32.0°C. The reaction was monitored by infrared spectroscopy, following the disappearance of the highest energy ($A_1$) carbonyl vibration at *ca.* 2105cm$^{-1}$. A plot of $\ln(I\infty/It)$ versus time yielded $k_{OBS}$ ($I\infty$ = intensity at time = ∞; It = intensity at time = t). An example is given in Appendix 2. The products all adopt a *cis* geometry. The reaction being followed is thus:

$$[Mn(R)(CO)_5] + PPh_3 \xrightarrow{k_{OBS}} cis\text{-}[Mn(COR)(CO)_4(PPh_3)] \qquad (10)$$

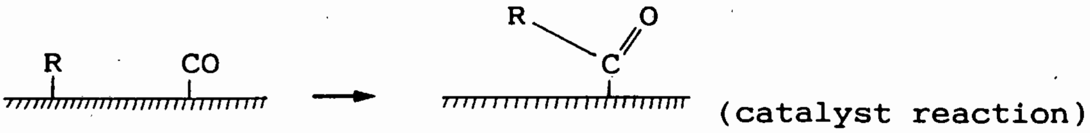
The results are given in Table 3.3 and a plot of n (in $[Mn\{(CH_2)_nCH_3\}(CO)_5]$) versus log k is given in Fig. 2.

From Fig. 2, one can see that the rate of alkyl migration/carbonyl insertion initially increases for n = 0 to n = 2 (*i.e.* R = $CH_3$ to n-propyl), then decreases rapidly until n = 6 (R = n-heptyl) and then levels off, decreasing very slowly till n = 17 (R = n-octadecyl). As with the decarbonylation process, this can be explained by a combination of steric and electronic effects. It is known that electron-donating substituents facilitate the alkyl migration reaction [2,3,5,19] and this is indeed the case as the rate increases for R = $CH_3$ to n-$C_3H_7$, *i.e.* the R group is becoming more electron-donating in nature which results in rate acceleration. However, when the R group becomes larger than n-propyl the electronic effect is more or less constant and steric effects start to take over, with rate retardation being observed. This occurs until R = n-heptyl, when the steric effects exerted by the alkyl group also become more or less constant and the addition of extra methylene ($CH_2$) groups has an almost negligible effect on the reaction rate. Again, the curve follows the same general trend as Beckhaus' [8]. This combination of steric and electronic factors that we have observed in the alkyl migration reactions of these manganese complexes may pertain to other alkyl complexes and also to alkyl intermediates in catalytic reactions. It could thus serve as a possible explanation for the observed deviation from the predicted Schulz-Flory product distribution above $C_{12}$ in the Fischer-Tropsch synthesis [23]. The fact that a lower proportion than was initially predicted of higher carbon-numbered products ($>C_{12}$) is obtained in the Fischer-Tropsch reaction [23] has been attributed to the lower mobility of these larger hydrocarbon groups. We have now shown this to be the case with these manganese alkyl model complexes. Thus, the alkyl migration process, as observed with these complexes, could be regarded as a model for a step leading to chain termination in catalytic polymerization reactions [23]. The reaction which interrupts chain growth and results in the formation of hydrocarbon oligomers is possibly a chain transfer reaction in the course of which the alkyl chain leaves the metal.

It could, however, also be a model for alkyl migration in chain growth processes [24] as shown in Scheme 4.



versus



Scheme 4

**Table 3.3**

**Kinetic Data for the Reaction of [Mn(R)(CO)$_5$] with PPh$_3$ at 32.0°C in Hexane**

| R | $k_{OBS}$ ($\times 10^4 sec^{-1}$) | log $k_{OBS}$ | $t_{1/2}$ (min) |
|---|---|---|---|
| $CH_3$ | 0.63 | -4.20 | 182.8 |
| $C_2H_5$ | 3.26 | -3.49 | 35.5 |
| n-$C_3H_7$ | 6.37 | -3.20 | 18.1 |
| n-$C_4H_9$ | 4.14 | -3.38 | 27.0 |
| n-$C_5H_{11}$ | 2.83 | -3.55 | 40.8 |
| n-$C_6H_{13}$ | 2.21 | -3.66 | 52.3 |
| n-$C_7H_{15}$ | 2.02 | -3.69 | 52.5 |
| n-$C_8H_{17}$ | 2.01 | -3.70 | 57.5 |
| n-$C_9H_{19}$ | 1.99 | -3.70 | 58.0 |
| n-$C_{11}H_{23}$ | 1.96 | -3.71 | 58.9 |
| n-$C_{13}H_{27}$ | 1.91 | -3.72 | 60.5 |
| n-$C_{15}H_{31}$ | 1.89 | -3.72 | 61.1 |
| n-$C_{17}H_{35}$ | 1.85 | -3.73 | 62.4 |
| n-$C_{18}H_{37}$ | 1.84 | -3.74 | 62.8 |
| $CH_3$a | 0.74 | -4.13 | 157.0 |

a:reaction done in $CDCl_3$ at 32.0°C, followed by $^1H$ NMR

A theoretical study on the migration of R in [Mn(R)(CO)$_5$] has been made [24] and it was found that migration of R should be facilitated with increasing chain length. However, this study only involved R = $CH_3$, $C_2H_5$ and n-$C_3H_7$ with no higher n-alkyl groups and is thus in line with our experimental results.

The carbonylation reactions of two of the binuclear alkyl compounds, [(CO)$_5$Mn(CH$_2$)$_n$Mn(CO)$_5$] (n = 8,10), as shown in

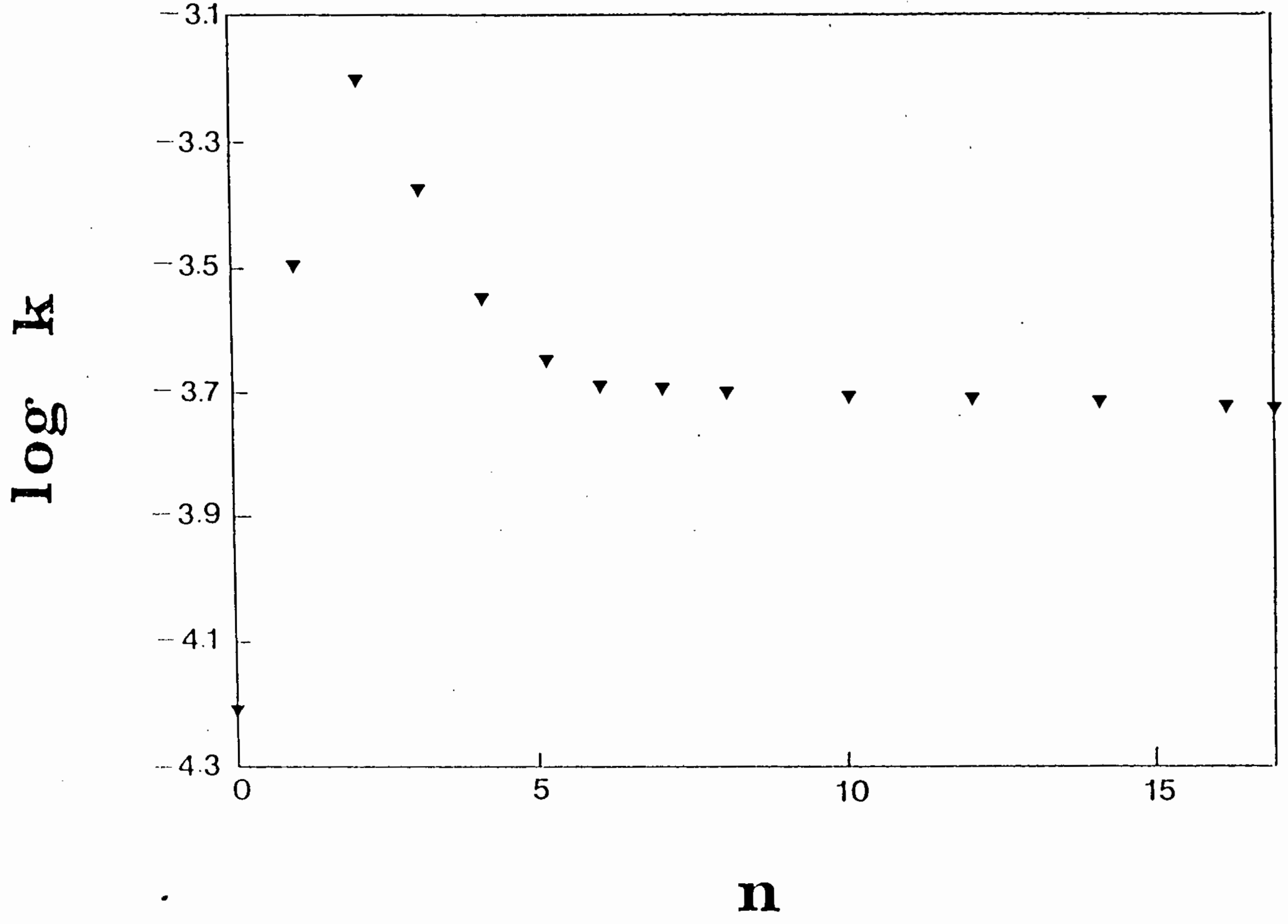


Fig. 2 Plot of n in $[Mn\{(CH_2)_nCH_3\}(CO)_5]$ versus log k for the Reaction $[Mn(R)(CO)_5] + PPh_3 \longrightarrow$ *cis*-$[Mn(COR)(CO)_4(PPh_3)]$

equation 11, were also followed kinetically

$$[(CO)_5Mn(CH_2)nMn(CO)_5] + 2PPh_3 \xrightarrow{k_1} \quad (11)$$
$$cis,cis\text{-}[(PPh_3)(CO)_4MnCO(CH_2)nCOMn(CO)_4)(PPh_3)]$$

Table 3.4

**Kinetic Data for the Reaction of $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ with $PPh_3$ at 32.0°C in Hexane**

| n | $k_1$ ($x10^4sec^{-1}$) | $k_3$ ($x10^4sec^{-1}$) | log $k_1$ | log $k_3$ | $t_{1/2(1)}$ (min) | $t_{1/2(3)}$ (min) |
|---|---|---|---|---|---|---|
| 8 | 1.59 | - | -3.80 | - | 72.6 | - |
| 10 | 2.06 | 0.98 | -3.69 | -4.01 | 56.0 | 117.5 |

The results are given in Table 3.4 and show the n = 8 compound to react in one identifiable step whereas the n = 10 compound reacts in two stages, with one end of the molecule reacting approximately twice as fast as the second end.

It can be seen from Tables 3.1 to 3.4 that the rates of CO insertion span a relatively larger range than the rates for the decarbonylation process. This is not unexpected since the rate determining step in the CO insertion reaction is the migration of R, whereas in the decarbonylation reaction it is loss of a terminal carbonyl group. It is thus understandable that the CO insertion process is more strongly affected by R than is the decarbonylation reaction. However, the manganese-terminal carbonyl bond strength is affected by the rest of the molecule and thus will be affected to some extent by R. The rate of decarbonylation does not level off, even with very large R groups. This can be explained by the proposal that, if the rate-determining step is loss of a terminal CO, the CO group has to dissociate from the rest of the molecule completely and will thus continue to be affected by larger and larger R groups. Larger R groups may make it increasingly difficult for the molecule of CO to completely remove itself from the increasingly larger coordination sphere of the metal.

## 3.3 **REACTION OF $[Mn\{(CH_2)_nCH_3\}(CO)_5]$ (n = 14,16) WITH $Ph_3CPF_6$**

$[Mn\{(CH_2)_{14}CH_3\}(CO)_5]$ and $[Mn\{(CH_2)_{16}CH_3\}(CO)_5]$ were both reacted with trityl salt, $Ph_3CPF_6$. It was anticipated that this reaction would give either cationic alkene complexes (by abstraction of ßH) or cationic carbene complexes (by abstraction of $\alpha$H). However, the only organometallic products that were isolated from the reaction (in *ca.* 40% yield) were the acyl compounds $[Mn\{CO(CH_2)_nCH_3\}(CO)_5]$. This is not altogether unsurprising, since it is known that $Ph_3CPF_6$ can in some instances act as an oxidizing agent [25]. Thus, it could react to give a product which would liberate CO upon decomposition, which could in turn react with the alkyl compounds $[Mn\{(CH_2)_nCH_3\}(CO)_5]$ to give the observed CO-inserted products. The oxidation of some transition metal alkyl compounds is also known to facilitate the alkyl migration reaction [26]. The products were identified on the basis of IR, $^1$H NMR, elemental analysis and melting points (see Table 3.5).

Table 3.5

Data for Products of the Reactions of $[Mn\{(CH_2)_nCH_3\}(CO)_5]$ with $Ph_3CPF_6$

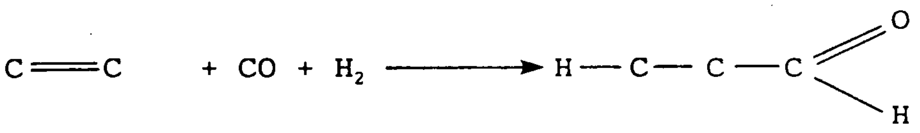
| n | yield | mp (°C) | IR $\nu$(CO) ($cm^{-1}$)[a] (hexane) | $^1$H NMR[a] ($CDCl_3$)[b] | Elemental Analysis[c] | |
|---|---|---|---|---|---|---|
| | | | | | C | H |
| 14 | 38 | 40–43 (44–46) | 2112, 2048, 2007, 2001, 1652<br>(2112, 2048, 2006, 2000, 1658) | 2.90tr, 1.48m, 1.22br, 0.86<br>(2.91, 1.48, 1.24, 0.87) | 58.9(58.1) | 7.4(7.2) |
| 16 | 40 | 46–48 (48–50) | 2111, 2048, 2006, 2006, 1656<br>(2112, 2048, 2006, 2000, 1658) | 2.91tr, 146m, 1.24br, 0.85<br>(2.90, 1.48, 1.24, 0.87) | 60.1(59.7) | 7.7(7.6) |

a:data for the previously characterized acyl compounds given in parentheses
b:relative to TMS ($\delta$ = 0.00 ppm) tr = triplet, m = multiplet, br = broad signal
c:calculated values in parentheses

## 3.4 SYNTHESIS GAS REACTIONS

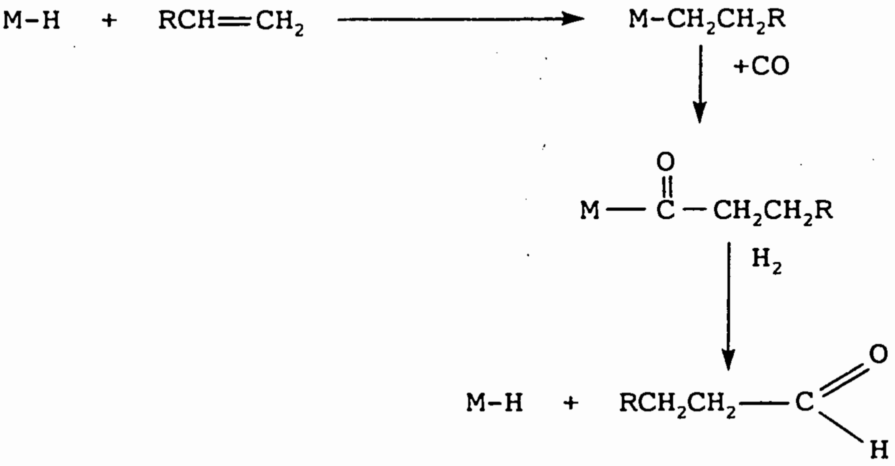
### 3.4.1 INTRODUCTION

The catalytic hydrogenation of carbon monoxide to give useful organic compounds such as hydrocarbons, alcohols, and other oxygen-containing products is a process of great importance in the chemical industry today [27]. Transition metal complexes are used as catalysts for this process. An example of a process which involves synthesis gas the conversion of carbon monoxide and hydrogen to hydrocarbons is the Fischer-Tropsch process [27]. At the present time, the SASOL operation in South Africa is the only large-scale Fischer-Tropsch synthesis plant [27]. Another example of a catalytic process which involves is the hydroformylation reaction. Hydroformylation is the oldest and one of the most important homogeneous catalytic reaction of olefins, generally leading to the formation of aldehydes as shown in equation 12.



(12)

The term "hydroformylation" was chosen [28] to indicate that the reaction involves the formal addition of the components of formaldehyde (H-CHO) to an olefinic double bond. The term "oxo reaction" is also sometimes used. An important extension of the hydroformylation reaction is the synthesis of alcohols from terminal olefins such as 1-octene [29]. This is one of the most important technical routes to alcohols, particularly those in the $C_3$ to $C_{13}$ range, which are required for the production of plasticizers, detergents, synthetic lubricants and as solvents [29]. The mechanism of the hydroformylation reaction was not unravelled until 1960 when Heck and Breslow [30] suggested the following general scheme:

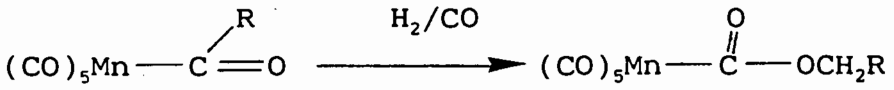


Scheme 5

Most industrial hydroformylation processes are run at 100-180°C with pressures of 100-300 atm. using cobalt catalysts, most commonly $[Co(H)(CO)_4]$. Many solvents can be used, in particular aliphatic, cycloaliphatic or aromatic hydrocarbons [29].

A great deal of research has been carried out on the reactions of transition metal complexes with synthesis gas [23,31-36] with the intention of gaining a better understanding of the mechanisms of a variety of catalytic processes, particularly the Fischer-Tropsch and hydroformylation reactions. This increased understanding could in turn lead to the development of more efficient and selective catalysts.

There are several examples in the literature dealing with the reaction of alkyl (and acyl) manganesepentacarbonyl complexes with synthesis gas [12,37-41]. However, since these reports were discussed in detail in Chapter One of this thesis, they will only be mentioned briefly here. The first report was published in 1978 by King *et al.* [37], although strictly speaking, this was not a reaction with synthesis gas. It involved the reaction of $[Mn(CH_3)(CO)_5]$ with CO (320 atm. at 50°C in tetradecane) to give $[Mn(COCH_3)(CO)_5]$. This was then reacted with $H_2$ (313 atm. at 95°C) to give $CH_3CHO$ and $[Mn_2(CO)_{10}]$. Thus, the authors obtained an aldehyde as the organic product. Then in 1979 Dombek [38] investigated the reactions of $[Mn(R)(CO)_5]$ ($R = H, CH_3, CH_2OCH_2CH_3, CH_2OC(O)CMe_3$) with synthesis gas in sulfolane. With $R = CH_3$, acetaldehyde was the only isolable organic product; when only $H_2$ (instead of $CO/H_2$) was used, ethanol was the organic product. The other complexes reacted similarly, giving either the aldehyde or the corresponding alcohol. It was proposed that the reaction proceeded *via* a complexed aldehyde species. Orchin and co-workers [39,40] found that in hydrocarbon solvents, synthesis gas became incorporated into the acyl compounds (which could be formed as intermediates when the alkyl complexes reacted with CO) to form alkoxycarbonyl compounds, as shown in equation 13.



$$(CO)_5Mn-\overset{R}{C}=O \xrightarrow{H_2/CO} (CO)_5Mn-\overset{O}{\overset{\|}{C}}-OCH_2R \qquad (13)$$

A labelling study [40] showed that the initial acyl group in the reactant was reduced exclusively to the methylene group of the product. In 1991, Mapolie and Moss [12] reported the reaction of $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ ($n = 4-6$) with synthesis gas (40 atm. at 70°C in THF) to give the diols, $HO-CH_2-(CH_2)_n-CH_2-OH$, as the organic products; $[Mn_2(CO)_{10}]$ was also formed. The most recent report [40] involves the reaction of benzyl manganesepentacarbonyl with $PhC\equiv CPh$ and $CO/H_2$ to give an aldehyde and $[Mn_2(CO)_{10}]$.

We now report our results on the reactions of (a) $[Mn\{(CH_2)_8CH_3\}(CO)_5]$ and $[Mn\{(CH_2)_{12}CH_3\}(CO)_5]$ with synthesis gas and (b) $[Mn_2(CO)_{10}]$ with 1-hexene and synthesis gas.

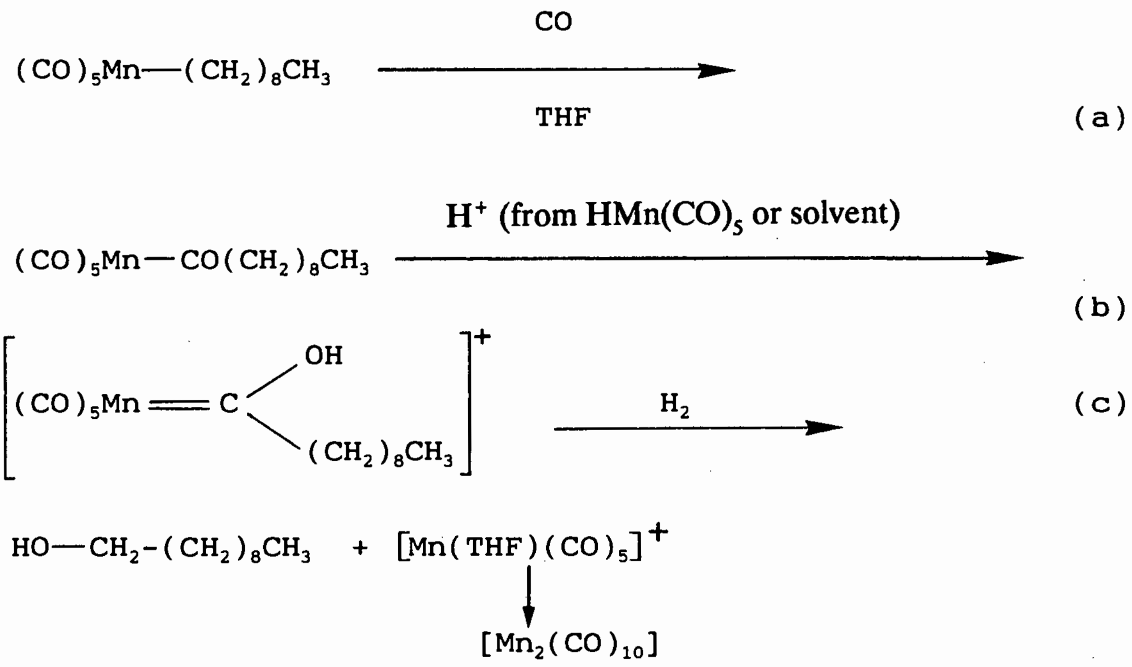
## 3.4.2 RESULTS AND DISCUSSION

Detailed experimental procedures are given in Chapter 7 and will thus not be elaborated upon here. Reactions were carried out in either freshly distilled THF or freshly distilled hexane in a Berghof Autoclave. Reaction (a) (i) was performed at 94 atm. at 55°C reaction (a) (ii) was performed at 70 atm. at 55°C and reaction (b) at 40 atm. and 74°C.

### 3.4.2 (a) (i) Reaction of $[Mn\{(CH_2)_8CH_3\}(CO)_5]$ with Synthesis Gas in Tetrahydrofuran

A solution of $[Mn\{(CH_2)_8CH_3\}(CO)_5]$ in THF was transferred to an autoclave and pressurized with $CO/H_2$ to 40 atm. and then heated at 55°C for 2.5h. During this time, the pressure rose rapidly to 94 atm. and thereafter remained constant at this value. The temperature remained at 55°C for the duration of the reaction.

The reaction gave 1-decanol, $CH_3(CH_2)_8CH_2OH$, in 46% yield as the only isolable organic product (no aldehyde was detected). The formation of the alcohol can be explained as follows,



Scheme 6 The formation of 1-decanol from n-nonyl manganesepentacarbonyl, $[Mn\{(CH_2)_8CH_3\}(CO)_5]$

The involvement of an intermediate acyl species, as shown in reaction (a) of Scheme 6, has been proved previously [12]. Also, the reaction of methyl [42] and acetyl [43] manganesepentacarbonyl with a nucleophile to form a hydroxycarbene complex, as represented in steps (a) to (c) is known. The 1-decanol was identified on the basis of its IR spectrum (neat film; 3380 (s,O-H--O stretch), 2900 (s), 1460 (s), 1370 (m), 1150 (m), 1050 (vs,$CH_2$-OH stretch), 712 (mw) $cm^{-1}$), $^1H$ NMR spectrum $CDCl_3$, $\delta$ = 0.89(s,$CH_3$), 1.28 (br,$(CH_2)_8$, shoulder at 1.61 ($CH_2OH$), 3.62(br,OH) and mass spectrum ($M^+$ = 158).

As can be seen from Scheme 6, $[Mn(THF)(CO)_5]^+$is a proposed product of the reaction, although it was not isolated. The only isolable organometallic product was $[Mn_2(CO)_{10}]$. However, it is known that $[Mn_2(CO)_{10}]$ is the main decomposition product of $[Mn(THF)(CO)_5]^+$[44].

Similar results, *i.e.* alcohol formation under almost identical conditions, using the binuclear compounds $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ (n = 4-6) were obtained by Mapolie and Moss [12].

In no case was incorporation of the synthesis gas into the alkyl compound observed, *i.e.* no alkoxycarbonyl compounds of the type $[Mn\{(O)CO(CH_2)_8CH_3\}(CO)_5]$ were detected. Compounds of this type have been reported by other workers in this field, especially by Orchin and co-workers [39,40] who reacted synthesis gas with $[Mn(COR)(CO)_5]$ species to form $[Mn\{(O)COCH_2R\}(CO)_5]$ compounds. However, Orchin used only non-polar hydrocarbon solvents such as hexane whereas we used THF, a polar solvent of fairly good coordinating ability. The difference then, between our results and those of Orchin, is presumably due to the different solvents used. In polar, coordinating solvents such as THF, the solvent could conceivably protonate the acyl intermediate formed in step (a) of Scheme 6 to give a hydroxycarbene species, as shown in step (b) of scheme 6, which can then undergo reaction with $H_2$. This would also explain the preferential formation of alcohols over aldehydes. All other workers in this field who observed the preferential formation of aldehydes over alcohols were using non-polar, non-coordinating solvents [12,38-41]. A similar reaction sequence has recently been reported by Cole-Hamilton and co-workers [45] using alcohols as solvents for a hydroformylation reaction. These authors found preferential formation of alcohols over aldehydes *via* a rhodium hydroxycarbene intermediate formed by donation of a proton from the solvent. Labelling studies by this group showed that aldehydes were not formed on the reaction pathway to the alcohols, which is in contrast to the results obtained by Dombek [38] and Orchin [39 40]. This then prompted Cole-Hamilton and co-workers to propose the formation of the hydroxycarbene intermediate. This agrees with our results and similar results (*i.e.* alcohol formation) obtained recently with binuclear alkyl manganesepentacarbonyl species [12]. Thus we suggest that with these manganese alkyl model complexes, alcohols may be formed directly on reaction with synthesis gas and not *via* aldehydes.

Thus, from our results it can be seen that the reactions of transition metal alkyl compounds could be models for the termination step in catalytic conversions of hydrocarbons to oxygenated products and that by changing the catalyst or reaction conditions it may be possible to selectively obtain alcohols rather than aldehydes in a hydroformylation reaction.

In order to test our proposal that the nature of the solvent is crucial in determining the reaction products, we reacted $[Mn\{(CH_2)_{12}CH_3\}(CO)_5]$ with synthesis gas in hexane.

### 3.4.2 (a) (ii) Reaction of [$Mn\{(CH_2)_{12}CH_3\}(CO)_5$] with Synthesis Gas in Hexane

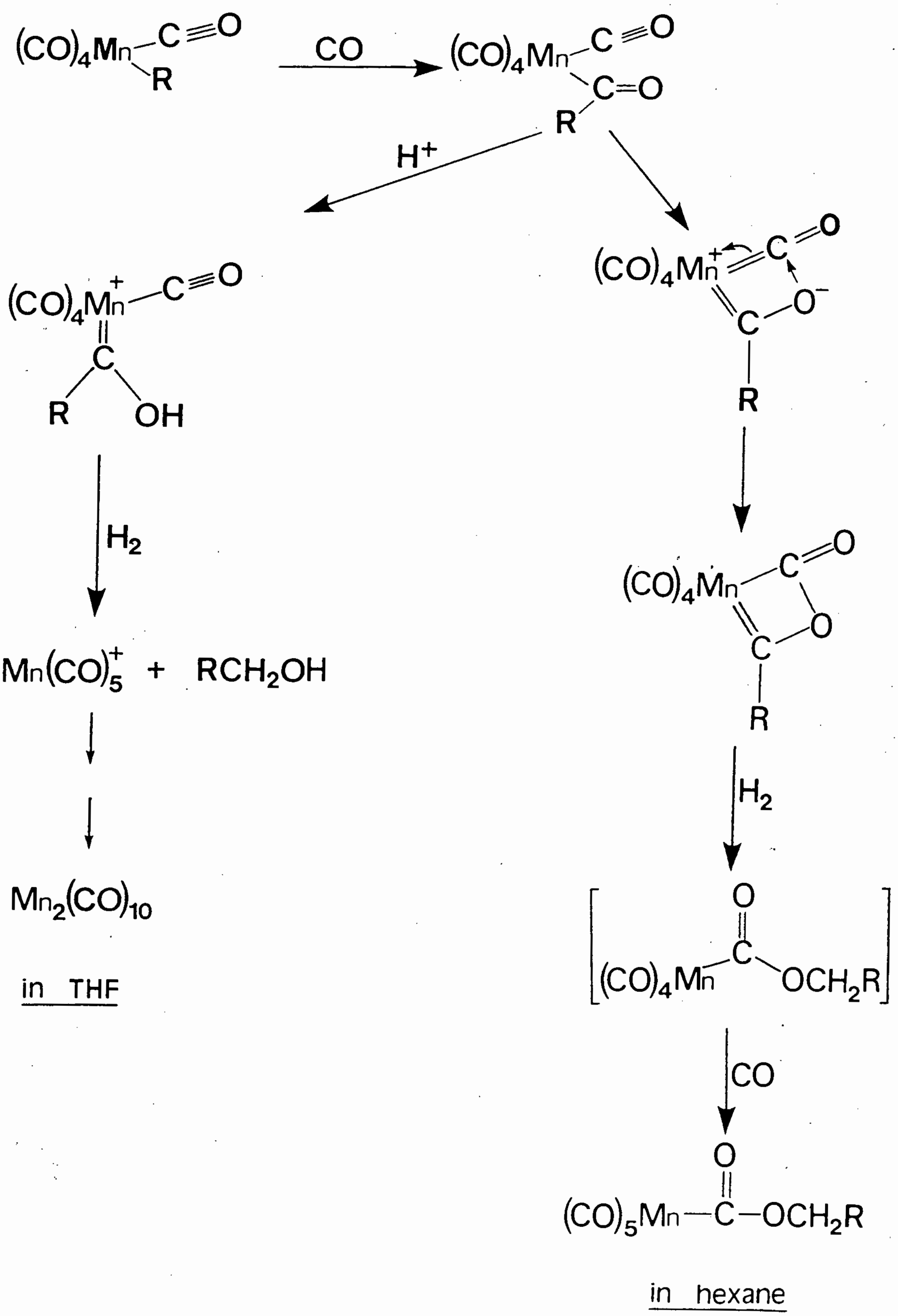
A solution of [$Mn\{(CH_2)_{12}CH_3\}(CO)_5$] in hexane was transferred to an autoclave and pressurized with $CO/H_2$ 40 atm. and then heated at 55°C for 2.5h. During this time the pressure rose rapidly to 70 atm. and thereafter remained at 70 atm.

The reaction gave the alkoxycarbonyl compound [$Mn\{CO(O)CH_2(CH_2)_{12}CH_3\}(CO)_5$] as the major isolated product (in 32% yield). A small amount of [$Mn_2(CO)_{10}$] was also obtained. The alkoxycarbonyl compound was characterized by IR $\nu$(CO) in $CH_2Cl_2$: 2126(mw), 2029(s), 2010(sh), 1657(w)), melting point (35-37°C) $^1H$ NMR (in $CDCl_3$, $\delta$ = 3.64 (tr,2H)$CO(O)CH_2$; $\delta$ = 1.58(quintet, 2H)$CO(O)CH_2CH_2$; $\delta$ = 1.26 (s,22H),$(CH_2)_{11}$, $\delta$ = 0.88(tr,3H)$CH_3$) and mass spectrum ($M^+$ = 436).

Thus, our results show that the solvent does indeed play a crucial role in determining the nature of the products obtained in a hydroformylation-type reaction. We propose that the solvent may alter the mechanism of the reaction as outlined in Scheme 7.

### 3.4.2 (b) Reaction of [$Mn_2(CO)_{10}$] with 1-hexene and Synthesis Gas in Tetrahydrofuran

While a wide variety of Group VIII metal carbonyl compounds are known to function as hydroformylation catalysts [46], very little is known about the catalytic activities of Group VII complexes such as [$Mn_2(CO)_{10}$]. It has been claimed that [$Mn(H)(CO)_5$] and [$CpMn(CO)_3$] can act as hydroformylation catalysts [47,48] but to the best of our knowledge there has only been one early report on the use of [$Mn_2(CO)_{10}$] as a hydroformylation catalyst, *i.e.* for the conversion of cyclohexene to cyclohexylmethanol [49].



<u>Scheme 7</u> Proposed Mechanism for Reaction of $[Mn\{(CH_2)_nCH_3\}(CO)_5]$ with Synthesis Gas in Different Solvents

Since it is known that $[Mn_2(CO)_{10}]$ will react with $H_2$ to form $[Mn(H)(CO)_5]$ [50], which can in turn insert an olefinic double bond [51] to form $[Mn(R)(CO)_5]$ species, we decided to test $[Mn_2(CO)_{10}]$ for catalytic activity in the hydroformylation reaction.

A solution of $[Mn_2(CO)_{10}]$ in THF was added to 1-hexene (a 6-molar excess). This was then transferred to an autoclave and pressurized with $CO/H_2$ to 40 atm. The reaction mixture was then heated at 74°C for 8.5h. The only isolable organic product from the reaction was 1-heptanol, identified on the basis of its IR, $^1H$ NMR and mass spectrum ($M^+$ = 116). The characterization data are shown in Table 3.6. The yield of 1-heptanol (27%) was not very high. However, $[Mn_2(CO)_{10}]$ was recovered in 88% yield meaning that only 0.103 mmoles of $[Mn_2(CO)_{10}]$ were lost. When one compares this to the 1.72 mmols of heptanol that were formed, it suggests that the reaction is in fact catalytic. In their early study on the use of $[Mn_2(CO)_{10}]$ as a hydroformylation catalyst [49], Weil *et al.* also observed the loss of some $[Mn_2(CO)_{10}]$, which they attributed to some catalyst having reacted with the oxo products or $H_2O$. Although our study was performed under considerably milder conditions (40 atm., 74°C) than that of Weil *et al.* (204 atm., 235°C), the different solvents used (Weil *et al.* used cyclohexane) should presumably account for the fact that we observed the catalytic formation of 1-heptanol from 1-hexene and $CO/H_2$ under relatively mild conditions. The use of a polar solvent such as THF should drive the reaction under much milder conditions as it will favour the formation of the proposed hydroxycarbene intermediate. We thus propose the catalytic cycle as shown in Fig. 3 for the conversion of 1-hexene to 1-heptanol in the presence of $[Mn_2(CO)_{10}]$.

Thus our results indicate that manganese carbonyl, $[Mn_2(CO)_{10}]$, has catalytic activity for the hydroformylation

Table 3.6

**Data for Reaction of [$Mn_2(CO)_{10}$] with $CO/H_2$ and 1-hexene**

| Proposed Product | IR[a] (neat film,$cm^{-1}$) | $^1H$ NMR[b] ($CDCl_3$) | Yield (%) (based on 1-hexene) |
|---|---|---|---|
| $CH_3(CH_2)_5CH_2OH$ | 3378(s,O-H---O stretch<br>2890(br,s)<br>1460(s)<br>1372(m)<br>1142(m)<br>1052(br,s,$CH_2$-OH stretch)<br>710(m) | 3.61(br,OH)<br>1.63(sh,$CH_2OH$)<br>1.29(br,$(CH_2)_5$)<br>0.89(br,$CH_3$) | 27 |

a:s = strong, br = broad, m = medium
b:br = broad signal, sh = shoulder

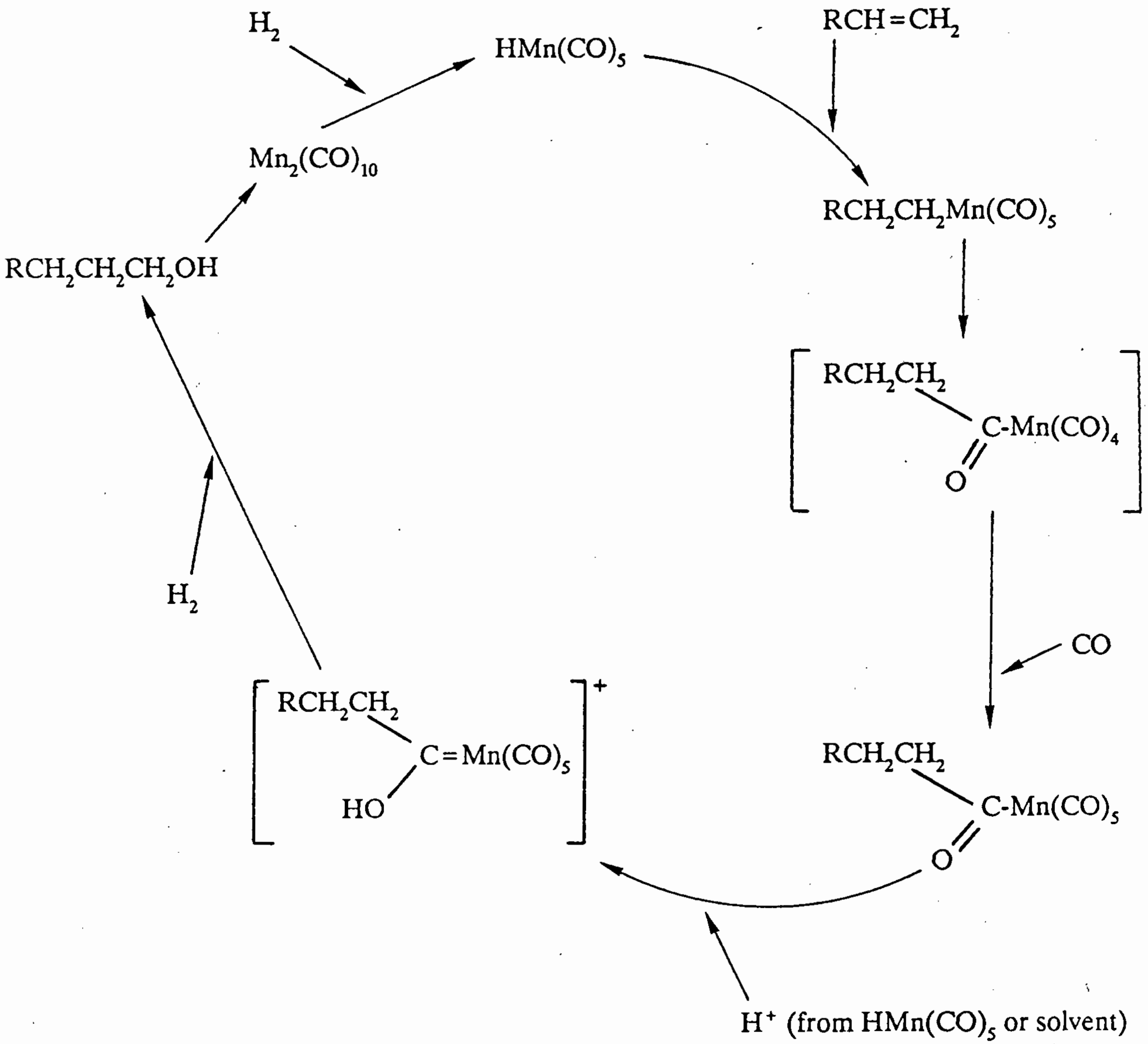


Fig. 3 **Proposed Catalytic Cycle for the Conversion of 1-Alkenes to Alcohols Using $[Mn_2(CO)_{10}]$**

reaction but that the products are alcohols rather than aldehydes. However, [$Mn_2(CO)_{10}$] is unlikely to replace the more efficient cobalt or rhodium carbonyl compounds as a hydroformylation catalyst owing to the [$Mn_2(CO)_{10}$]-catalyzed reaction requiring fairly vigorous conditions and giving rather low yields. Further investigations need to be undertaken to optimize the conditions. The loss of expensive [$Mn_2(CO)_{10}$] would also be an unfavourable factor.

## 3.5 CONCLUSIONS

Rates have been measured for the decarbonylation reactions of an extensive series of manganesepentacarbonyl acyl complexes and for the reactions of the corresponding series of n-alkyl complexes with $PPh_3$(an alkyl migration reaction). The results obtained by us for both types of reaction show a dependence of the rates of the reactions on the nature of the alkyl group. We propose that both steric and electronic factors are important in determining the reactivity patterns of these compounds. These reactions have been shown to have relevance as models for catalytic reactions such as hydroformylation and the Fischer-Tropsch synthesis.

[$Mn_2(CO)_{10}$] has been shown to be an active hydroformylation catalyst for the conversion of 1-hexene to 1-heptanol. The reactions of [$Mn(R)(CO)_5$] compounds with synthesis gas thus have important applications in this field. New information has been obtained on this process, *viz.* that the solvent plays a crucial role in determining the selectivity of the catalyst.

## 3.6 REFERENCES

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# CHAPTER 4

# ACYL AND ALKYL RHENIUMPENTACARBONYL COMPLEXES : SYNTHESIS, CHARACTERIZATION AND REACTIVITY

## 4.1 INTRODUCTION

Until now, the only known mononuclear rheniumpentacarbonyl species of the type $[Re(R)(CO)_5]$ (where R is a hydrocarbyl ligand) have been $[Re(CH_3)(CO)_5]$, $[Re(C_6H_5)(CO)_5]$, $[Re(CH_2C_6H_5)(CO)_5]$[1], $[Re(C_2H_5)(CO)_5]$ [2], $[Re(C_2H_4)(CO)_5]^+$ [3,4], $[Re(i\text{-}Bu)(CO)_5]$[5] and some substituted benzyl and phenyl derivatives $[Re(CH_2C_6H_{5-n}X_n)(CO)_5]$[6], $[Re(p\text{-}XC_6H_4)(CO)_5]$ (X = Cl,Br,I)[7], [Re(o-,m- and p-$ClC_6H_4)(CO)_5]$[8] and [Re(m- and p-Me-$C_6H_4)(CO)_5]$[9]. The acyl complexes $[Re(COCH_3)(CO)_5]$, $[Re(COC_6H_5)(CO)_5]$, $[Re(COCH_2C_6H_5)(CO)_5]$[1], $[Re(COC_2H_5)(CO)_5]$[2], $[Re(p\text{-}XC_6H_4CO)(CO)_5]$ (X = Cl,Br,I) [7], [Re(o-,m- and p-$ClC_6H_4CO)(CO)_5]$ [8] and $[Re(p\text{-}MeC_6H_4CO)(CO)_5]$ [9] are also known. $[Re(o\text{-}MeC_6H_4CO)(CO)_5]$ gives $[Re_2(CO)_{10}]$ upon heating, rather than $[Re(o\text{-}tolyl)(CO)_5]$[9], thus, the o-tolyl derivative is not known.

Only three μ-alkanediyl complexes of rhenium are known, *viz.* μ-(1,2)-ethanediyl-bis-rheniumpentacarbonyl, $[(CO)_5ReCH_2CH_2Re(CO)_5]$, prepared by the reaction of $Na[Re(CO)_5]$ with $[Re(C_2H_4)(CO)_5]^+$[10], $[(CO)_5Re(CH_2)_3Re(CO)_5]$, prepared by the reaction of $Na[Re(CO)_5]$ with $CF_3SO_2O(CH_2)_3OSO_2CF_3$ [11] and the 1,4-butanediyl complex, $[(CO)_5Re(CH_2)_4Re(CO)_5]$, prepared by decarbonylation of the corresponding acyl derivative [11].

Although numerous reactions have been reported for $[Mn(R)(CO)_5]$ compounds [12] (especially $[Mn(CH_3)(CO)_5]$) very few are in fact known for the corresponding [Re(R)$(CO)_5$] species. It has been observed that alkyl complexes of third row transition metals undergo alkyl migrations or substitution reactions at rates much slower than those of first row metals [13,14]. This is partly due to the higher strength of the metal-carbon bond in [Re(R)$(CO)_5$] than in [Mn(R)$(CO)_5$] [15], which has been correlated with an increase in the bonding overlaps between the 2σR and the (p,d)-hybrid $\sigma ML_n$ on the metal centre [16].

The reactions of the μ-butanediyl complex [$(CO)_5Re(CH_2)_4Re(CO)_5$] with tertiary phosphines, $PR_3$ ($PR_3$ = $PPh_3$, $PPh_2Me$, $PPhMe_2$, $PMe_3$) have been reported [11], the products of the reaction are the phosphine-substituted species [$(CO)_4(PR_3)Re(CH_2)_4Re(PR_3)(CO)_4$]. Treatment of [Re(p-$ClC_6H_4$)$(CO)_5$] or [Re(p-$ClC_6H_4CO$)$(CO)_5$] with $PPh_3$ gives [Re(p-$ClC_6H_4$)$(CO)_4(PPh_3)$][17]. Reaction of [Re$(CH_3)(CO)_5$] with CO (320atm., 140°C) resulted only in the eventual formation of [$Re_2(CO)_{10}$] (at 200°C)[18]. [$(CO)_5Re(CH_2)_4Re(CO)_5$] reacts with synthesis gas (1:1 $CO/H_2$) (40 atm., 70°C) to give a mixture of [$(CO)_5Re(CH_2)_4Re(CO)_5$], [$(CO)_5ReCO(CH_2)_4CORe(CO)_5$], the bifunctional aldehyde $OHC(CH_2)_4CHO$ and 1,6-hexanediol, $HO-CH_2(CH_2)_4CH_2-OH$ [19].

In view of the fact that we had synthesized higher n-alkyl derivatives of [Mn$(CO)_5$] and found them to be relatively stable [20], we were interested to investigate the rhenium analogues and particularly to determine the effect of (a) changing the metal atom in [M(R)$(CO)_5$] (and [M(COR)$(CO)_5$)]), and (b) varying the length of the alkyl chain in [Re(R)$(CO)_5$] (and [Re(COR)$(CO)_5$]). It was hoped that this would generate new information on the alkyl migration reaction and on transition metal alkyl compounds in general.

## 4.2 SYNTHESIS AND CHARACTERIZATION

### 4.2.1 MONONUCLEAR ACYL COMPOUNDS $[Re(COR)(CO)_5]$ (R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

The acyl compounds $[Re(COCH_3)(CO)_5]$ 1, [1] and $[Re(COC_2H_5)(CO)_5]$ 2, [2] have previously been reported. The syntheses of the new acyl compounds $[Re(COR)(CO)_5]$ (R = n-$C_3H_7$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$), 3-13, are now described. These complexes were prepared by the reaction of $Na[Re(CO)_5]$ with the appropriate acyl chloride (equation 1). Compounds 1 and 2 were also prepared in the same manner by us.

$$Na[Re(CO)_5] + RCOCl \xrightarrow[25°C]{THF} [Re(COR)(CO)_5] + NaCl \qquad (1)$$

(R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

All the compounds were isolated as pale-yellow microcrystalline solids which are stable in air in closed containers for several months. They are also fairly stable in solution when kept under nitrogen. They have been fully characterized by IR, $^1H$ and $^{13}C$ NMR, elemental analysis, mass spectroscopy and differential scanning calorimetry (DSC) (for R = $C_2H_5$, n-$C_3H_7$,n-$C_6H_{13}$,n-$C_7H_{15}$,n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$). The data are listed in Tables 4.1 - 4.5.

**IR**

The IR spectra in the $\nu$(CO) region (see Table 4.1) are in good agreement with the reported spectrum for $[Re(COCH_3)(CO)_5]$[1] and show the expected number of peaks for $[M(COR)(CO)_5]$ compounds [21], *viz.*. $A_1$ ($2130cm^{-1}$), B ($2059cm^{-1}$), E($2014cm^{-1}$), $A_1$ ($1998cm^{-1}$) and acyl ($1622cm^{-1}$). It can be seen that there is no significant variation in $\nu$ (CO) upon changing the length of the alkyl chain.

Table 4.1

## DATA FOR $[Re(COR)(CO)_5]^-$

| R | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) ($cm^{-1}$)[a] | Elemental Analysis C; found (calcd) | H; found (calcd) |
|---|---|---|---|---|---|---|
| $CH_3$ | 1 | 45 | 79-82 | 2131w, 2060w, 2016s, 1999ms, 1621w | 22.1(22.8) | 0.8(0.8) |
| $C_2H_5$ | 2 | 58 | 90[b] | 2130w, 2059w, 2015s, 1998ms, 1625w | 24.6(25.0) | 1.2(1.3) |
| n-$C_3H_7$ | 3 | 61 | 68-72 | 2130w, 2059w, 2014s, 1998ms, 1624w | 27.1(27.2) | 1.7(1.8) |
| n-$C_4H_9$ | 4 | 65 | 70-73 | 2130w, 2058w, 2015s, 1998ms, 1622w | 29.1(29.2) | 2.3(2.2) |
| n-$C_5H_{11}$ | 5 | 62 | 62-64 | 2130w, 2059w, 2015s, 1998ms, 1620w | 31.4(31.1) | 2.6(2.6) |
| n-$C_6H_{13}$ | 6 | 71 | 53-56 | 2129w, 2058w, 2014s, 1998ms, 1622w | 32.5(32.8) | 2.8(3.0) |
| n-$C_7H_{15}$ | 7 | 58 | 49-53 | 2129w, 2059w, 2014s, 1998ms, 1625w | 34.1(34.4) | 3.1(3.3) |
| n-$C_8H_{17}$ | 8 | 60 | 48-51 | 2129w, 2058w, 2014s, 1998ms, 1624w | 35.6(36.0) | 3.4(3.7) |
| n-$C_9H_{19}$ | 9 | 72 | 43-47 | 2130w, 2059w, 2015s, 1999ms, 1615w | 37.4(37.4) | 3.9(4.0) |
| n-$C_{11}H_{23}$ | 10 | 74 | 42-45 | 2129w, 2058w, 2014s, 1998ms, 1625w | 40.2(40.1) | 4.5(4.6) |
| n-$C_{13}H_{27}$ | 11 | 67 | 50-53 | 2129w, 2058w, 2014s, 1998ms, 1625w | 42.6(42.5) | 5.2(5.1) |
| n-$C_{15}H_{31}$ | 12 | 65 | 60-62 | 2129w, 2059w, 2014s, 1998ms, 1622w | 44.5(44.6) | 5.3(5.5) |
| n-$C_{17}H_{35}$ | 13 | 74 | 61-63 | 2129w, 2058w, 2014s, 1998ms, 1624w | 46.4(46.5) | 5.9(5.9) |

a: in hexane, w = weak, ms = medium/strong, s = strong
b: sublimed first at 64°C

## $^1$H and $^{13}$C NMR

Assignments of the $^1$H and $^{13}$C NMR data were made by comparison of all of the NMR data for these compounds and comparison of these data with the NMR data of the analogous [Mn(COR)(CO)$_5$] compounds [22]. As an example of the results obtained, the $^1$H and $^{13}$C NMR spectra of [Re{CO(CH$_2$)$_5$CH$_3$}(CO)$_5$] are shown in Figures 1 and 2, respectively.

### $^1$H NMR

From the $^1$H NMR data (Table 4.2) it can be seen that separate resonances are observed for the methyl protons of the alkyl chain and the $\alpha$ and $\beta$ protons in these acyl compounds. The remaining methylene protons appear as a complex signal (sometimes a broad singlet). There is no significant variation in chemical shift with variation in the length of the alkyl chain. For this reason, integration of the peaks is therefore the only way to distinguish between the compounds using $^1$H NMR measurements. The same was found for the analogous manganese compounds [22] and for related long chain alkyl iron and ruthenium compounds [23]

### $^{13}$C NMR

The $^{13}$C NMR spectra are reported in Table 4.3. The $^{13}$C NMR spectrum of [Re(COCH$_3$)(CO)$_5$] has previously been reported [24]. The carbonyl resonances (terminal and acyl) are at the expected positions and are independent of the alkyl chain length. The terminal carbonyl groups give rise to two signals, appearing at *ca.* $\delta$ = 183.5 ppm and $\delta$ = 181 ppm. The observation of two signals is a result of one of the carbonyls being *trans* to the alkyl chain while the remaining four carbonyls are *cis* to the alkyl chain. The signal at $\delta$ = 183.5 ppm can be assigned to the *cis* carbonyls while the signal at $\delta$ = 181 ppm is due to the *trans* carbonyl. These assignments were made on the basis of relative intensities of the peaks, which was found to be

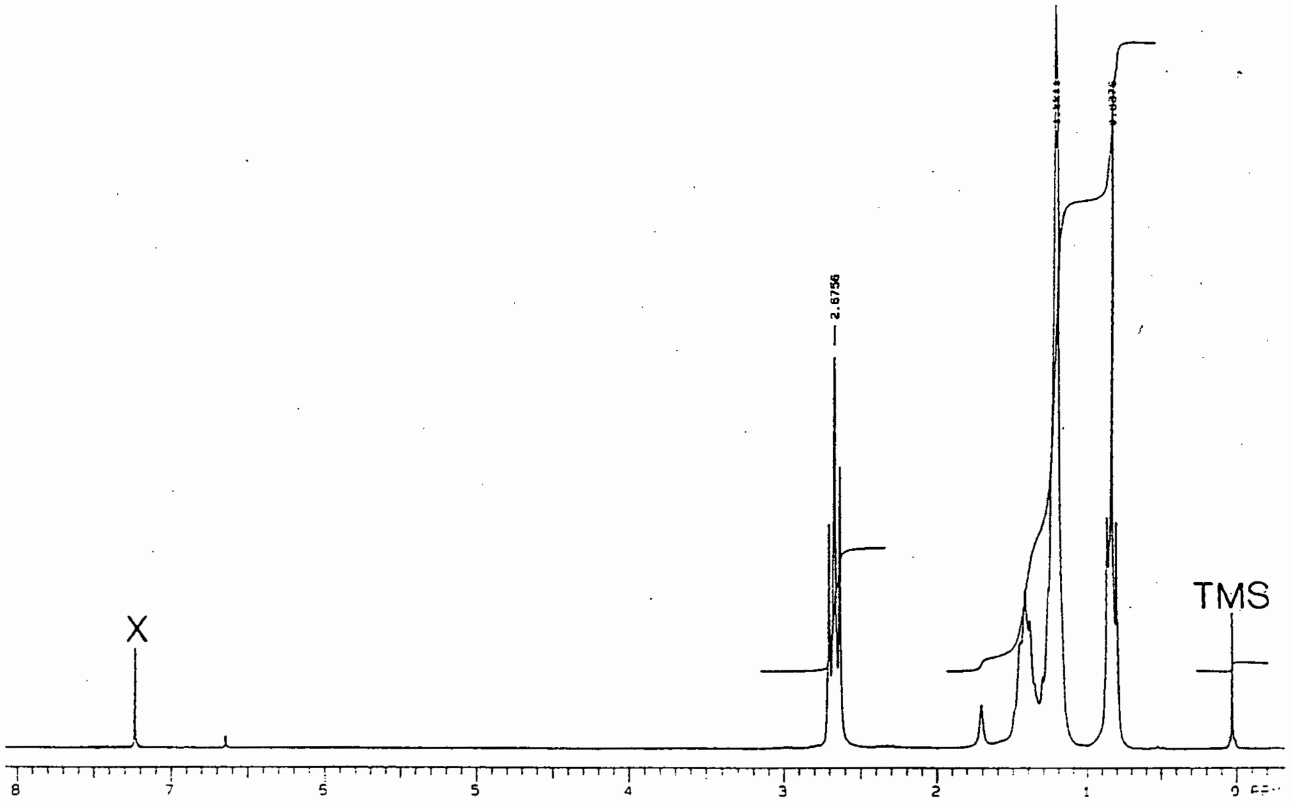

Figure 1 $^1H$ NMR Spectrum of [Re{CO(CH$_2$)$_5$CH$_3$}(CO)$_5$]
(X = solvent (CDCl$_3$) impurity)

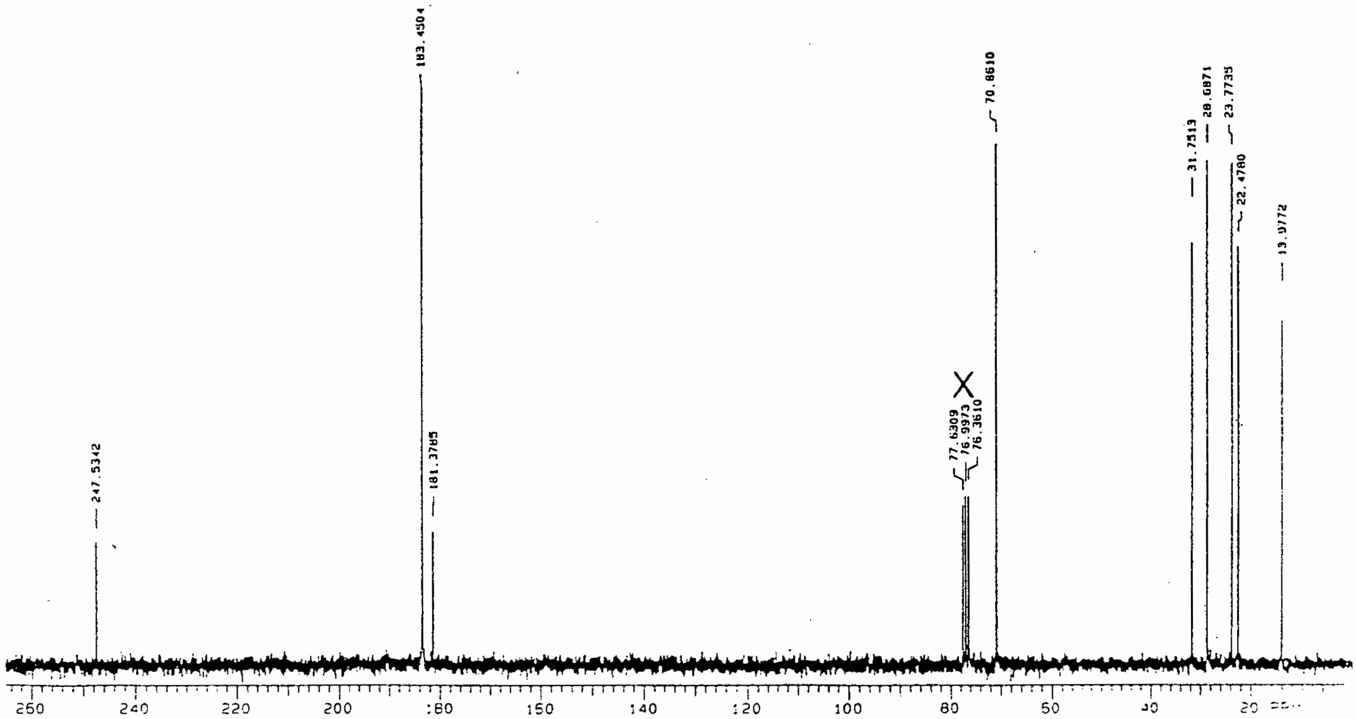

Figure 2 $^{13}C$ NMR Spectrum of [Re{CO(CH$_2$)$_5$CH$_3$}(CO)$_5$]

approximately 4:1. This compares well to what is obtained for other complexes of the type $[Re(X)(CO)_5]$ [24]. The signal at *ca.* δ = 247 ppm is due to the acyl carbonyl group. For compounds **1-9** all the carbon atoms of the alkyl chain were assigned. For compounds **10-13**, the peaks due to the central carbon atoms were not resolved, as is found for substituted n-alkanes, $CH_3(CH_2)_nX$[23]. Effects of the metal are only evident in the first two carbon atoms of the alkyl chain. Thus, the influence that the metal has on the chemical shifts of carbon atoms in the methylene chain diminishes along the chain and is only really apparent in the α and ß methylene positions.

## MASS SPECTRA

The mass spectra of **1-13** are reported in Table 4.4 and are all similar. They all show parent molecular ions with the predominant fragmentation pathway being sequential loss of carbonyl groups followed by sequential loss of methylene fragments. Some evidence is seen for remote functionalization in the higher mass peaks of the longer chain compounds. Thus, for $[Re\{CO(CH_2)_{16}CH_3\}(CO)_5]$, peaks are observed for $[M-6CO-H]^+$, $[M-6CO-C_2H_5-H]^+$, $[M-6CO-C_3H_7-H]^+$ and $[M-6CO-C_4H_9-H]^+$. The expected 37% $^{185}Re$:63% $^{187}Re$ isotope distribution was seen for the rhenium-containing peaks.

## DSC DATA

Differential Scanning Calorimetry (DSC) was used to obtain some quantitative information about the thermal decomposition of these rheniumpentacarbonyl acyl compounds. To our knowledge, no DSC studies have previously been reported for any $[Re(COR)(CO)_5]$ species. The DSC data for compounds **2,4,6,7** and **10-13** are given in Table 4.5. The DSC trace of **11**, $[Re\{CO(CH_2)_{12}CH_3\}(CO)_5]$ is shown in Fig. 3. All of the compounds show a sharp endotherm at low temperatures which corresponds to the melting point (mp) of

Table 4.2

$^1$H NMR Data for $[Re(COR)(CO)_5]^a$

| R | Cmpd No | $ReCO\underline{CH_2}$ | $ReCOCH_2\underline{CH_2}$ | $ReCOCH_2CH_2\underline{(CH_2)_x}$ | $CH_3$ |
|---|---|---|---|---|---|
| $CH_3$ | 1 | | | | 2.53s |
| $C_2H_5$ | 2 | 2.70q(2H) | | | 0.87tr(3H) |
| $n$-$C_3H_7$ | 3 | 2.65tr(2H) | 1.44q(2H) | | 0.83tr(3H) |
| $n$-$C_4H_9$ | 4 | 2.68tr(2H) | 1.40q(2H) | 1.22q(2H) | 0.85tr(3H) |
| $n$-$C_5H_{11}$ | 5 | 2.62tr(2H) | 1.49c(2H) | 1.20c(4H) | 0.81tr(3H) |
| $n$-$C_6H_{13}$ | 6 | 2.68tr(2H) | 1.42c(2H) | 1.22c(6H) | 0.84tr(3H) |
| $n$-$C_7H_{15}$ | 7 | 2.69tr(2H) | 1.44c(2H) | 1.24c(8H) | 0.85tr(3H) |
| $n0C_8H_{17}$ | 8 | 2.69tr(2H) | 1.44c(2H) | 1.24c(10H) | 0.85tr(3H) |
| $n$-$C_9H_{19}$ | 9 | 2.70tr(2H) | 1.46c(2H) | 1.24c(12H) | 0.86tr(3H) |
| $n$-$C_{11}H_{23}$ | 10 | 2.66tr(2H) | 1.40c(2H) | 1.17c(16H) | 0.81tr(3H) |
| $n$-$C_{13}H_{27}$ | 11 | 2.64tr(2H) | 1.41c(2H) | 1.18c(20H) | 0.81tr(3H) |
| $n$-$C_{15}H_{31}$ | 12 | 2.69tr(2H) | 1.44c(2H) | 1.24c(24H) | 0.87tr(3H) |
| $n$-$C_{17}H_{35}$ | 13 | 2.70tr(2H) | 1.43c(2H) | 1.24c(28H) | 0.87tr(3H) |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm), s = singlet, tr = triplet, q = quartet, c = complex signal

## Table 4.3

$^{13}C$ NMR Data for $[Re(COR)(CO)_5]^a$

| R | Cmpd No | ReCO (acyl) | ReCO (*cis*)[b] | ReCO (*trans*)[b] | Re-CO$\underline{C}H_2$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{17}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | 1 | 245.0 | 182.9 | 181.1 | 57.4 | | | | | | | | | | | | | | | | |
| $C_2H_5$ | 2 | 246.9 | 183.4 | 181.3 | 64.0 | 8.2 | | | | | | | | | | | | | | | |
| n-$C_3H_7$ | 3 | 247.2 | 183.5 | 181.4 | 72.8 | 17.2 | 13.5 | | | | | | | | | | | | | | |
| n-$C_4H_9$ | 4 | 247.3 | 183.5 | 181.4 | 70.5 | 25.9 | 22.1 | 13.9 | | | | | | | | | | | | | |
| n-$C_5H_{11}$ | 5 | 247.6 | 183.4 | 181.4 | 70.8 | 31.2 | 23.5 | 22.6 | 13.9 | | | | | | | | | | | | |
| n-$C_6H_{13}$ | 6 | 247.5 | 183.5 | 181.4 | 70.9 | 31.8 | 28.7 | 23.8 | 22.5 | 14.0 | | | | | | | | | | | |
| n-$C_7H_{15}$ | 7 | 247.3 | 183.3 | 181.2 | 70.7 | 31.5 | 29.0 | 28.8 | 23.6 | 22.4 | 13.8 | | | | | | | | | | |
| n-$C_8H_{17}$ | 8 | 247.6 | 183.4 | 181.3 | 70.8 | 31.7 | 29.5 | 29.1 | 29.0 | 23.8 | 22.5 | 14.0 | | | | | | | | | |
| n-$C_9H_{19}$ | 9 | 247.4 | 183.3 | 181.2 | 70.7 | 31.7 | 29.4 | 29.3 | 29.1 | 28.0 | 23.6 | 22.5 | 13.9 | | | | | | | | |
| n-$C_{11}H_{23}$ | 10 | 247.8 | 183.4 | 181.4 | 70.8 | 31.9 | {29.6 → | | | | | → 28.8}[c] | 23.8 | 22.6 | 14.0 | | | | | | |
| n-$C_{13}H_{27}$ | 11 | 248.3 | 183.4 | 181.4 | 70.8 | 31.9 | {29.6 → | | | | | | | → 28.9}[c] | 23.9 | 22.7 | 14.1 | | | | |
| n-$C_{15}H_{31}$ | 12 | 248.3 | 184.2 | 182.1 | 71.6 | 32.6 | {30.4 → | | | | | | | | | → 29.8}[c] | 24.5 | 23.4 | 14.8 | | |
| n-$C_{17}H_{35}$ | 13 | 248.1 | 184.2 | 182.0 | 71.6 | 32.6 | {30.4 → | | | | | | | | | | → 29.8}[c] | 26.38 | 24.5 | 23.4 | 14.8 |

a: in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm)
b: relative to the alkyl chain
c: peaks were not resolved

the individual compounds. The second Tmax (endo) at *ca.* 200°C (seen only for **10** and **11**) may be due to decomposition which results in the loss of the hydrocarbon chain. The third Tmax (endo) at *ca.* 280°C (seen for **7**,**10**,**11** and **12**) is probably due to the decomposition of $[Re_2(CO)_{10}]$ which has Tmax (endo) at *ca.* 190°C under these conditions.

The thermograms of the compounds with only one Tmax (endo) (**2**,**4** and **6**) all show 100% mass loss over the range 80°-130°C; this could be due to sublimation. The compounds with more than one Tmax (endo) (**7**,**10-13**) show steps in their TGA's corresponding to initial loss of $[Re(CO)_3]$, followed by loss of the remaining three carbonyls and fragments of the alkyl chain (except for 13, which showed initial loss of $[Re(CO)_6]$). These results confirm that the second (or third) endotherms in the DSC's may be due to loss of alkyl fragments. A plot of melting point (mp)(measured by conventional means) versus chain length (n = number of carbon atoms in the alkyl chain) is given in Figure 4 which shows that the mp (with the exception of $[Re(COCH_3)(CO)_5]$ initially decreases with increasing chain length (as found for the series $[Fp(CH_2)_nFp]$ (n = 3-10)[25] and $[Rp(CH_2)_nRp]$(n = 3-10)[26,27]) until n = 11, and then increases with increasing chain length. This behaviour is also found in the series $[Fp(CH_2)_nFp]$ *i.e.* the mp decreases with increasing chain length until n = 10 (for n even and n odd) and then increases sharply for n = 11 and n = 12 [25]. No other trends could be found in the DSC data.

## 4.2.2 BINUCLEAR ACYL COMPOUNDS, $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$ (n = 4-8;10)

The binuclear acyl compound $[(CO)_5ReCO(CH_2)_4CORe(CO)_5]$, **14**, has previously been reported [11]. We now report the syntheses of the new compounds $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$ (n = 5-8,10), **15-19**. These compounds, and compound **14**, were prepared by the reaction of $Na[Re(CO)_5]$ with the appropriate diacyl chloride,

Table 4.4

Mass Spectral Data for $[Re(COR)(CO)_5]^a$

| Possible Assignments[b] | Relative Peak Intensities[c] | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| Parent, M | 12 | 12 | 10 | 8 | 5 | 8 | 4 | 4 | 10 | 13 | 9 | 2 | 7 |
| M-CO | 83 | 91 | 81 | 81 | 75 | 78 | 82 | 80 | 76 | 83 | 80 | 70 | 80 |
| M-2CO | 50 | 53 | 48 | 60 | 58 | 55 | 51 | 50 | 61 | 60 | 57 | 63 | 51 |
| M-3CO | 35 | 30 | 32 | 34 | 41 | 33 | 38 | 43 | 42 | 35 | 36 | 40 | 36 |
| M-4CO | 38 | 42 | 38 | 36 | 33 | 40 | 42 | 36 | 44 | 43 | 35 | 43 | 43 |
| M-5CO | 34 | 40 | 33 | 32 | 39 | 38 | 36 | 41 | 37 | 32 | 39 | 41 | 36 |
| M-6CO | 38 | 40 | 43 | 38 | 37 | 46 | 42 | 40 | 43 | 38 | 35 | 39 | 42 |
| M-6CO-H | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 3 | 0 | 12 | 5 | 13 |
| M-6CO-$CH_3$ | 100 | 0 | 0 | 0 | 3 | 4 | 2 | 1 | 2 | 2 | 5 | 3 | 6 |
| M-6CO-$C_2H_5$ | - | 100 | 3 | 3 | 5 | 8 | 5 | 18 | 14 | 24 | 28 | 27 | 32 |
| M-6CO-$C_2H_5$-H | - | - | 0 | 0 | 3 | 2 | 2 | 4 | 3 | 6 | 5 | 7 | 11 |
| M-6CO-$C_3H_7$ | - | - | 100 | 3 | 5 | 4 | 18 | 20 | 14 | 12 | 14 | 18 | 21 |

Table 4.4 (... continued)

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M-6CO-$C_3H_7$-H | - | - | - | 2 | 0 | 3 | 2 | 0 | 0 | 2 | 0 | 5 | 6 |
| M-6CO-$C_4H_9$ | - | - | - | - | 6 | 10 | 10 | 20 | 14 | 31 | 35 | 61 | 78 |
| M-6CO-$C_4H_9$-H | - | - | - | - | 0 | 3 | 0 | 4 | 10 | 8 | 3 | 30 | 23 |
| M-6CO-$C_5H_{11}$ | - | - | - | - | 100 | 0 | 12 | 0 | 0 | 3 | 0 | 2 | 4 |
| M-6CO-$C_7H_{15}$ | - | - | - | - | - | - | 100 | 10 | 8 | 14 | 12 | 18 | 21 |
| M-6CO-$C_9H_{19}$ | - | - | - | - | - | - | - | - | 100 | 28 | 30 | 27 | 32 |
| M-6CO-$C_{11}H_{23}$ | - | - | - | - | - | - | - | - | - | 100 | 38 | 42 | 43 |
| M-6CO-$C_{12}H_{25}$ | - | - | - | - | - | - | - | - | - | - | 18 | 10 | 3 |
| M-6CO-$C_{13}H_{27}$ | - | - | - | - | - | - | - | - | - | - | 90 | 31 | 24 |
| M-6CO-$C_{14}H_{29}$ | - | - | - | - | - | - | - | - | - | - | - | 17 | 16 |
| M-6CO-$C_{15}H_{31}$ | - | - | - | - | - | - | - | - | - | - | - | 100 | 30 |
| M-6CO-$C_{16}H_{33}$ | - | - | - | - | - | - | - | - | - | - | - | - | 17 |
| Re | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| $C_9H_{19}$ | - | - | - | - | - | - | - | 10 | 8 | 8 | 6 | 11 | 7 |

**Table 4.4 (... continued)**

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_8H_{17}$ | - | - | - | - | - | - | - | 49 | 13 | 17 | 10 | 12 | 13 |
| $C_7H_{15}$ | - | - | - | - | - | - | 71 | 18 | 29 | 32 | 21 | 16 | 28 |
| $C_6H_{13}$ | - | - | - | - | - | 62 | 37 | 41 | 40 | 31 | 24 | 34 | 37 |
| $C_5H_{11}$ | - | - | - | - | 71 | 33 | 40 | 38 | 29 | 33 | 18 | 38 | 44 |
| $C_4H_9$ | - | - | - | 58 | 12 | 21 | 18 | 24 | 38 | 46 | 17 | 70 | 82 |
| $C_3H_7$ | - | - | 21 | 17 | 18 | 12 | 23 | 18 | 24 | 36 | 41 | 23 | 84 |
| CO | 100 | 100 | 80 | 95 | 90 | 100 | 100 | 96 | 80 | 78 | 100 | 83 | 100 |

a:ion intensity listed is that of the most abundant isotope combination
b:all ions have a single positive charge
c:peak intensities relative to base peaks at m/e 187 and m/e 28

Table 4.5

DSC Data for [Re(COR)(CO)$_5$] (°C)

| R | Cmpd No | mp[a] | Tmax (endo) (melting) | ΔH endo (kJmol$^{-1}$)[b] (melting) | Tmax (endo) | Tmax (endo) | Tmax (endo) |
|---|---|---|---|---|---|---|---|
| $C_2H_5$ | 2 | 90 | 89.4 | 22.0 | | | |
| n-$C_4H_9$ | 4 | 70-73 | 74.9 | 19.5 | | | |
| n-$C_6H_{13}$ | 6 | 53-56 | 57.2 | 13.7 | | | |
| n-$C_7H_{15}$ | 7 | 49-53 | 56.0 | 18.6 | | 292.3 | |
| n-$C_{11}H_{23}$ | 10 | 42-45 | 44.4 | 33.1 | 204.5 | 286.6 | 311.0 |
| n-$C_{13}H_{27}$ | 11 | 50-53 | 53.3 | 22.5 | 202.5 | 282.4 | 358.3 |
| n-$C_{15}H_{31}$ | 12 | 60-62 | 62.8 | 42.2 | | 278.4 | 389.6 |
| n-$C_{17}H_{35}$ | 13 | 61-63 | 63.1 | 31.9 | | | 431.8 |

a:measured on a Kofler hot stage microscope
b:determined by Perkin-Elmer PC Series DS7 Instrument (in J.g$^{-1}$)

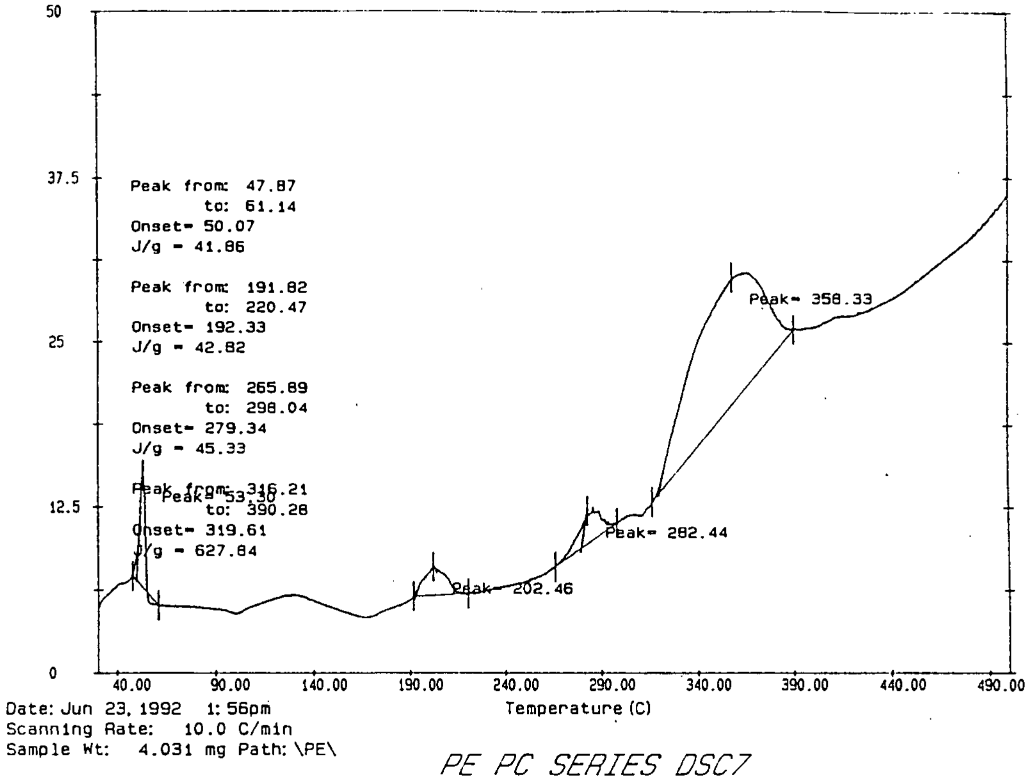

Fig. 3 DSC Trace of 11, [Re{CO$(CH_2)_{12}CH_3$}$(CO)_5$]

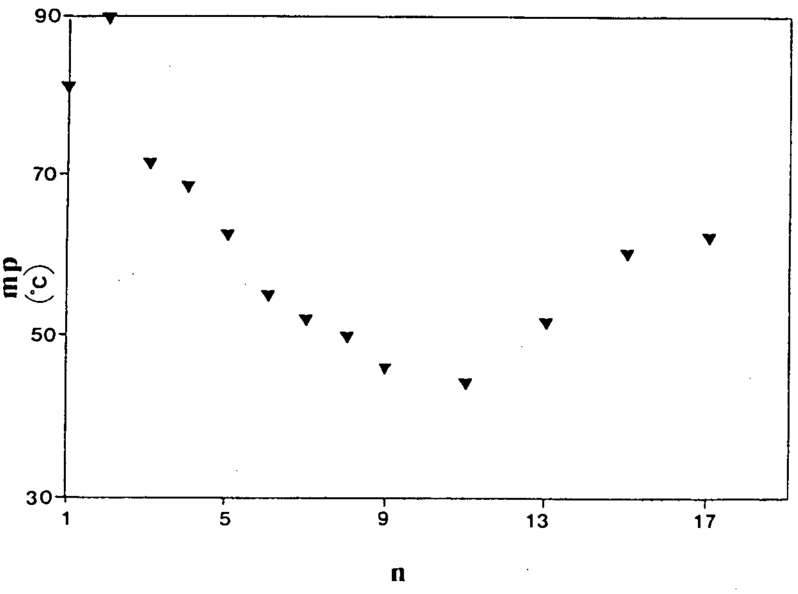

Fig. 4 Melting Point versus Length of Alkyl Chain (n = number of carbon atoms in the alkyl chain) for Mononuclear Rheniumpentacarbonyl Acyl Compounds

$ClCO(CH_2)_nCOCl$ (equation 2)

$$2Na[Re(CO)_5] + ClCO(CH_2)_nCOCl \xrightarrow[25°C]{THF} 2\ NaCl + [(CO)_5ReCO(CH_2)_nCORe(CO)_5] \quad (2)$$

$$(n = 4\text{-}8;10)$$

All the compounds were isolated as off-white microcrystalline solids which, like their mononuclear analogues, are stable in air for several months and in solution when kept under nitrogen. They have been fully characterized by IR, $^1H$ and $^{13}C$ NMR, elemental analysis, mass spectroscopy and DSC (for n = 8 and 10). The data are listed in Tables 4.6 - 4.10.

## IR

The IR spectra in the $\nu(CO)$ region are in good agreement with the reported spectrum for $[(CO)_5ReCO(CH_2)_4CORe(CO)_5]$[11] and show the expected number of peaks for $[M(COR)(CO)_5]$ species [21], *viz.* $A_1$(2132cm$^{-1}$), B(2062cm$^{-1}$), E and $A_1$(2021cm$^{-1}$) and acyl(1605cm$^{-1}$). There is no significant variation in $\nu(CO)$ upon varying the length of the bridging hydrocarbyl chain.

## $^1H$ and $^{13}C$ NMR

Assignments of the $^1H$ and $^{13}C$ NMR spectra for 14-19 were made by comparison of all of the NMR data for these compounds and by comparison of this data with the NMR data of $[(CO)_5ReCO(CH_2)_4CORe(CO)_5]$[11] and of the mononuclear analogues, $[Re(COR)(CO)_5]$.

Table 4.6

Data for $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$

| n | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) ($cm^{-1}$)[a] | Elemental Analysis<br>C;found(calcd) | <br>H;found(calcd) |
|---|---|---|---|---|---|---|
| 4 | 14 | 48 | 144-147 | 2132w,2062mw,2021sbr,1605w | 25.1(25.1) | 1.0(1.1) |
| 5 | 15 | 46 | 117-120 | 2132w,2062mw,2021sbr,1605w | 26.4(26.2) | 1.4(1.3) |
| 6 | 16 | 52 | 129-132 | 2132w,2062mw,2021sbr,1605w | 27.3(27.3) | 1.6(1.5) |
| 7 | 17 | 53 | 96-104 | 2132w,2062mw,2020sbr,1605w | 28.5(28.3) | 1.9(1.7) |
| 8 | 18 | 58 | 122-125 | 2132w,2062mw,2014sbr,1605w | 29.1(29.3) | 1.9(2.0) |
| 10 | 19 | 50 | 106-110 | 2132w,2062mw,2019sbr,1605w | 31.3(31.7) | 2.3(2.4) |

a: in $CHCl_3$, w = weak, mw = medium/weak, sbr = strong/broad

## $^1$H NMR

From the $^1$H NMR data (Table 4.7) it can be seen that, as for the mononuclear compounds, separate resonances are observed only for the $\alpha$ and $\beta$ methylene groups. The remaining methylene protons resonate as a complex signal. It can be seen that there is no significant variation in chemical shift when changing the length of the bridging hydrocarbon chain. Therefore, integration is the only way to distinguish between these compounds using $^1$H NMR measurements.

**Table 4.7**

**$^1$H NMR Data for $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]^a$**

| n | Cmpd No | $ReCO\underline{CH_2}$ | $ReCOCH_2\underline{CH_2}$ | $ReCOCH_2CH_2(\underline{CH_2})_x$ |
|---|---|---|---|---|
| 4 | 14 | 2.69tr | 1.40tr | |
| 5 | 15 | 2.69tr | 1.43tr | 1.23c(2H) |
| 6 | 16 | 2.69tr | 1.44c | 1.22c(4H) |
| 7 | 17 | 2.68tr | 1.43c | 1.22c(6H) |
| 8 | 18 | 2.69tr | 1.44c | 1.22c(8H) |
| 10 | 19 | 2.69tr | 1.43c | 1.22c(12H) |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm), tr = triplet, c = complex signal

## $^{13}$C NMR

The $^{13}$C NMR data are reported in Table 4.8. The $^{13}$C NMR spectrum of $[(CO)_5ReCO(CH_2)_4CORe(CO)_5]$ has not been reported previously. The carbonyl resonances (terminal and acyl)

**Table 4.8**

$^{13}$C NMR Data for $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]^a$

| n | Cmpd No | ReCO (acyl) | ReCO (*cis*)$^b$ | ReCO (*trans*)$^b$ | $ReCO\underline{C}H_2$ | C2 | C3 | C4 | C5 |
|---|---|---|---|---|---|---|---|---|---|
| 4 | 14 | 248.1 | 183.2 | 181.6 | 70.4 | 23.0 | | | |
| 5 | 15 | 247.7 | 183.2 | 181.2 | 70.5 | 23.5 | 28.2 | | |
| 6 | 16 | 247.0 | 183.3 | 181.2 | 70.6 | 23.5 | 28.8 | | |
| 7 | 17 | 247.7 | 183.3 | 181.2 | 70.7 | 23.5 | 28.6 | 29.3 | |
| 8 | 18 | 247.2 | 183.3 | 181.2 | 70.7 | 23.6 | 28.8 | 29.2 | |
| 10 | 19 | 247.2 | 183.3 | 181.2 | 70.7 | 23.6 | 28.8 | 29.2 | 29.3 |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm)
b:relative to the alkyl chain

are at the expected positions. The peaks due to the *cis* and *trans* CO groups were assigned on the basis of relative intensities (4:1). This is in agreement with the assignments made for the mononuclear analogues. All of the carbon atoms in the bridging alkyl chain were assigned. Since these binuclear compounds are symmetrical, some of the carbon atoms in the alkyl chain are equivalent and will resonate at identical positions, *e.g.* for $[(CO)_5ReCO(CH_2)_7CORe(CO)_5]$ only four peaks were observed for the alkyl chain as a result of three pairs of identical carbon atoms. The central carbon atom is unique and is only half the intensity of the other methylene peaks. As with the analogous mononuclear compounds, $[Re(COR)(CO)_5]$, the influence of the metal atom is only really apparent in the $\alpha$ and ß methylene positions.

## MASS SPECTRA

The mass spectra of **14**-**19** are reported in Table 4.9. They are all similar and relatively simple. No parent molecular ions were seen for any of the compounds; the parent ion in all cases was $[M-5CO]^+ ( = M')$. The predominant fragmentation pathway was loss of carbonyl groups (from $M'$) followed by successive loss of methylene fragments.

## DSC DATA

Differential Scanning Calorimetry was used to obtain some information about the thermal stability of these binuclear acyl compounds relative to their mononuclear analogues. The DSC data for compounds **18** and **19** is given in Table 4.10. Both compounds show a sharp endotherm at low temperatures, corresponding to their melting point. The second Tmax(endo) at *ca.* 200°C may, as for the mononuclear compounds, be due to decomposition arising from the loss of

## Table 4.9

## Mass Spectral Data for $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$[a]

| Possible Assignments[b] | Relative Peak Intensities[c d] | | | | | |
|---|---|---|---|---|---|---|
| | n = 4 | 5 | 6 | 7 | 8 | 10 |
| M | 0 | 0 | 0 | 0 | 0 | 0 |
| M-5CO = M′ | 12 | 14 | 21 | 18 | 10 | 8 |
| M′-CO | 18 | 9 | 7 | 10 | 12 | 9 |
| M′-2CO | 7 | 20 | 11 | 18 | 16 | 14 |
| M′-3CO | 17 | 24 | 10 | 10 | 10 | 13 |
| M′-4CO | 12 | 10 | 9 | 8 | 15 | 21 |
| M′-5CO | 24 | 21 | 13 | 14 | 10 | 17 |
| M′-6CO | 31 | 8 | 10 | 12 | 17 | 12 |
| M′-7CO | 11 | 16 | 13 | 15 | 12 | 19 |
| M′-2CO-$(CH_2)_n$-Re | 28 | 32 | 23 | 41 | 46 | 34 |
| M′-7CO-$C_2H_4$ | 12 | 4 | 4 | 8 | 0 | 9 |
| M′-7CO-$C_3H_6$ | 0 | 0 | 3 | 0 | 0 | 7 |
| M′-7CO-$C_4H_8$ | 14 | 9 | 0 | 0 | 10 | 3 |
| M′-7CO-$C_5H_{10}$ | – | 21 | 0 | 6 | 7 | 0 |
| M′-7CO-$C_6H_{12}$ | – | – | 18 | 4 | 0 | 4 |
| M′-7CO-$C_7H_{14}$ | – | – | – | 16 | 3 | 8 |
| M′-7CO-$C_8H_{16}$ | – | – | – | – | 20 | 10 |
| M′-7CO-$C_9H_{18}$ | – | – | – | – | – | 0 |
| M′-7CO-$C_{10}H_{20}$ | – | – | – | – | – | 24 |
| [Re] | 100 | 100 | 100 | 100 | 68 | 100 |
| [CO] | 82 | 23 | 42 | 100 | 100 | 29 |

a:peaks due to $[Re(CO)_n]$(n = 2 – 6) were seen in all of these mass spectra
b:all ions have a single positive charge
c:peak intensities relative to base peak for $[Re]^+$ or $[CO]^+$
d:intensity given is that of the most abundant isotope distribution

the hydrocarbon chain. The third Tmax(endo) is probably due to the decomposition of $[Re_2(CO)_{10}]$.

The thermogram of **18** showed a sharp loss in mass over the temperature range 100°-180°C, corresponding to the loss of $[(CO)_5ReCO(CH_2)_8CO]$. This was then followed by loss of 3CO over the range 240°C-300°C. The thermogram of **19** showed a sharp loss in mass over the range 90°-180°C corresponding to the loss of $[(CO)_5ReCO(CH_2)_6]$.

A plot of melting point (mp) (measured by conventional means) versus chain length (n = number of carbon atoms in hydrocarbon chain) is given in Figure 5. A regular alternation of mp between the compounds with n even and those with n odd is observed. The mps of the n odd compounds of the series are assumed to lie on a line which is below the curve formed by the mps of n even. Similar variations in mp are observed for analogous iron compounds [25] and in homologous series of aliphatic compounds, *e.g.* the series of n-paraffins [28]. The regular alternation of mp may arise from differences in structural types between the n odd and n even members of the series. The higher mps of the n even compounds than their odd homologues indicates that these compounds may have structures with closer packing of the molecules than the compounds with n odd.

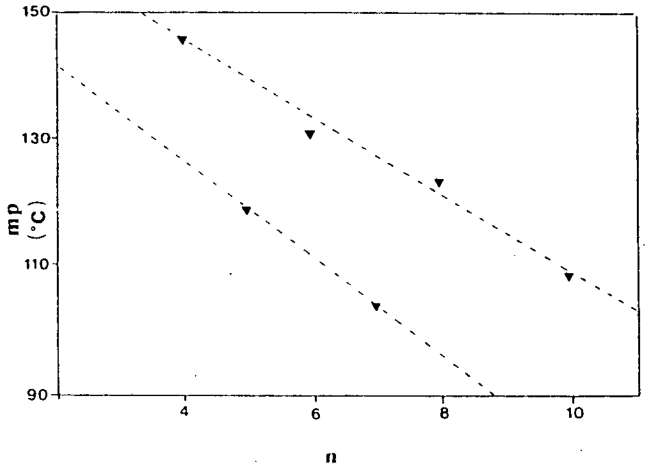

Fig. 5 Melting Point versus length of Alkyl Chain for Compounds of the Type $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$

Table 4.10

DSC Data for $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$ (°C)

| n | Cmpd No | mp[a] | Tmax(endo) (melting) | ΔHendo(kJ.mol$^{-1}$)[b] (melting) | Tmax(endo) | Tmax(endo) |
|---|---|---|---|---|---|---|
| 8 | 18 | 122-125 | 126.4 | 134.8 | 207.3 | 285.2 |
| 10 | 19 | 106-110 | 117.7 | 94.5 | 182.0 | 285.2 |

a:measured on a Kofler hot stage microscope
b:determined by Perkin-Elmer PC Series DS7 Instrument (in J.g$^{-1}$)

### 4.2.3 MONONUCLEAR ALKYL COMPOUNDS, $[Re(R)(CO)_5]$ ($R = C_2H_5$ to $n-C_{18}H_{37}$)

The alkyl compounds $[Re(CH_3)(CO)_5]$[1], $[Re(C_2H_5)(CO)_5]$[2] and $[Re(i-Bu)(CO)_5]$[5] have been reported previously. Some substituted benzyl derivatives of rheniumpentacarbonyl, $[Re(CH_2C_6H_4X)(CO)_5]$, are also known [6-9]. We now report the synthesis and characterization of the new n-alkyl compounds $[Re(R)(CO)_5]$, where R = n-propyl to n-octadecyl. Two synthetic strategies were used, the first being the thermal decarbonylation of the acyl species, $[Re(COR)(CO)_5]$, as shown in equation 3, and the second being the direct reaction of the rheniumpentacarbonyl anion with the appropriate n-alkyl bromide, as shown in equation 4.

$$[Re(COR)(CO)_5] \xrightarrow[110^\circ C]{toluene} [Re(R)(CO)_5] + CO \qquad (3)$$

($R = C_2H_5$ to $n-C_9H_{19}$; $n-C_{11}H_{23}$; $n-C_{13}H_{27}$; $n-C_{15}H_{31}$; $n-C_{17}H_{35}$)

$$Na[Re(CO)_5] + RBr \xrightarrow[25^\circ C]{THF} [Re(R)(CO)_5] + NaBr \qquad (4)$$

($R = n-C_{10}H_{21}$; $n-C_{12}H_{25}$; $n-C_{14}H_{29}$; $n-C_{16}H_{33}$; $n-C_{18}H_{37}$)

All the compounds were isolated as either yellow oils or pale yellow solids. They are stable both thermally and to air. They have been characterized by IR, $^1H$ and $^{13}C$ NMR, elemental analysis and mass spectroscopy. The results are given in Tables 4.11 to 4.14.

The fact that $[Re(C_2H_5)(CO)_5]$ synthesized by us was relatively stable (it does not decompose when kept under nitrogen at 0°C for several months) is further evidence that ethyl manganesepentacarbonyl decomposes by a process other than ß-hydride elmination; in Chapter Two of this thesis we have suggested that this decomposition is probably a very rapid carbonylation process. Ethyl rheniumpentacarbonyl contains ß-hydrogen atoms and yet is relatively stable; it is also known that $[Re(R)(CO)_5]$ species undergo alkyl migration to form CO-inserted products more slowly than $[Mn(R)(CO)_5]$ compounds [14], which may be largely due to a much stronger rhenium-carbon *i.e.* $Re-CH_2$ bond [15]. This is therefore a possible reason for the increased stability of $[Re(C_2H_5)(CO)_5]$ over $[Mn(C_2H_5)(CO)_5]$, *i.e.* that the rhenium compound undergoes the alkyl migration/ carbonylation reaction more slowly than the analogous manganese compound.

### IR

As was observed for the mononuclear acyl compounds, $[Re(COR)(CO)_5]$, the IR spectra in the $\nu$(CO) region (see Table 4.11) show the expected number of peaks for $[M(R)(CO)_5]$ species [21], *viz* $A_1$ (2112cm$^{-1}$), E (2009cm$^{-1}$) and $A_1$ (1982cm$^{-1}$). There was no detectable variation in $\nu$(CO) upon changing the length of the alkyl chain. The spectra were, in fact, remarkably similar. The IR data are in good agreement with those reported for $[Re(CH_3)(CO)_5]$[1] and $[Re(C_2H_5)(CO)_5]$[2].

### $^1$H and $^{13}$C NMR

Assignments of the $^1$H and $^{13}$C NMR spectra were made by comparison of the NMR data for this series of compounds with the NMR data for the mononuclear acyl species, $[Re(COR)(CO)_5]$ and with the NMR data reported for $[Re(CH_3)(CO)_5]$ [1,24] and $[Re(C_2H_5)(CO)_5]$[2]. As an example of the results obtained, the $^1$H and $^{13}$C NMR spectra of $[Re\{(CH_2)_{15}CH_3\}(CO)_5]$ are shown in Figures 6 and 7, respectively.

### $^1$H NMR

The $^1$H NMR data are reported in Table 4.12. It can be seen that separate resonances are observed for the methyl protons and the α and ß protons of the alkyl chain. The remaining methylene protons appear as a broad singlet. This was also observed for the acyl complexes, $[Re(COR)(CO)_5]$ and similar behaviour was also observed for the analogous $[Mn(COR)(CO)_5]$ and $[Mn(R)(CO)_5]$ complexes.

The α protons of the alkyl chain (*i.e.* those attached to the carbon atom which is directly bonded to rhenium) resonate at a very similar position to the methyl protons; in fact, for compound **21**, $[Re(CH_2CH_2CH_3)(CO)_5]$, these two resonances are superimposed, *i.e.* the methyl and α protons are equivalent in this case. This behaviour is due to the strong shielding effect of the rhenium atom, which is also observed in the $^{13}$C NMR spectra.

There was no detectable variation in chemical shift upon changing the length of the alkyl chain; thus, integration is the only way to distinguish between these compounds using $^1$H NMR measurements.

### $^{13}$C NMR

The $^{13}$C NMR data are presented in Table 4.13. The carbonyl resonances are at the expected positions and are independent of alkyl chain length. The signal at *ca.* -9.2 ppm was assigned to the α-carbon atom of the alkyl chain, ie that carbon atom which is directly bonded to rhenium. This shows that the metal atom is exerting a very strong shielding effect. For compounds **20** to **28** (*i.e.* R = ethyl to n-decyl), separate resonances are seen for all of the carbon atoms of the alkyl chain. For compounds **29** to **36** (R = n-undecyl to n-octadecyl) the peaks due to the central methylene carbon atoms were not resolved, as is

Table 4.11

Data for [Re(R)(CO)$_5$]

| R | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) (cm$^{-1}$)$^a$ | Elemental Analysis | |
|---|---|---|---|---|---|---|
| | | | | | C; found(calcd) | H; found(calcd) |
| $C_2H_5$ | 20 | 31 | Oil | 2123(w),2009(s),1982(m) | 23.2(23.7) | 1.1(1.4) |
| n-$C_3H_7$ | 21 | 48 | Oil | 2122(w),2009(s),1982(m) | 25.8(26.0) | 1.8(1.9) |
| n-$C_4H_9$ | 22 | 47 | Oil | 2122(w),2009(s),1982(m) | 28.0(28.2) | 2.1(2.4) |
| n-$C_5H_{11}$ | 23 | 52 | Oil | 2122(w),2009(s),1982(m) | 30.4(30.2) | 2.9(2.8) |
| n-$C_6H_{13}$ | 24 | 61 | 53-55 | 2123(w),2009(s),1982(m) | 32.1(32.1) | 3.1(3.2) |
| n-$C_7H_{15}$ | 25 | 38 | 54-57 | 2122(w),2009(s),1982(m) | 33.7(33.9) | 3.5(3.6) |
| n-$C_8H_{17}$ | 26 | 67 | 92-94 | 2122(w),2009(s),1982(m) | 35.5(35.6) | 3.8(3.9) |
| n-$C_9H_{19}$ | 27 | 71 | 26-29 | 2122(w),2009(s),1982(m) | 37.4(37.1) | 4.2(4.2) |
| n-$C_{10}H_{21}$ | 28 | 62 | 48-53 | 2122(w),2009(s),1982(m) | 38.4(38.5) | 4.4(4.5) |
| n-$C_{11}H_{23}$ | 29 | 74 | 28-30 | 2122(w),2008(s),1982(m) | 39.7(39.9) | 4.7(4.8) |
| n-$C_{12}H_{25}$ | 30 | 74 | 41-43 | 2122(w),2009(s),1982(m) | 41.3(41.2) | 5.1(5.1) |
| n-$C_{13}H_{27}$ | 31 | 82 | 29-31 | 2122(w),2009(s),1982(m) | 42.5(42.4) | 5.2(5.3) |
| n-$C_{14}H_{29}$ | 32 | 78 | 38-39 | 2122(w),2009(s),1982(m) | 43.8(43.7) | 5.4(5.6) |

Table 4.11 (.... continued)

| | | | | | | |
|---|---|---|---|---|---|---|
| n-$C_{15}H_{31}$ | 33 | 74 | 30-32 | 2122(w),2009(s),1982(m) | 44.5(44.7) | 5.6(5.8) |
| n-$C_{16}H_{33}$ | 34 | 71 | 34-36 | 2122(w),2009(s),1982(m) | 45.4(45.7) | 6.1(6.0) |
| n-$C_{17}H_{35}$ | 35 | 80 | 32-34 | 2122(w),2009(s),1982(m) | 46.4(46.5) | 6.0(6.2) |
| n-$C_{18}H_{37}$ | 36 | 81 | 37-40 | 2122(w),2009(s),1982(m) | 47.6(47.7) | 6.5(6.4) |

a:in hexane; w=weak, s=strong, m=medium

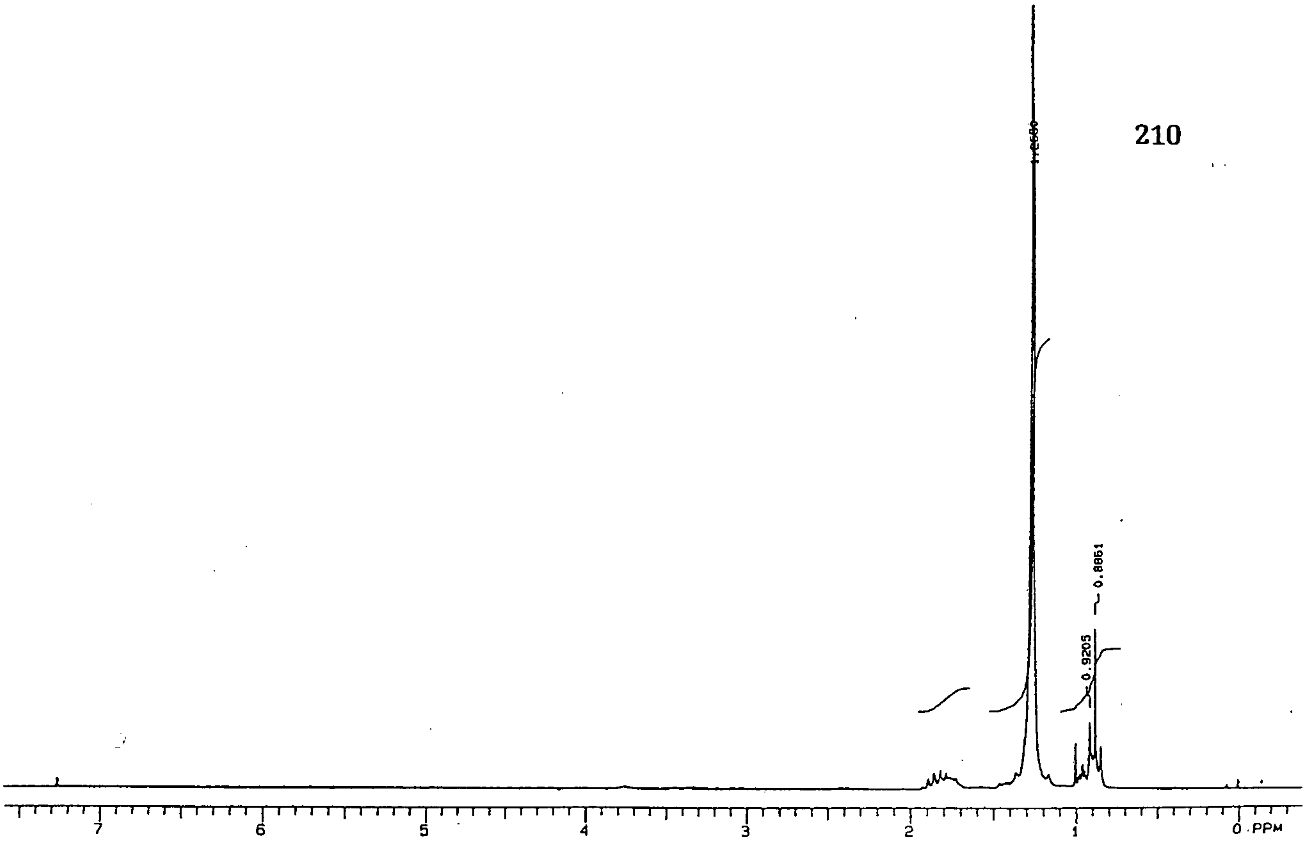

**Fig. 6** $^1H$ NMR Spectrum of $[Re\{(CH_2)_{15}CH_3\}(CO)_5]$

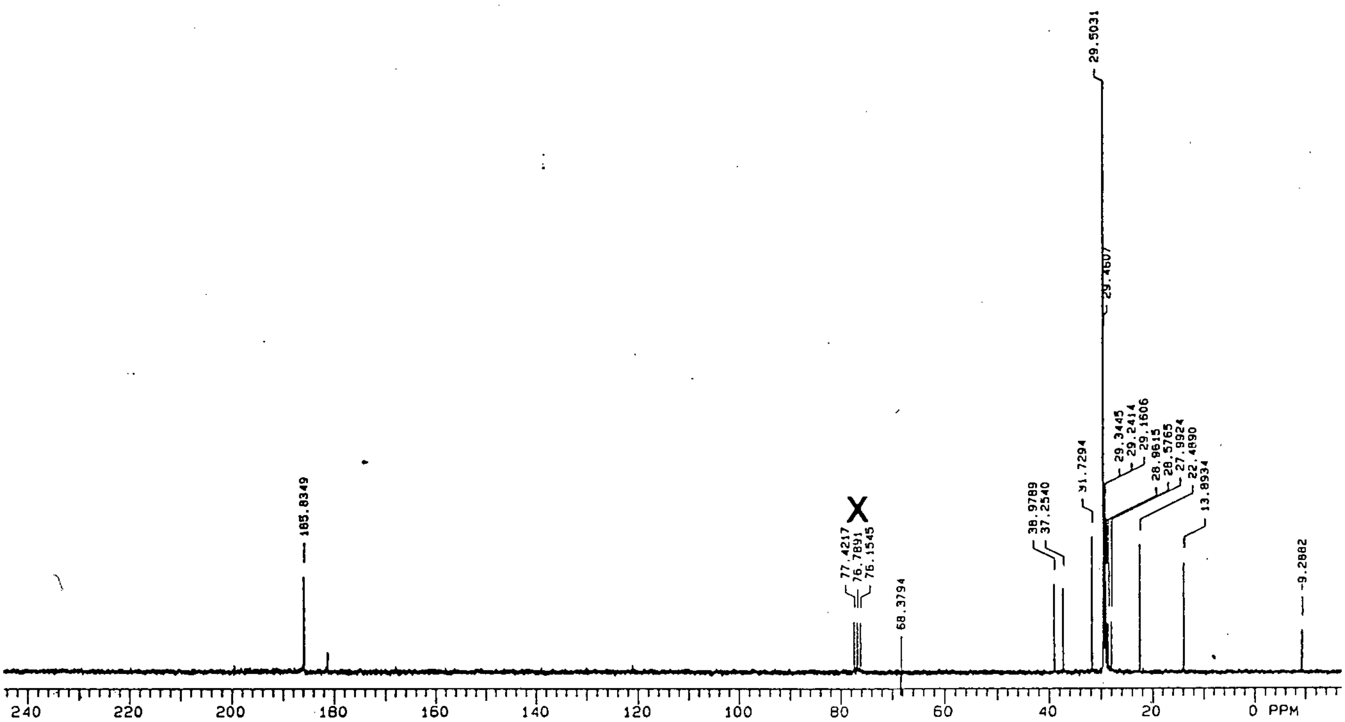

**Fig.7** $^{13}C$ NMR Spectrum of $[Re\{(CH_2)_{15}CH_3\}(CO)_5]$
(X=solvent ($CDCl_3$))

Table 4.12

$^1$H NMR Data for $[Re(R)(CO)_5]^a$

| R | Cmpd No | $\mathrm{Re\underline{CH_2}}$ | $\mathrm{ReCH_2\underline{CH_2}}$ | $\mathrm{ReCH_2CH_2\underline{(CH_2)_x}}$ | $\mathrm{CH_3}$ |
|---|---|---|---|---|---|
| $C_2H_5$ | 20 | 1.01(q,2H) | | | 1.75(tr,3H) |
| n-$C_3H_7$ | 21 | 0.95(tr,5H) | 1.80(m,2H) | | 0.95(tr,5H) |
| n-$C_4H_9$ | 22 | 0.93(m,2H) | 1.79(m,2H) | 1.30(brs,2H) | 0.90(tr,3H) |
| n-$C_5H_{11}$ | 23 | 0.93(m,2H) | 1.78(m,2H) | 1.30(brs,4H) | 0.90(tr,3H) |
| n-$C_6H_{13}$ | 24 | 0.97(m,2H) | 1.75(m,2H) | 1.30(brs,6H) | 0.90(tr,3H) |
| n-$C_7H_{15}$ | 25 | 0.97(m,2H) | 1.78(m,2H) | 1.26(brs,8H) | 0.86(tr,3H) |
| n-$C_8H_{17}$ | 26 | 0.98(m,2H) | 1.82(m,2H) | 1.28(brs,10H) | 0.89(tr,3H) |
| n-$C_9H_{19}$ | 27 | 0.96(m,2H) | 1.79(m,2H) | 1.22(brs,12H) | 0.83(tr,3H) |
| n-$C_{10}H_{21}$ | 28 | 0.92(m,2H) | 1.70(m,2H) | 1.21(brs,14H) | 0.81(tr,3H) |
| n-$C_{11}H_{23}$ | 29 | 0.92(m,2H) | 1.74(m,2H) | 1.30(brs,16H) | 0.86(tr,3H) |
| n-$C_{12}H_{25}$ | 30 | 0.95(m,2H) | 1.74(m,2H) | 1.24(brs,18H) | 0.85(tr,3H) |
| n-$C_{13}H_{27}$ | 31 | 0.93(m,2H) | 1.75(m,2H) | 1.28(brs,20H) | 0.85(tr,3H) |
| n-$C_{14}H_{29}$ | 32 | 0.92(m,2H) | 1.72(m,2H) | 1.21(brs,22H) | 0.84(tr,3H) |
| n-$C_{15}H_{31}$ | 33 | 0.95(m,2H) | 1.77(m,2H) | 1.27(brs,24H) | 0.86(tr,3H) |
| n-$C_{16}H_{33}$ | 34 | 0.96(m,2H) | 1.73(m,2H) | 1.27(brs,26H) | 0.87(tr,3H) |
| n-$C_{17}H_{35}$ | 35 | 0.96(m,2H) | 1.77(m,2H) | 1.25(brs,28H) | 0.88(tr,3H) |
| n-$C_{18}H_{37}$ | 36 | 0.95(m,2H) | 1.80(m,2H) | 1.24(brs,30H) | 0.87(tr,3H) |

a:in $CDCl_3$, relative to TMS ($\delta$ = 0.00ppm); q = quartet, tr = triplet, m = complex multiplet, brs = broad singlet

found for substituted n-alkanes [23] and related long chain alkyl complexes of manganese [22], iron and ruthenium [23]. The effects of the metal are only evident in the first two carbon atoms of the alkyl chain.

Beyond $C_3$, the $^{13}$C NMR spectra of corresponding acyl and alkyl compounds are very similar, although this is more or less to be expected.

## Table 4.13

## $^{13}C$ NMR Data for $[Re(R)(CO)_5]^a$

| R | Cmpd No | CO (*cis*)$^b$ | CO (*trans*)$^b$ | $ReCH_2$ *i.e.* $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{17}$ | $C_{18}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_5$ | 20 | 186.07 | 181.52 | 1.03 | 22.88 | | | | | | | | | | | | | | | | |
| $n-C_3H_7$ | 21 | 186.02 | 181.50 | -6.20 | 32.24 | 21.98 | | | | | | | | | | | | | | | |
| $n-C_4H_9$ | 22 | 186.04 | 181.48 | -9.46 | 41.45 | 30.30 | 13.51 | | | | | | | | | | | | | | |
| $n-C_5H_{11}$ | 23 | 186.06 | 181.48 | -9.17 | 39.61 | 38.76 | 22.14 | 14.14 | | | | | | | | | | | | | |
| $n-C_6H_{13}$ | 24 | 185.51 | 180.90 | -9.65 | 38.58 | 36.54 | 30.86 | 22.22 | 13.55 | | | | | | | | | | | | |
| $n-C_7H_{15}$ | 25 | 186.04 | 181.47 | -9.38 | 39.29 | 36.81 | 31.23 | 29.10 | 22.34 | 14.10 | | | | | | | | | | | |
| $n-C_8H_{17}$ | 26 | 186.05 | 181.46 | -9.09 | 39.17 | 37.44 | 31.75 | 29.43 | 29.11 | 22.69 | 14.08 | | | | | | | | | | |
| $n-C_9H_{19}$ | 27 | 186.05 | 181.43 | -9.13 | 39.20 | 37.39 | 31.82 | 29.61 | 29.34 | 29.29 | 22.68 | 14.13 | | | | | | | | | |
| $n-C_{10}H_{21}$ | 28 | 186.05 | 181.49 | -9.08 | 39.19 | 37.46 | 31.94 | 29.78 | 29.71 | 29.37 | 29.16 | 22.70 | 14.11 | | | | | | | | |
| $n-C_{11}H_{23}$ | 29 | 186.10 | 181.51 | -9.20 | 39.18 | 37.51 | 31.94 | {29.77 → | | | | → 29.23}$^c$ | 22.67 | 13.99 | | | | | | | |
| $n-C_{12}H_{25}$ | 30 | 186.04 | 181.49 | -9.08 | 39.19 | 37.46 | 36.94 | {29.78 → | | | | | → 29.37}$^c$ | 22.70 | 14.10 | | | | | | |
| $n-C_{13}H_{27}$ | 31 | 186.21 | 181.40 | -9.13 | 39.13 | 37.44 | 31.94 | {29.76 → | | | | | | → 29.34}$^c$ | 22.71 | 14.04 | | | | | |
| $n-C_{14}H_{29}$ | 32 | 185.83 | 181.26 | -9.28 | 38.99 | 37.26 | 31.89 | {29.58 → | | | | | | | → 29.17}$^c$ | 22.49 | 13.88 | | | | |
| $n-C_{15}H_{31}$ | 33 | 186.10 | 181.22 | -9.21 | 38.97 | 37.29 | 31.70 | {29.61 → | | | | | | | | → 29.20}$^c$ | 22.64 | 14.12 | | | |
| $n-C_{16}H_{33}$ | 34 | 185.83 | 181.22 | -9.29 | 38.98 | 37.25 | 31.73 | {29.50 → | | | | | | | | | → 29.16}$^c$ | 22.49 | 13.89 | | |
| $n-C_{17}H_{35}$ | 35 | 186.05 | 181.20 | -8.98 | 39.19 | 37.46 | 31.94 | {29.71 → | | | | | | | | | | → 29.17}$^c$ | 22.70 | 14.11 | |
| $n-C_{18}H_{37}$ | 36 | 185.96 | 181.14 | -9.11 | 39.10 | 37.38 | 31.85 | {29.62 → | | | | | | | | | | | → 29.28}$^c$ | 22.61 | 14.02 |

a:in $CDCl_3$ relative to TMS (δ = 0.00ppm)
b:relative to the alkyl chain
c:peaks were not resolved

## Table 4.14

## Mass Spectral Data for $[Re(R)(CO)_5]$[a]

| Possible Assignments[b] | Relative Peak Intensities[c] | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cmpd No | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 |
| M | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| M-CO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| M-2CO | 3 | 1 | 2 | 4 | 1 | 7 | 5 | 0 | 1 | 3 | 7 | 8 | 0 | 0 | 0 | 0 |
| M-3CO | 0 | 4 | 1 | 3 | 3 | 9 | 0 | 4 | 0 | 4 | 9 | 8 | 5 | 0 | 0 | 0 |
| M-4CO | 2 | 5 | 4 | 7 | 7 | 4 | 5 | 2 | 2 | 3 | 0 | 12 | 1 | 3 | 4 | 7 |
| M-5CO | 100 | 80 | 72 | 100 | 100 | 100 | 100 | 58 | 100 | 100 | 72 | 100 | 100 | 29 | 100 | 100 |
| M-5CO-H | 0 | 0 | 0 | | 0 | 0 | 0 | 8 | 0 | 0 | 2 | 0 | 2 | 0 | 5 | 2 |
| M-5CO-$CH_3$ | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 4 | 0 | 0 | 8 | 0 | 0 | 2 | 0 |
| M-5CO-$C_2H_5$ | 3 | 8 | 10 | 4 | 7 | 5 | 11 | 12 | 18 | 5 | 7 | 11 | 9 | 3 | 17 | 4 |
| M-5CO-$C_3H_7$ | 51 | 3 | 0 | 4 | 11 | 18 | 12 | 3 | 14 | 12 | 5 | 7 | 3 | 9 | 4 | 11 |
| M-5CO-$C_4H_9$ | - | 34 | 1 | 10 | 3 | 8 | 21 | 12 | 0 | 11 | 12 | 7 | 4 | 0 | 8 | 9 |
| M-5CO-$C_5H_{11}$ | - | - | 56 | 7 | 9 | 0 | 4 | 14 | 8 | 0 | 9 | 6 | 8 | 5 | 0 | 10 |
| M-5CO-$C_6H_{13}$ | - | - | - | 86 | 2 | 3 | 5 | 18 | 7 | 8 | 3 | 8 | 0 | 2 | 1 | 12 |
| M-5CO-$C_7H_{15}$ | - | - | - | - | 71 | 10 | 12 | 11 | 5 | 4 | 4 | 0 | 10 | 6 | 14 | 0 |
| M-5CO-$C_8H_{17}$ | - | - | - | - | - | 59 | 9 | 7 | 0 | 10 | 8 | 14 | 1 | 8 | 8 | 8 |
| M-5CO-$C_9H_{19}$ | - | - | - | - | - | - | 38 | 4 | 3 | 11 | 10 | 8 | 4 | 3 | 7 | 10 |
| M-5CO-$C_{10}H_{21}$ | - | - | - | - | - | - | - | 82 | 7 | 8 | 8 | 5 | 6 | 0 | 4 | 11 |

Table 4.14 (.... continued)

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M-5CO-$C_{11}H_{23}$ | - | - | - | - | - | - | - | - | 27 | 5 | 5 | 0 | 8 | 10 | 5 | 0 |
| M-5CO-$C_{12}H_{25}$ | - | - | - | - | - | - | - | - | - | 37 | 4 | 8 | 7 | 10 | 3 | 10 |
| M-5CO-$C_{13}H_{27}$ | - | - | - | - | - | - | - | - | - | - | 14 | 11 | 9 | 7 | 4 | 8 |
| M-5CO-$C_{14}H_{29}$ | - | - | - | - | - | - | - | - | - | - | - | 29 | 12 | 6 | 6 | 3 |
| M-5CO-$C_{15}H_{31}$ | - | - | - | - | - | - | - | - | - | - | - | - | 72 | 5 | 9 | 9 |
| M-5CO-$C_{16}H_{33}$ | - | - | - | - | - | - | - | - | - | - | - | - | - | 21 | 5 | 7 |
| M-5CO-$C_{17}H_{35}$ | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 35 | 4 |
| M-5CO-$C_{18}H_{37}$ | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 19 |
| [$Re(CO)_5$] | 71 | 100 | 100 | 51 | 44 | 92 | 33 | 100 | 70 | 78 | 100 | 60 | 54 | 100 | 68 | 71 |
| [Re] | 51 | 34 | 54 | 86 | 71 | 59 | 38 | 82 | 27 | 77 | 14 | 29 | 72 | 21 | 35 | 19 |
| [CO] | 14 | 24 | 15 | 22 | 31 | 18 | 10 | 51 | 24 | 13 | 14 | 17 | 12 | 12 | 15 | 17 |

a:the mass spectrum of [$Re(C_2H_5)(CO)_5$] was not obtained
b:all ions have a single, positive charge
c:peak intensities relative to base peak for $[M-5CO]^+$ or $[Re(CO)_5]^+$
d:the peak intensities reported are those for the most abundant isotope combination

## MASS SPECTRA

The mass spectral data for compounds **21** to **36** are reported in Table 4.14. The mass spectra were all similar and relatively simple. Parent molecular ions were not seen for any of the compounds. The major fragmentation pathway was loss of carbonyl groups followed by sequential loss of methylene fragments. Some evidence for remote functionalization (a very weak peak corresponding to $[M-5CO-H]^+$) was seen in compounds **28**, **31**, **33**, **35** and **36**.

## 4.2.4 BINUCLEAR ALKYL COMPOUNDS $[(CO)_5Re(CH_2)_nRe(CO)_5]$ (n = 4 to 10)

The binuclear alkyl compounds $[(CO)_5Re(CH_2)_nRe(CO)_5]$ (n = 2 to 4) have previously been reported [10,11]. We now report the syntheses of the n = 4 compound, and the new compounds $[(CO)_5Re(CH_2)_nRe(CO)_5]$ (n=5 to 10). As with the mononuclear alkyl compounds, $[Re(R)(CO)_5]$, two synthetic strategies were used. The first involved the thermal decarbonylation of the acyl precursors, as shown in equation 5, while the second procedure involved direct reaction of $Na[Re(CO)_5]$ with a dibromoalkane, as shown in equation 6.

$$[(CO)_5ReCO(CH_2)_nCORe(CO)_5] \xrightarrow[110^\circ C]{\text{toluene}} [(CO)_5Re(CH_2)_nRe(CO)_5] + 2CO \quad (n = 4 \text{ to } 8,10) \qquad (5)$$

$$2Na[Re(CO)_5] + Br(CH_2)_9Br \xrightarrow[25^\circ C]{\text{THF}} [(CO)_5Re(CH_2)_9Re(CO)_5] + 2NaBr \qquad (6)$$

The above compounds were all isolated as off-white solids which are stable in air and in solution when kept under nitrogen. They have been characterized by IR, $^1$H and $^{13}$C NMR, elemental analysis and mass spectroscopy. The data are listed in Tables 4.15 to 4.18.

### IR

The IR spectra in the $\nu$(CO) region (see Table 4.15) are in good agreement with the spectra reported for $[(CO)_5Re(CH_2)_nRe(CO)_5]$ (n = 3,4)[19], and show the expected number of peaks for $[M(R)(CO)_5]$ species [21] (where R = $(CH_2)_nRe(CO)_5]$), *viz.* $A_1$ (2122cm$^{-1}$), E (2008cm$^{-1}$) and $A_1$ (1977cm$^{-1}$). There was no detectable variation in $\nu$(CO) upon changing the length of the alkyl chain.

### $^1$H and $^{13}$C NMR

Assignments of the $^1$H and $^{13}$C NMR spectra for 37 to 43 were made by comparison of all of the NMR data for these compounds with the data reported for $[(CO)_5Re(CH_2)_nRe(CO)_5]$ (n = 3,4)[19], the analogous manganese complexes $[(CO)_5Mn(CH_2)_nMn(CO)_5]$[22] and that obtained for the mononuclear compounds $[Re(R)(CO)_5]$ (see section 4.2.2). As an example of the results obtained, the $^1$H and $^{13}$C NMR spectra of $[(CO)_5Re(CH_2)_9Re(CO)_5]$ are shown in Figures 8 and 9, respectively.

### $^1$H NMR

The $^1$H NMR data are given in Table 4.16. This shows that separate resonances are seen for the $\alpha$ and $\beta$ protons (and the $\gamma$ protons of the n = 5 and n = 6 compounds only) of the bridging alkyl group. The remaining methylene protons (of the n = 7 to 10 compounds) resonate as a broad singlet at *ca.* $\delta$ = 1.27 ppm. There is no detectable variation in chemical shift upon changing the chain length of the

Table 4.15

Data for $[(CO)_5Re(CH_2)_nRe(CO)_5]$

| n | Cmpd No | Yield (%) | mp (°C) | IR $\nu$(CO) ($cm^{-1}$)$^a$ | Elemental Analysis | |
|---|---|---|---|---|---|---|
| | | | | | C;found(calcd) | H;found(calcd) |
| 4 | 37 | 42 | 170-172 | 2122(mw), 2010(s), 1977(m) | 23.8(23.7) | 1.0(1.1) |
| 5 | 38 | 58 | 141-143 | 2123(mw), 2008(s), 1977(m) | 24.9(24.9) | 1.3(1.4) |
| 6 | 39 | 62 | 162-164 | 2122(mw), 2009(s), 1978(m) | 25.8(26.1) | 1.3(1.6) |
| 7 | 40 | 69 | 122-127 | 2122(mw), 2008(s), 1977(m) | 27.1(27.2) | 1.9(1.9) |
| 8 | 41 | 54 | 151-155 | 2122(mw), 2008(s), 1978(m) | 28.1(28.3) | 2.0(2.1) |
| 9 | 42 | 40 | 104-106 | 2123(MW), 2007(s), 1978(m) | 29.0(29.3) | 1.9(2.3) |
| 10 | 43 | 71 | 138-140 | 2122(mw), 2007(s), 1978(m) | 30.1(30.3) | 2.2(2.5) |

a:in $CHCl_3$; mw = medium weak, s = strong, m = medium

**Table 4.16**

**$^1$H NMR Data for $[(CO)_5Re(CH_2)_nRe(CO)_5]^a$**

| n | Cmpd No | $ReC\underline{H_2}$ | $ReCH_2C\underline{H_2}$ | $ReCH_2CH_2(\underline{CH_2})_x$ |
|---|---|---|---|---|
| 4 | 37 | 1.01(tr,4H) | 1.78(br,4H) | |
| 5 | 38 | 0.98(tr,4H) | 1.76(br,4H) | 1.30(brs,2H) |
| 6 | 39 | 0.91(tr,4H) | 1.70(br,4H) | 1.26(brs,4H) |
| 7 | 40 | 0.96(tr,4H) | 1.76(br,4H) | 1.28(brs,6H) |
| 8 | 41 | 0.99(tr,4H) | 1.77(br,4H) | 1.27(brs,8H) |
| 9 | 42 | 0.96(tr,4H) | 1.78(br,4H) | 1.27(brs,10H) |
| 10 | 43 | 0.96(tr,4H) | 1.77(br,4H) | 1.27(brs,12H) |

a:in $CDCl_3$ relative to TMS (δ = 0.00ppm); tr = triplet, br = broad signal, brs = broad singlet

bridging alkyl group.

**$^{13}$C NMR**

The $^{13}$C NMR data are shown in Table 4.17. The $^{13}$C NMR spectra were all very similar to each other, and relatively simple. The carbonyl resonances were at the expected positions and did not vary upon changing the length of the μ-hydrocarbyl group. Separate resonances were seen for all of the carbon atoms in the alkyl chain. The signal at *ca.* -9.1 ppm was assigned to Cα, *i.e.* the carbon atom in the alkyl chain which is directly bonded to the rhenium atoms. Thus, the rhenium atom is again exerting a very strong shielding effect, more so than the manganese atom in the analogous $[Mn(R)(CO)_5]$ and $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ compounds, where the signal for Cα appears at *ca.* 7ppm.

The $^{13}$C NMR spectra of these binuclear compounds are very similar to the spectra obtained for the mononuclear analogues $[Re(R)(CO)_5]$ (see section 4.2.3) and are also in good agreement with the $^{13}$C NMR spectra reported for

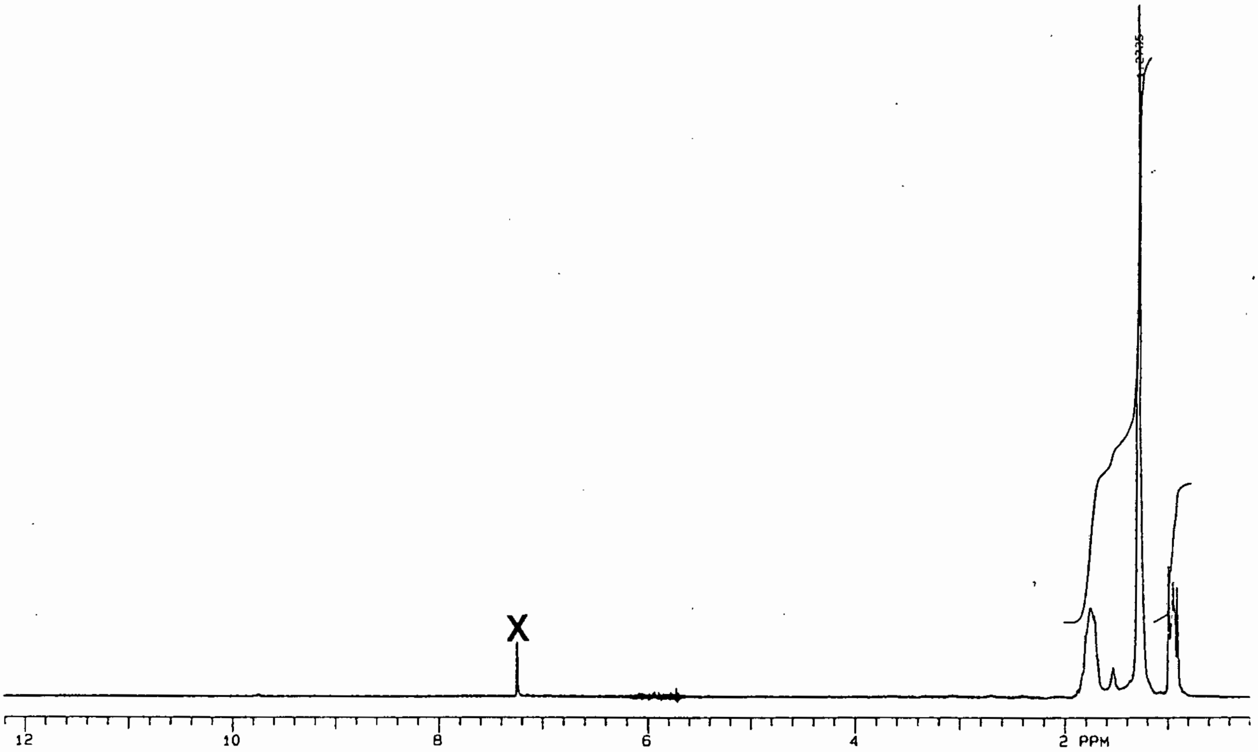

Fig. 8 $^1$H NMR Spectrum of $[(CO)_5Re(CH_2)_9Re(CO)_5]$
(X = solvent ($CDCl_3$) impurity)

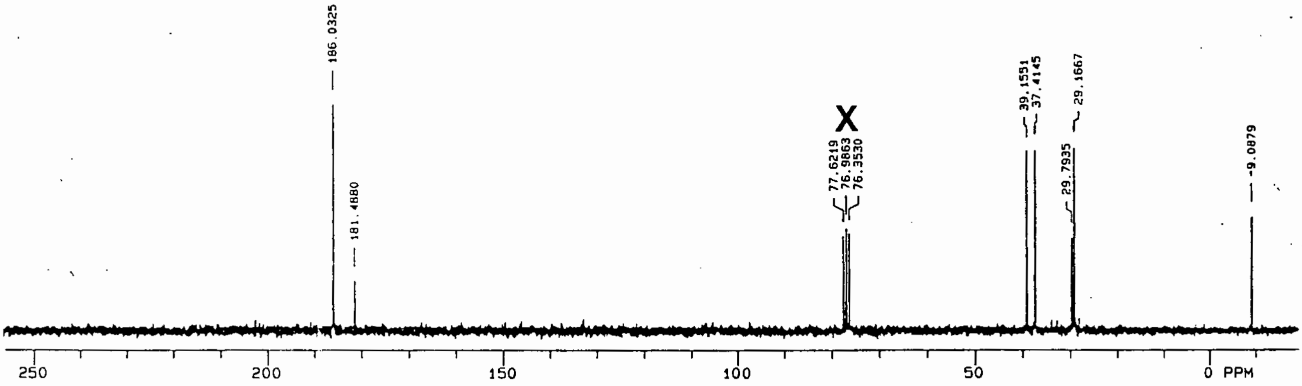

Fig. 9 $^{13}$C NMR spectrum of $[(CO)_5Re(CH_2)_9Re(CO)_5]$
(X = solvent ($CDCl_3$))

Table 4.17

$^{13}$C NMR Data for [(CO)$_5$Re(CH$_2$)$_n$Re(CO)$_5$]$^a$

| n | Cmpd No | ReCO (*cis*)$^b$ | ReCO (*trans*)$^b$ | ReCH$_2$ | C$_2$ | C$_3$ | C$_4$ | C$_5$ |
|---|---|---|---|---|---|---|---|---|
| 4 | 37 | 186.1 | 181.4 | -9.5 | 49.9 | | | |
| 5 | 38 | 186.1 | 181.4 | -9.2 | 40.3 | 37.8$^c$ | | |
| 6 | 39 | 186.0 | 181.5 | -9.1 | 39.1 | 37.1 | | |
| 7 | 40 | 186.1 | 181.5 | -9.1 | 39.2 | 37.3 | 29.6$^c$ | |
| 8 | 41 | 186.0 | 181.5 | -9.1 | 39.1 | 37.5 | 29.7 | |
| 9 | 42 | 186.0 | 181.5 | -9.1 | 39.2 | 37.4 | 29.2 | 29.8$^c$ |
| 10 | 43 | 186.0 | 181.5 | -9.0 | 39.2 | 37.5 | 29.1 | 29.8 |

a:in CDCl$_3$, relative to TMS ($\delta$ = 0.00ppm)
b:relative to the alkyl chain
c:assignments were made on the basis of relative intensities

$[(CO)_5Re(CH_2)_nRe(CO)_5]$ (n = 3,4)[19].

## MASS SPECTRA

The mass spectral data are given in Table 4.18. All compounds showed weak molecular ions, with the major fragmentation pathway being successive loss of the carbonyl groups. A second pathway involves initial loss of the bridging alkyl group, $(CH_2)_n$, followed by successive loss of carbonyl groups.

**Table 4.18**
**Mass Spectral Data for $[(CO)_5Re(CH_2)_nRe(CO)_5]$**

| Possible Assignments[a] | Relative Intensities[b] | | | | | | |
|---|---|---|---|---|---|---|---|
| | n=4 | 5 | 6 | 7 | 8 | 9 | 10 |
| M | 8 | 4 | 6 | 10 | 3 | 12 | 4 |
| M-CO | 5 | 10 | 0 | 12 | 4 | 6 | 0 |
| M-2CO | 0 | 7 | 9 | 0 | 12 | 8 | 0 |
| M-3CO | 10 | 12 | 7 | 9 | 0 | 0 | 5 |
| M-4CO | 10 | 0 | 6 | 4 | 8 | 9 | 6 |
| M-5CO | 28 | 12 | 18 | 22 | 14 | 17 | 28 |
| M-6CO | 24 | 22 | 17 | 14 | 21 | 27 | 20 |
| M-7CO | 30 | 32 | 21 | 14 | 35 | 28 | 20 |
| M-8CO | 32 | 14 | 18 | 31 | 27 | 26 | 22 |
| M-9CO | 24 | 28 | 22 | 24 | 24 | 23 | 14 |
| M-10CO | 28 | 30 | 31 | 30 | 38 | 28 | 27 |
| M-$(CH_2)_n$ | 0 | 0 | 7 | 2 | 8 | 4 | 8 |
| M-CO-$(CH_2)_n$ | 10 | 4 | 6 | 3 | 14 | 8 | 20 |
| M-2CO-$(CH_2)_n$ | 10 | 8 | 18 | 11 | 21 | 6 | 20 |
| M-3CO-$(CH_2)_n$ | 28 | 4 | 17 | 7 | 35 | 7 | 22 |
| M-4CO-$(CH_2)_n$ | 24 | 5 | 21 | 10 | 27 | 3 | 14 |
| M-5CO-$(CH_2)_n$ | 30 | 8 | 18 | 10 | 24 | 12 | 27 |
| M-6CO-$(CH_2)_n$ | 32 | 6 | 22 | 12 | 38 | 4 | 8 |
| M-7CO-$(CH_2)_n$ | 24 | 7 | 31 | 7 | 20 | 13 | 12 |
| M-8CO-$(CH_2)_n$ | 28 | 12 | 21 | 17 | 18 | 12 | 21 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| M-9CO-$(CH_2)_n$ | 18 | 10 | 14 | 18 | 19 | 17 | 14 |
| M-10CO-$(CH_2)_n$ | 28 | 31 | 28 | 37 | 42 | 29 | 40 |
| M-10CO-$(CH_2)_n$-Re | 44 | 61 | 58 | 48 | 38 | 54 | 41 |
| M-$(CH_2)_n$-Re$(CO)_5$ | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| M-10CO-Re | 20 | 12 | 21 | 18 | 14 | 29 | 20 |
| M-$(CH_2)_n$-Re-6CO | 32 | 41 | 24 | 48 | 33 | 31 | 38 |
| M-$(CH_2)_n$-Re-7CO | 30 | 35 | 54 | 41 | 27 | 27 | 36 |
| M-$(CH_2)_n$-Re-8CO | 50 | 28 | 38 | 23 | 40 | 43 | 30 |
| M-$(CH_2)_n$-Re-9CO | 42 | 20 | 21 | 37 | 22 | 34 | 31 |
| M-$(CH_2)_n$-Re-10CO | 24 | 28 | 20 | 20 | 29 | 20 | 18 |
| M-Re$(CO)_5$ | 31 | 26 | 28 | 20 | 28 | 34 | 14 |
| M-Re$(CO)_5$-CO | 10 | 7 | 11 | 8 | 10 | 7 | 9 |
| M-Re$(CO)_5$-2CO | 21 | 18 | 14 | 16 | 28 | 10 | 17 |
| M-Re$(CO)_5$-3CO | 20 | 21 | 31 | 26 | 22 | 18 | 27 |
| M-Re$(CO)_5$-4CO | 30 | 24 | 30 | 28 | 18 | 32 | 30 |
| [CO] | 18 | 14 | 28 | 22 | 50 | 14 | 10 |

a:all ions have a single, positive charge
b:peak instensities relative to base peak for $[Re(CO)_5]^+$

## 4.3 REACTIVITY STUDIES

The decarbonylation reactions of $[Re(COR)(CO)_5]$ compounds (equation 7) were followed by IR spectroscopy, as outlined in Chapter 3.

$$[Re(COR)(CO)_5] \xrightarrow[94^\circ C]{toluene} [Re(R)(CO)_5] + CO \qquad (7)$$

However, although it was established that the reaction went to completion, it was difficult to obtain reliable rate data. The use of toluene as a solvent resulted in broad peaks being observed in the IR spectra; thus, intensity readings were not always reliable. This may have accounted for the fact that less than satisfactory reproducibility was observed. Analysis of the rate data was thus more informative from a qualitative, rather than quantitative, point of view. The following observations were made:

(i) a slight dependence (very much less than for the analogous $[Mn(COR)(CO)_5]$ system) of reaction rate on alkyl chain length was observed;

(ii) this dependence followed the same general pattern as that obtained for the analogous manganese system;

(iii) although the rate constants we obtained were not very reliable, estimates indicated that they fell in the range $1.5 \times 10^{-4}s^{-1}$ (for R = $CH_3$) to $4 \times 10^{-4}s^{-1}$ (for R = n-$C_9H_{19}$). A table of estimates of these rate constants for various R groups appears in Appendix 4a.

### 4.3.2 Reaction of $[Re(R)(CO)_5]$ with $PPh_3$

The reactions of $[Re(R)(CO)_5]$ with triphenylphosphine (equation 8) were followed by IR spectroscopy.

$$[Re(R)(CO)_5] + PPh_3 \xrightarrow[94°C]{toluene} cis\text{-}[Re(R)(CO)_4(PPh_3)] + CO \qquad (8)$$

Some characterization data are given in Chapter 7. It was established that the reaction went to completion, but, as was observed for the decarbonylation reactions, reliable rate data were not obtained. The use of toluene as a solvent resulted in broad peaks in the IR spectra resulting in unreliable intensity readings. Higher temperatures and longer reaction times (relative to the manganese system) may also lead to side reactions. However, the following facts were established:

(i) only a very slight dependence of reaction rate on alkyl chain length was observed;

(ii) this dependence followed the same general pattern as that of the $[Mn(R)(CO)_5]$ system;

(iii) estimates of rate constants indicated that they fell in the range $0.15 \times 10^{-4}s^{-1}$ (for R = $C_2H_5$ ) to $0.3 \times 10^{-4}s^{-1}$ (for R = n-$C_8H_{17}$). These rate constants span a very much narrower range than those measured for the $[Mn(R)(CO)_5]$ system. A table of estimates of these rate constants for various R groups appears in Appendix 4b;

(iv) no evidence was obtained for acyl species being formed in the course of the reaction. This, in addition to fact (i) above, implies that the reaction of $[Re(R)(CO)_5]$ compounds with $PPh_3$ may therefore be simple substitution reactions in which a terminal carbonyl group is replaced by $PPh_3$, which most probably proceeds *via* initial loss of a terminal carbonyl group.

Thus, different products were obtained from the reactions of (a) manganese and (b) rhenium long chain alkyl complexes. This may be largely a result of the much stronger rhenium-carbon (alkyl) bond compared to the manganese-carbon (alkyl) bond [15] *i.e.* 222.6 $kJ.mol^{-1}$ for $Re-CH_3$ in $[Re(CH_3)(CO)_5]$ and 116.1 $kJ.mol^{-1}$ for $Mn-CH_3$ in $[Mn(CH_3)(CO)_5]$.

The use of a high-boiling saturated hydrocarbon solvent such as n-octane may alleviate the problem of broad peaks (resulting in unreliable intensity measurements) in the IR spectra. Thus, further experiments need to be performed on this system in order to obtain satisfactory rate data.

## 4.4 CONCLUSIONS

We have synthesized and characterized several new alkyl and acyl complexes of rhenium of the types $[Re(R)(CO)_5]$, $[(CO)_5Re(CH_2)_nRe(CO)_5]$, $[Re(COR)(CO)_5]$ and $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$. These complexes, and the ethyl derivative, $[Re(C_2H_5)(CO)_5]$, were all relatively stable, both thermally and to air. No evidence for $[Re(C_2H_5)(CO)_5]$ undergoing a carbonylation reaction was obtained. Thus, $[Re(C_2H_5)(CO)_5]$ may be more stable than $[Mn(C_2H_5)(CO)_5]$ due to a rapid carbonylation process not being a viable mode of decomposition (for $[Re(C_2H_5)(CO)_5]$). This is possibly due to the rhenium-carbon bond being considerably stronger than the manganese-carbon bond [15].

The rates of decarbonylation of $[Re(COR)(CO)_5]$ are much slower than for the analogous manganese complexes and the rates of reaction of $[Re(R)(CO)_5]$ with $PPh_3$ are also much slower.

The alkyl complexes, $[Re(R)(CO)_5]$, undergo reaction with $PPh_3$ to form the alkyl $PPh_3$-substituted products, *cis*-$[Re(R)(CO)_4(PPh_3)]$, which implies that an alternative reaction pathway to that observed for the analogous $[Mn(R)(CO)_5]$ complexes may be in operation.

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# CHAPTER 5

# THE SYNTHESIS AND REACTIVITY OF SOME TRANSITION METAL BENZYL COMPOUNDS OF THE TYPES $[Mn(CH_2C_6H_4X)(CO)_5]$ AND $[CpFe(CH_2C_6H_4X)(CO)_2]$

## 5.1 INTRODUCTION

The first reported synthesis of benzyl manganesepentacarbonyl, $[Mn(CH_2C_6H_5)(CO)_5]$ was in 1957 by Closson et al [1] and that of the cyclopentadienyliron analogue, $[CpFe(CH_2C_6H_5)(CO)_2]$, followed in 1966 by Bibler and Wojcicki [2]. Since then, several mono-substituted benzyl derivatives of these two metal ligand systems, $[Mn(CH_2C_6H_4X)(CO)_5]$ and $[CpFe(CH_2C_6H_4X)(CO)_2]$, have been reported, including X = o-CN, m-CN and p-CN [3], p-F [4], o-$CH_3$ and p-$CH_3$ [5], m-$CH_3$, o-i-Pr, p-i-Pr, o-t-Bu, o-Cl, m-Cl, p-Cl, o-F, m-F, o-$OCH_3$, m-$OCH_3$, p-$OCH_3$, o-$CF_3$, m-$CF_3$ and p-$CF_3$ [6] for the manganese system and X = p-$OCH_3$ [7], o-CN [3] and p-F [4] for the iron system. The majority of the syntheses involved reaction of the metal anion ($[Mn(CO)_5]^-$ or $[CpFe(CO)_2]^-$) with the relevant benzyl halide. As a ligand, the substituted benzyl group provides for a wide variation in steric and electronic parameters. As a result, these compounds have been subjected to numerous reactivity studies. Meta- and para-substituted benzyl systems are especially useful as a discrete analysis of electronic effects is made possible by the relatively constant steric environment at the reacting centre in the benzyl substituent. The manganese system has been subjected to more reactivity studies (especially studies on the carbonyl insertion reaction) than the iron system owing to the greater ability of $[Mn(R)(CO)_5]$ species over $[CpFe(R)(CO)_2]$ species to undergo carbonyl insertion/alkyl migration. The most extensive studies have been produced by the research group of J. D. Cotton [5,6,8-10].

Two reaction pathways for the ligand-induced insertion of carbon monoxide into a transition metal-carbon σ-bond, leading to a ligand-substituted acyl product have been proposed and are represented in Scheme 1 (L = ligand).

$$\mathrm{RM(CO)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{[M\text{-}COR]} \underset{k_{-2}\ (-\mathrm{L})}{\overset{k_2(+\mathrm{L})}{\rightleftharpoons}} \mathrm{(L)M(COR)} \qquad \mathrm{(a)}$$

$$\mathrm{RM(CO)} + \mathrm{L} \xrightarrow{k_3} \mathrm{(L)M(COR)} \qquad \mathrm{(b)}$$

M = $Mn(CO)_4$ or CpFe(CO)

Scheme 1

The first pathway, (a), operates in polar solvents and the coordinatively unsaturated acyl intermediate is often solvated. Thus, in the first step, a polar solvent molecule induces the formation of an acyl intermediate from which the coordinated solvent is displaced by the nucleophilic ligand in the second step. The alternative pathway, (b), which is favoured in non-polar solvents, involves the direct reaction of the nucleophile with the metal alkyl species. Thus, in polar solvents such as DMSO or acetonitrile, pathway (a) predominates and the contribution from pathway (b) can generally be ignored. The observed rate constant, $k_{OBS}$, is given by equation (1) [11].

$$k_{OBS} = k_1k_2[L]/(k_{-1}+k_2[L]) \qquad (1)$$

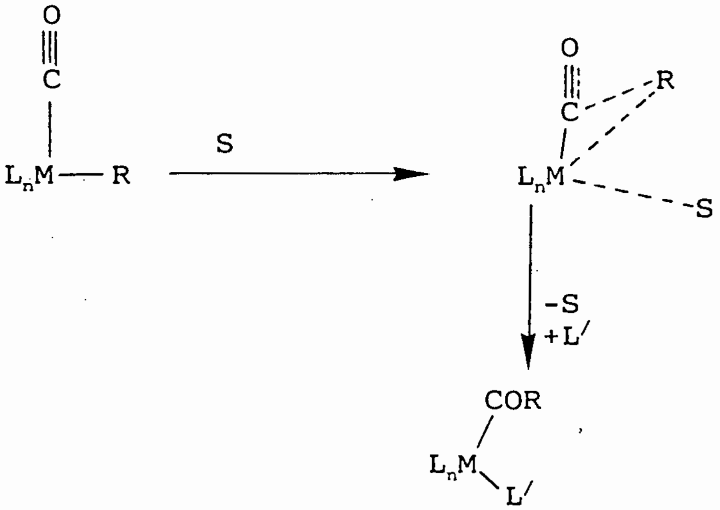
The derivation assumes that a steady-state concentration of the solvated intermediate exists and that the reaction proceeds to completion. At high concentrations of L, $k_2[L] >> k_{-1}$ and $k_{OBS} \approx k_1$. Thus, if $[L] >> [RM(CO)]$, the reaction is pseudo-first order in the metal alkyl species.

The direct influence of the solvent on $k_1$ has been shown in the reaction of [CpMo($CH_3$)($CO)_3$] with $PPh_2Me$ in a series of $\alpha$-substituted $THF_s$ [12] and the following reactivity order was found: THF>2-MeTHF>>2,5-$Me_2$THF. However the dependance of $k_1$ on the solvent is modest when compared to the effect of differing incoming nucleophiles (L) on the rates of bimolecular displacement reactions [13] and the extent of solvent involvement is presumably small. Theoretical analyses [14,15] have led to different conclusions as to whether such stabilization exists.

A recent report by Bent and Cotton [10] raised the question of whether the reaction of [Mn(R)($CO)_5$] species with tertiary phosphines proceeded after prior dissociation of a solvent molecule from the intermediate. The separate measurement of $k_2$ using a variety of solvents has not yet been achieved in any system. Evidence for a dissociative process has however been presented in a kinetic study of the reaction between [Mn($CH_2C_6H_4$-p-OMe)($CO)_5$], *cis*-[Mn(H)($CO)_4$($PPhMe_2$)] and carbon monoxide, which gave p-$MeOC_6H_4CH_2CHO$ and *ax*-[$Mn_2$($CO)_9$($PPhMe_2$)] [16].

Numerous studies on the reactivities of alkyl metal carbonyl species have shown that carbonyl insertion becomes more difficult as the electron-withdrawing ability of the substituent increases [17-20]. In a study by Cawse et al [21], the use of a common $CH_2$ attachment to the metal centre ([Mn($CO)_5$] or [Fe($CO)_4]^-$) yielded a good linear free energy relationship (LFER) correlation over a range of substituents (R in $MCH_2R = H$ ,$CH_3$, $C_2H_5$, $C_6H_5$ for Mn and n-heptyl, n-octyl, $C_6H_5$ for Fe). The two systems (Fe and Mn) showed large, similar effects of polar substituents on the carbonyl insertion reaction. The very large $\rho$ values (see later) (-8.7 for Mn and -8.8 for Fe) demonstrate the profound effect of electron-withdrawing groups in slowing down the reaction. An electron-withdrawing group would be expected to have its greatest effect on the formation, *via* alkyl migration, of the coordinatively unsaturated intermediate. The observed $\rho$ values for both the Fe and Mn systems are very similar, thus a fairly large, negative $\rho$ may be a common feature of carbonyl insertion reactions. The magnitude of $\rho$, the sensitivity parameter, (a reaction constant) is essentially a measure of the susceptibility of a reaction to the polar effect of substituents. The larger the value of $\rho$, the greater is the susceptibility of the reaction. The sign of $\rho$ is also of diagnostic use. A negative $\rho$ indicates the development of positive charge (or, of course, the removal of negative charge) at the reaction centre in the transition state for the rate-determining step (RDS) of the overall reaction. A positive $\rho$ value indicates the development of negative charge in the transition state [22].

Mechanistic studies [17,23] on the CO insertion reaction for $[CpFe(R)(CO)_2]$ show an increase in rate with increase in phosphine concentration, but only up to a certain limiting value. This is indicative of a reversible, nucleophile-independent insertion to give a low concentration of a coordinatively unsaturated acyl intermediate which undergoes a bimolecular reaction with the phosphine [24]. The solvent and the nature of the phosphine play only minor roles, however the rate is very dependant on the nature of R, decreasing in the order R=i-Pr>Et>Me. Isotopic labelling studies [25] have shown that the migration takes place to a *cis* carbonyl ligand. Cotton et al [26] investigated the DMSO-promoted reaction of $[CpFe(R)(CO)_2]$ compounds with $PPh_3$ (R=Me,Et,n-Pr,n-Bu,n-hexyl,n-octyl, i-Bu,s-Bu). The major substituent effect was seen in $k_1$ and reflects mostly steric enhancement of the reaction with the following reactivity order being observed: s-Bu>i-Pr> i-Bu>Et>n-Pr n-Bu n-hexyl n-octyl>$CH_3$. These results were also found to be compatible with a solvent-assisted process. Cotton's explanation of the observed steric enhancement for the $[CpFe(R)(CO)_2]$ system involved the concept of proportionally greater release of steric strain within the transition state leading to the formation of the DMSO-substituted acyl intermediate as the size of the alkyl group is increased. In the transition state, as the partial bond to the solvent is formed, the metal-carbon σ-bond becomes longer and the large substituent is partially removed from the crowded environment at the metal centre, as shown in Scheme 2



Scheme 2

Cotton et al [5,6,8,9] have performed an extensive series of studies on substituted benzyl manganesepentacarbonyl systems (eqn. 2), using a variety of substituents in order

$$[Mn(CH_2C_6H_4X)(CO)_5] + PR_3 \xrightarrow[30°C]{CH_3CN} cis\text{-}[Mn(COCH_2C_6H_4X)(CO)_4(PR_3) \qquad (2)$$

to provide a wide variation in electronic and steric parameters. The rate data were analyzed in terms of the reaction pathways proposed in Scheme 1. In the majority of cases, there was no detectable contribution from the $k_3$

pathway. The rate constant, $k_{OBS}$, (effectively $k_1$) was found to increase significantly with increasing electron-donating ability of the substituent. The most reactive substituent among those studied, p-$OCH_3$, reacted *ca.* five times faster than the least reactive, p-$CF_3$. The results were analyzed in terms of Hammett $\sigma$ substituent parameters, giving a rather modest value (-0.97) of $\rho$, the reaction parameter. This enhancement of the CO insertion reaction by electron-donating substituents observed by Cotton agrees with earlier observations made by Calderazzo [19,27] for the $[Mn(R)(CO)_5]$ system, with the following order being found: $CH_3$>$CH_2F$>$CH_3$. However, the conclusion regarding electronic effects in Calderazzo's studies required qualification because of the rather substantial change in the steric environment at the reacting carbon centre. Cotton's results for CO insertion in $[CpFe(R)(CO)_2]$ (in DMSO) [26] suggested that steric enhancement of such reactions can occur. If this is also the case for $[Mn(R)(CO)_5]$ systems, then the steric and electronic factors along the series $CH_3$,$CH_2F$,$CF_3$ would operate in opposite directions and the above conclusions regarding electronic effects would no longer be ambiguous.

Cotton attributed the steric enhancement he observed in the $[CpFe(R)(CO)_2]$ systems to the weakening of the iron-alkyl bond with increasing intramolecular interaction. However, for benzyl manganesepentacarbonyl systems, the following reactivity order is observed: p-$CH_3$>m-$CH_3$>o-$CH_3$. This order is incompatible with the concept of steric enhancement. It is also at variance with that predicted on electronic grounds. Although the electronic effect of the methyl group is small, the group is both inductively and by resonance electron-donating, thus its influence should be greater from the ortho position than from the para position. However, as the steric influence in the ortho position is increased, rate enhancement is observed *e.g.* $k_1$ for X = o-i-Pr $\sim$ $k_1$ for X = p-i-Pr *ie* the "ortho-inhibition" observed for the methyl substituent has been overcome. The low reactivity of the o-$CH_3$ compound may reflect competition between two opposing steric effects. In addition to the enhancement arising from non-bonded interactions in the starting material which will weaken the metal-carbon bond in the ground state, inhibition can also arise from interactions in the transition state associated with migration of the benzyl ligand to an adjacent carbonyl group. This effect is demonstrated by the large decreases in $k_1$ for the large alkyl group, di-ortho-substituted [$CpMo(CH_2C_6H_3X_2)(CO)_3$] compounds [28], compared to their mono-substituted counterparts. For the manganese complexes studied by Cotton, the limiting size necessary for the onset of this latter effect as a major influence on reactivity was not reached or observed [6]. For the concept of two competing influences to be valid, the profile of each effect with respect to the substituent would have to be very different and the profile would also have to vary from metal to metal. Cotton proposed [5,6] that the overall effect was to create a "steric window" within which the reactivity is enhanced. Comparison of the relative reactivities of the manganese [5,6,9,10] and molybdenum [28,29] systems studied by Cotton suggests that the "window" for the manganese compounds encompasses larger alkyl groups and that overall, the manganese compounds are less sterically congested.

The $k_1$ values for the o-halobenzyl manganesepentacarbonyl compounds show similar trends. The $k_1$ value for the o-Cl compound is significantly less than $k_1$ for the p-Cl compound. This is as expected, due to the higher contribution from the electron-withdrawing inductive effect from the ortho position. Although the $CF_3$ group is electron-withdrawing by induction and resonance from ortho and para positions which, on electronic grounds, should result in $k_1$ for the o-$CF_3$ compound being much lower than for the p-$CF_3$ compound, the difference is, in reality, very small. This is consistent with the onset of an enhancing steric effect for this larger substituent.

An investigation into the effect of solvent on the $[Mn(CH_2C_6H_4X)(CO)_5]$ system [9] showed that the $k_1$ values were less sensitive to the solvent than in the $[CpMo(R)(CO)_3]$ system [9]. This is consistent with the previously observed [5,6], relatively lower influence of steric factors in the reactivity of $[Mn(CH_2C_6H_4X)(CO)_5]$ complexes.

In a separate study of $[Mn(CH_2C_6H_4X)(CO)_5]$ [9], Cotton et al observed a wide variation in $k_3$ values (for the direct reaction pathway) with variation in $PR_3$. The $k_3$ values (in toluene) were found to increase with a decrease in the Tolman electronic parameter [30], *ie* with increasing electron-donating ability of the nucleophile. The fact that the major effect of $PR_3$ is electronic and not steric is of considerable significance in relation to the observed dependence of $k_2$ on steric factors [6]. The $k_3$ pathway is necessarily associative and is thus expected to show a more pronounced steric effect than the $k_2$ step if, as is claimed [16,31], this step involves attack of the nucleophile on a coordinatively unsaturated species formed by prior dissociation of a polar solvent molecule. Cotton proposed that the $k_2$ process is in fact associative [9], albeit with a substantial degree of bond breaking from the solvent molecule, before bond formation to the incoming nucleophile occurs.

While our work on these manganesepentacarbonyl benzyl species was in progress, Cotton reported a study on this same metal-ligand system [6,9]. Some of the substituents reported in his study were the same as we had been studying *i.e.* o-$CH_3$, m-$CH_3$, p-$CH_3$, o-Cl, m-Cl and p-Cl. Thus we do not report or discuss these compounds, with the exception of the p-$CH_3$ derivative which has been included in order to provide a point of comparison between electron-withdrawing and electron-donating substituents. We now report the synthesis and characterization of several new benzyl compounds of the types $[Mn(CH_2C_6H_4X)(CO)_5]$ and $[CpFe(CH_2C_6H_4X)(CO)_2]$. We have carried out carbonyl insertion reactions on some of these compounds under the same conditions as reported by Cotton, *ie* a concentration of 0.008M in 10ml of $CH_3CN$ at 30°C with a *ca.* 15-fold molar excess of $PPh_3$ and we compare our results with those of Cotton.

## 5.2 RESULTS AND DISCUSSION

### 5.2.1 MANGANESEPENTACARBONYL BENZYL DERIVATIVES $[Mn(CH_2C_6H_4X)(CO)_5]$ (X=H, p-$CH_3$, o-Br, m-Br, p-Br, o-$NO_2$, m-$NO_2$, p-$NO_2$) - SYNTHESIS AND CHARACTERIZATION

We now report the synthesis and characterization of the manganesepentacarbonyl benzyl derivatives, $[Mn(CH_2C_6H_4X)(CO)_5]$ (X=H, p-$CH_3$, o-Br, m-Br, p-Br, o-$NO_2$, m-$NO_2$ and p-$NO_2$; compounds 1-8). The unsubstituted benzyl compound [1], the para-methyl derivative [5] and the para-nitro derivative [32] have previously been reported. These complexes were all prepared by the reaction of $Na[Mn(CO)_5]$ with the relevant benzyl bromide derivative, $BrCH_2C_6H_4X$, as shown in equation 3.

$$Na[Mn(CO)_5] + BrCH_2C_6H_4X \xrightarrow[25°C]{THF} [Mn(CH_2C_6H_4X)(CO)_5] + NaBr \qquad (3)$$

(X = H, p-$CH_3$, o-Br, m-Br, p-Br, o-$NO_2$, m-$NO_2$, p-$NO_2$)

All the compounds were isolated as pale yellow crystalline solids which melt below 130°C. They are stable both thermally and to air and are fairly stable in solution (except for the p-$NO_2$ derivative) when kept under nitrogen. They were all soluble in most organic solvents, with the exception of compound **8**, the p-$NO_2$ derivative, which was not soluble in hexane or other hydrocarbon solvents. Compounds **1-8** were characterized by IR, $^1H$ and $^{13}C$ NMR, elemental analysis and mass spectrometry. The data are presented in Tables 5.1 - 5.4.

## IR

The IR data in the $\nu(CO)$ region (see Table 5.1) show the peaks predicted for $[Mn(R)(CO)_5]$ compounds [33], *viz.* $A_1$ (2108cm$^{-1}$), E (split: 2017cm$^{-1}$, 2013cm$^{-1}$) and $A_1$ (1990cm$^{-1}$). One can see that there is a slight variation in $\nu(CO)$ upon changing X. For example, when changing X from the electron-donating para-$CH_3$ group to the electron-withdrawing meta-$NO_2$ group, the highest energy carbonyl vibration ($A_1$) shifts in frequency from 2105cm$^{-1}$ to 2109cm$^{-1}$ and the lower energy $A_1$ vibration shifts from 1988cm$^{-1}$ to 1998cm$^{-1}$. This shift to a higher wavenumber is indicative of a stronger Mn-benzylic $CH_2$ bond. Thus, from the IR data one can draw the conclusion that electron-withdrawing substituents strengthen the Mn-$CH_2$ bond. This should result in decreased reactivity of the compounds with electron-withdrawing substituents as was found to be the case [5,6,9].

## $^1H$ and $^{13}C$ NMR

Assignments of the $^1H$ and $^{13}C$ NMR data were made by comparison of all of the NMR data for these compounds with those reported for $[Mn(CH_2C_6H_5)(CO)_5]$[34], $[Mn(CH_2C_6H_4\text{-p-}Cl)(CO)_5]$[32], $[Mn(CH_2C_6H_4\text{-p-}NO_2)(CO)_5]$[32] and the o-, m- and p-cyano derivatives, $[Mn(CH_2C_6H_4CN)(CO)_5]$[3]. Despite the plethora of $[Mn(CH_2C_6H_4X)(CO)_5]$ compounds described by Cotton *et al* [5,6,8,9,10], very little characterization data has

## Table 5.1

## Data for [$Mn(CH_2C_6H_4X)(CO)_5$]

| X | Cmpd No | Yield (%) | mp (°C) | IR $\nu(CO)$ ($cm^{-1}$)[a] | Elemental Analysis | |
|---|---|---|---|---|---|---|
| | | | | | C; found(calcd) | H; found(calcd) |
| H | 1 | 58 | 36–38[b] | 2106(mw), 2015(vs), 2008(vs), 1990(s) | 50.4(50.4) | 2.6(2.5) |
| p-$CH_3$ | 2 | 60 | 50–51 | 2105(mw), 2014(vs), 2007(vs), 1988(s) | 52.1(52.0) | 3.0(3.0) |
| o-Br | 3 | 64 | 86–89 | 2108(mw), 2017(vs), 2013(vs), 1990(s) | 39.4(39.5) | 1.6(1.7) |
| m-Br | 4 | 68 | 47–50 | 2107(mw), 2017(vs), 2011(vs), 1994(s) | 39.3(39.5) | 1.6(1.7) |
| p-Br | 5 | 71 | 66–70 | 2107(mw), 2017(vs), 2009(vs), 1993(s) | 39.5(39.5) | 1.5(1.7) |
| o-$NO_2$ | 6 | 70 | 88–91 | 2108(mw), 2017(vs), 2013(vs), 1990(s) | 43.4(43.5) | 1.8(1.8) |
| m-$NO_2$ | 7 | 65 | 70–73 | 2109(mw), 2019(vs), 2013(vs), 1998(s) | 43.3(43.5) | 1.7(1.8) |
| p-$NO_2$ | 8 | 11 | 116–120 (decomp) | 2109(mw), 2014(br,s)[c] | d | d |

a:in hexane, mw = medium/weak, vs = very strong, s = strong, br = broad
b:corresponds well to literature value [1] of 37.5–38.5°C
c:in $CHCl_3$
d:elemental analysis not obtained for this compound

been reported and no NMR data (for the mono-substituted benzyl compounds) has yet been published, as far as we are aware. As an example of the results that we have obtained, the $^1H$ and $^{13}C$ NMR spectra of $[Mn(CH_2C_6H_4\text{-m-Br})(CO)_5]$ are shown in Figures 1 and 2, respectively.

### $^1H$ NMR

The $^1H$ NMR data are shown in Table 5.2. The assignments for the aromatic protons were made using the numbering scheme shown in Figure 3.

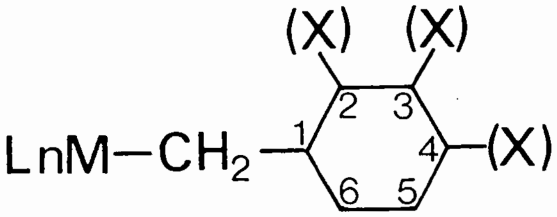


Figure 3 (X denotes the substituent)

The $^1H$ NMR spectra for these compounds in the aromatic region is fairly complicated, especially for the ortho and meta derivatives where all the protons on the benzene ring are rendered inequivalent by the substituent. Thus an ABCD spin system [35] exists which may or may not be resolved. For example, four separate signals are observed for the aromatic protons of the ortho-Br derivative. When the bromine atom is in the meta position however, only three signals are seen - an ABCD spin system still exists, but the signals are not all resolved. When the substituent is in the para position, an AA$'$BB$'$ spin system exists [35] which, in most cases, manifests itself as a doublet of unsymmetrical doublets.

No significant variation in chemical shift was observed when changing either the position of the substituent on the benzene ring or its electron-withdrawing/donating

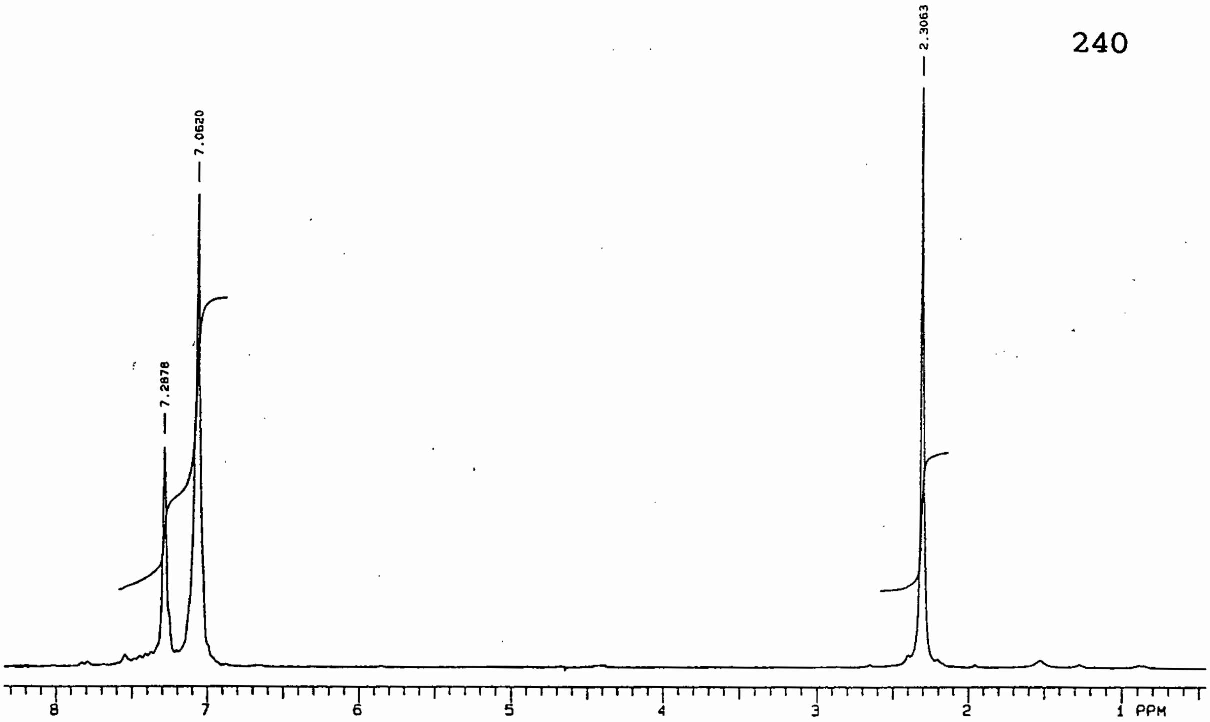


Figure 1 $^{1}H$ NMR Spectrum of $[Mn(CH_2C_6H_4\text{-m-Br})(CO)_5]$

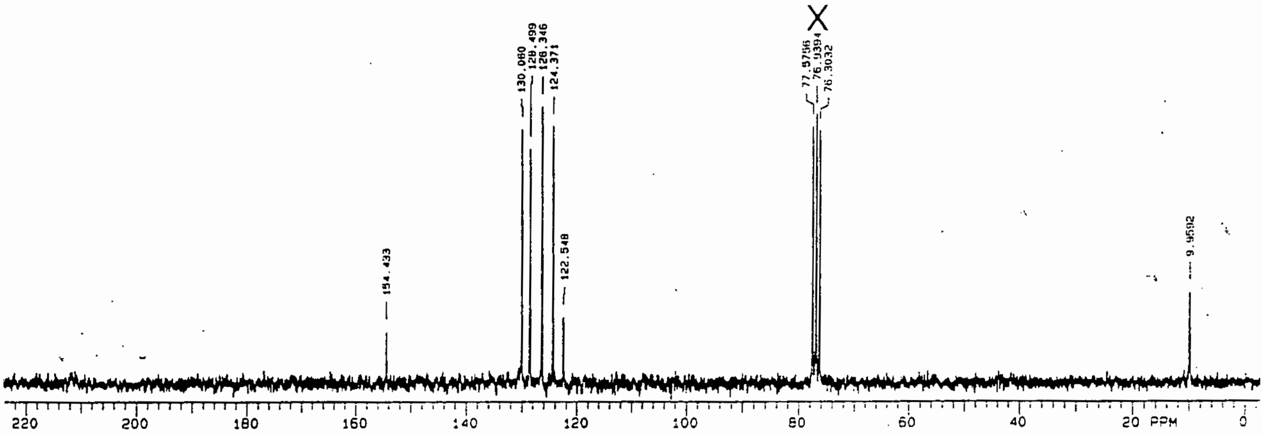


Figure 2 $^{13}C$ NMR Spectrum of $[Mn(CH_2C_6H_4\text{-m-Br})(CO)_5]$
(X=solvent ($CDCl_3$))

Table 5.2

$^1$H NMR Data for $[Mn(CH_2C_6H_4X)(CO)_5]^a$

| X | Cmpd No | $CH_2$ | ArH$^b$ | $CH_3$ |
|---|---|---|---|---|
| H | 1 | 2.38(s,2H) | 7.11(c,6H) | - |
| p-$CH_3$ | 2 | 2.39(s,2H) | 7.00(c,4H)6.83(tr,1H,$H_3$);7.13(c,1H,$H_4$) | 2.25(s,3H) |
| o-Br | 3 | 2.40(s,2H) | 7.25(c,1H,$H_5$);7.45(c,1H,$H_6$) | - |
| m-Br | 4 | 2.31(s,2H) | 7.06(br,s,3H,$H_4$,$H_5$,$H_6$);7.29(br,s,1H,$H_2$) | - |
| p-Br | 5 | 2.30(s,2H) | 6.66(ud,2H,$H_3$,$H_5$);7.14(ud,2H,$H_2$,$H_6$) | - |
| o-$NO_2$ | 6 | 2.58(s,2H) | 7.09(tr,1H,$H_3$);7.42(c,2H,$H_4$,$H_5$);<br>7.96(tr,1H,$H_6$) | - |
| m-$NO_2$ | 7 | 2.39(s,2H) | 7.41(c,3H,$H_4$,$H_5$,$H_6$);7.83(c,1H,$H_2$) | - |
| p-$NO_2$ | 8 | 4.46(s,2H) | 7.53(ud,2H,$H_3$,$H_5$);8.14(ud,2H,$H_2$,$H_6$) | - |

a:in $CDCl_3$, relative to TMS ($\delta$ = 0.00ppm), s = singlet, ud = unsymmetrical doublet, tr = triplet, c = complex signal, br = broad

b:see Fig 3 for numbering system

capabilities.

The $^1$H NMR spectra of $[Mn(CH_2C_6H_5)(CO)_5]$ [36] and $[Mn(CH_2C_6H_4\text{-}p\text{-}NO_2)(CO)_5]$ [32] have previously been reported. Our values are in good agreement with those which appear in the literature, *viz* $\delta$ = 2.36ppm ($CH_2$) and $\delta$ = 7.07ppm (ArH) for $[Mn(CH_2C_6H_5)(CO)_5]$ and $\delta$ = 4.57ppm ($CH_2$) and $\delta$ = 7.95 (ArH) for $[Mn(CH_2C_6H_4\text{-}p\text{-}NO_2)(CO)_5]$.

## $^{13}$C NMR

The $^{13}$C NMR data are given in Table 5.3. No significant variation in the chemical shifts of any of the carbon nuclei was detected when varying the nature or position of X. The para-carbon atom of the benzene ring could be assigned only when the substituent was in the para position, on the basis of relative intensities. In all other cases, only the $CH_2$-substituted *i.e.* ipso carbon atom could be assigned unambiguously because of its characteristic chemical shift. The $^{13}C$ NMR spectrum of $[Mn(CH_2C_6H_5)(CO)_5]$ has previously been reported [34] and was in good agreement with the spectrum obtained by us. Separate resonances were observed for the *cis* and *trans* carbonyls (at $\delta$ = 211.1ppm and $\delta$ = 209.1ppm, respectively) only at low temperatures (-87°C) [34]. Presumably, the *cis* and *trans* carbonyls in our spectra appeared as one broad peak as a result of the molecules being fluxional at 25°C, the temperature at which our spectra were recorded.

**Table 5.3**

**$^{13}C$ NMR Data for $[Mn(CH_2C_6H_4X)(CO)_5]^{a,b}$**

| X | Cmpd No | $CH_2$ | ArC$^{c}$ | $CH_3$ |
|---|---|---|---|---|
| H | 1 | 11.0 | 151.74($C_1$);128.59,125.80($C_2$,$C_3$,$C_5$,$C_6$); 123.45($C_4$)$^{d}$ | - |
| p-$CH_3$ | 2 | 10.85 | 148.29($C_1$);129.17,125.77($C_2$,$C_3$,$C_5$,$C_6$); 132.81($C_4$)$^{d}$ | 20.84 |
| o-Br | 3 | 9.90 | 150.83($C_1$);132.83,127.96,127.62,124.70 122.70($C_2$,$C_3$,$C_4$,$C_5$,$C_6$) | - |
| m-Br | 4 | 9.96 | 154.43($C_1$);130.06,128.50,126.35,124.37 122.55($C_2$,$C_3$,$C_4$,$C_5$,$C_6$) | - |
| p-Br | 5 | 10.04 | 150.82($C_1$);131.49,127.45($C_2$,$C_3$,$C_5$,$C_6$); 116.43($C_4$)$^{d}$ | - |
| o-$NO_2$ | 6 | 8.16 | 150.36($C_1$);133.01,131.07,128.89,126.28 124.63($C_2$,$C_3$,$C_4$,$C_5$,$C_6$) | - |
| m-$NO_2$ | 7 | 10.27 | 155.01($C_1$);132.53,130.08,120.75,119.01 117.24($C_2$,$C_3$,$C_4$,$C_5$,$C_6$) | - |
| p-$NO_2$ | 8 | 10.57 | 152.26($C_1$);125.83,124.41($C_2$,$C_3$,$C_5$,$C_6$) 123.77($C_4$)$^{d}$ | - |

a:in $CDCl_3$ relative to TMS ($\delta$ = 0.00ppm)
b:broad, weak peaks were seen for the carbonyl groups at *ca.* 210ppm
c:for numbering system, see Fig 3
d:assigned on the basis of relative intensities

## MASS SPECTRA

The mass spectra of **1-8** are reported in Table 5.4 and are all similar. They all show parent molecular ions, with the predominant fragmentation pathway being successive loss of carbonyl groups. A second pathway involves the initial loss of the benzyl group followed by loss of the carbonyl groups.

## 5.2.2 CYCLOPENTADIENYLIRONDICARBONYL BENZYL DERIVATIVES, $[CpFe(CH_2C_6H_4X)(CO)_2]$ (X=H, o-$CH_3$, m-$CH_3$, p-$CH_3$, o-Cl, m-Cl, p-Cl, o-Br, m-Br, p-Br) - SYNTHESIS AND CHARACTERIZATION

The unsubstituted benzyl derivative, $[CpFe(CH_2C_6H_5)(CO)_2]$, has been reported previously [2]. We also report the synthesis and characterization of this compound, **9**, and in addition, we report the synthesis and characterization of the new compounds $[CpFe(CH_2C_6H_4X)(CO)_2]$ (X=o-$CH_3$, m-$CH_3$, p-$CH_3$, o-Cl, m-Cl, p-Cl, o-Br, m-Br and p-Br) **10-18** and the synthesis of the related compounds $[CpFe(CH_2CH_2C_6H_5)(CO)_2]$, **19**, and $[CpFe(CH_2CH_2CH_2C_6H_5)(CO)_2]$, **20** Compound **19** has been reported previously [37].

These complexes were all prepared by the reaction of $Na[CpFe(CO)_2]$ with the appropriate benzyl bromide derivative, $BrCH_2C_6H_4X$, as shown in equation 4.

$$Na[CpFe(CO)_2] + BrCH_2C_6H_4X \xrightarrow[25°C]{THF} [CpFe(CH_2C_6H_4X)(CO)_2] + NaBr \quad (4)$$

(X = H, o-$CH_3$, m-$CH_3$, p-$CH_3$, o-Cl, m-Cl, p-Cl, o-Br, m-Br, p-Br)

Table 5.4

Mass Spectral Data for [Mn($CH_2C_6H_4X$)($(CO)_5$)]

| Possible Assignments[a] | Cmpd No | | | Relative Peak Intensities[b] | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| [M][c] | 11 | 13 | 20 | 15 | 30 | 0 | 10 | 0 |
| [M-CO][c] | 20 | 17 | 28 | 0 | 26 | 8 | 12 | 10 |
| [M-2CO][c] | 10 | 8 | 8 | 17 | 21 | 6 | 8 | 12 |
| [M-3CO)[c] | 8 | 6 | 21 | 5 | 29 | 20 | 27 | 18 |
| [M-4CO][c] | 17 | 10 | 32 | 21 | 42 | 28 | 31 | 14 |
| [M-5CO][c] | 82 | 43 | 100 | 100 | 100 | 100 | 100 | 58 |
| [M-4CO-X] | 0 | 0 | 0 | 0 | 20 | 0 | 0 | 0 |
| [M-5CO-X] | 0 | 0 | 72 | 73 | 84 | 0 | 0 | 0 |
| [$CH_2C_6H_4X$][c] | 100 | 100 | 11 | 15 | 20 | 7 | 10 | 0 |
| [Mn$(CO)_5$] | 0 | 0 | 5 | 8 | 16 | 4 | 8 | 0 |
| [Mn$(CO)_4$] | 3 | 0 | 12 | 11 | 0 | 0 | 0 | 6 |
| [Mn$(CO)_3$] | 6 | 3 | 8 | 6 | 20 | 0 | 0 | 0 |
| [Mn$(CO)_2$] | 6 | 3 | 0 | 6 | 18 | 7 | 0 | 0 |
| [Mn(CO)] | 5 | 4 | 6 | 12 | 30 | 22 | 4 | 7 |
| [Mn] | 68 | 20 | 61 | 86 | 100 | 57 | 16 | 100 |
| [CO] | 71 | 18 | 0 | 0 | 21 | 0 | 72 | 0 |

a:all ions have a single positive charge
b:peak intensities relative to base peaks for [M-5CO]$^+$ or [$CH_2C_6H_4X$]$^+$ or [Mn]$^+$
c:these peaks exhibited doublets due to $^{79}$Br and $^{81}$Br for compounds 3,4, or 5

Compounds **19** and **20** were prepared in a similar manner. All the compounds (**9-20**) were isolated as yellow-orange crystalline solids melting below 120°C. As with their manganese analogues, they are stable both thermally and to air and in solution when kept under nitrogen. They are also soluble in most organic solvents. They have been fully characterized by IR, $^1H$ and $^{13}C$ NMR, elemental analysis and mass spectroscopy. The data are presented in Tables 5.5 - 5.8. The o-, m- and p-$NO_2$ derivatives were not prepared. A number of attempts were made to synthesize these compounds but extensive decomposition to $[CpFe(CO)_2]_2$ (as the only isolable product) resulted in every case.

## IR

The IR spectra in the $\nu(CO)$ region (see Table 5.5) show the expected [38] number of peaks (two) at the expected positions. One can see that there is a slight increase in $\nu(CO)$ when X is changed from an electron-donating to an electron-withdrawing group. This may be taken as being indicative of a stronger Fe-benzylic $CH_2$ bond for the benzyl compounds with electron-withdrawing substituents.

## $^1H$ and $^{13}C$ NMR Data

Assignments of the $^1H$ and $^{13}C$ NMR data were made by comparison of all of the NMR data for these compounds with those of the related benzyl manganesepentacarbonyl compounds and with the $^1H$ NMR data reported for $[CpFe(CH_2C_6H_5)(CO)_2]$[2], $[CpFe(CH_2CH_2C_6H_5)(CO)_2$[37] and $[CpFe(CH_2C_6H_4\text{-o-CN})(CO)_2]$[3]. No $^{13}C$ NMR data for cyclopentadienyl irondicarbonyl benzyl derivatives was found in the literature. As an example of the results obtained, the $^1H$ and $^{13}C$ NMR spectra of $[CpFe(CH_2C_6H_4\text{-m-}CH_3)(CO)_2]$ are shown in Figures 4 and 5, respectively.

Table 5.5

Data for [CpFe($CH_2C_6H_4X$)$(CO)_2$] and [CpFe{$(CH_2)_nC_6H_5$}$(CO)_2$]

| X | n | Cmpd No | Yield (%) | mp (°C) | IR ν(CO) ($cm^{-1}$)[a] | Elemental Analysis C:found(calcd) | H:found(calcd) |
|---|---|---|---|---|---|---|---|
| H | 1 | 9 | 56 | 55-57[b] | 2009(s),1958(s) | 62.7(62.7) | 4.2(4.1) |
| o-$CH_3$ | 1 | 10 | 62 | 64-67 | 2010(s),1960(s) | 63.8(63.9) | 5.0(5.0) |
| m-$CH_3$ | 1 | 11 | 68 | 95-97 | 2009(s),1957(s) | 63.8(63.9) | 5.1(5.0) |
| p-$CH_3$ | 1 | 12 | 71 | 89-91 | 2008(s),1956(s) | 63.7(63.9) | 5.1(5.0) |
| o-Cl | 1 | 13 | 72 | 80-82 | 2012(s),1963(s) | 55.5(55.6) | 3.7(3.7) |
| m-Cl | 1 | 14 | 70 | 81-84 | 2012(s),1961(s) | 55.6(55.6) | 3.6(3.7) |
| p-Cl | 1 | 15 | 81 | 68-70 | 2011(s),1960(s) | 55.8(55.6) | 3.8(3.7) |
| o-Br | 1 | 16 | 76 | 70-72 | 2012(s),1962(s) | 48.4(48.5) | 3.2(3.2) |
| m-Br | 1 | 17 | 70 | 84-86 | 2012(s),1961(s) | 48.6(48.5) | 3.2(3.2) |
| p-Br | 1 | 18 | 64 | 115-119 | 2011(s),1960(s) | 48.6(48.5) | 3.0(3.2) |
| H | 2 | 19 | 50 | 77-80[c] | 2009(s),1955(s) | 63.9(63.9) | 5.1(5.0) |
| H | 3 | 20 | 48 | 48-50 | 2009(s),1955(s) | 64.7(64.9) | 5.6(5.5) |

a:in hexane, s=strong
b:corresponds well to literature value of 55°C[2]
c:corresponds well to literature value of 75°C[37]

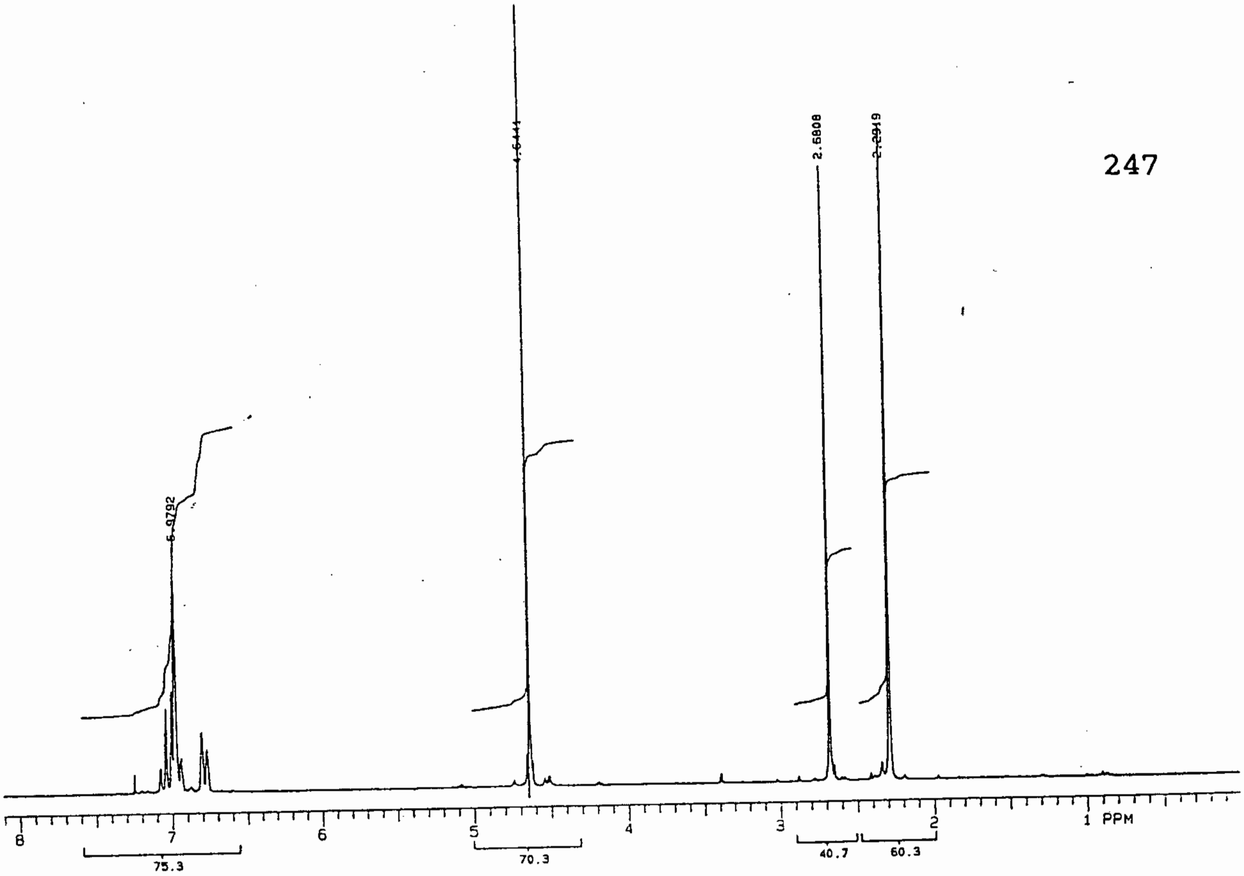


Figure 4 $^1$H NMR Spectrum of $[CpFe(CH_2C_6H_4\text{-m-}CH_3)(CO)_2]$ (in $CDCl_3$)

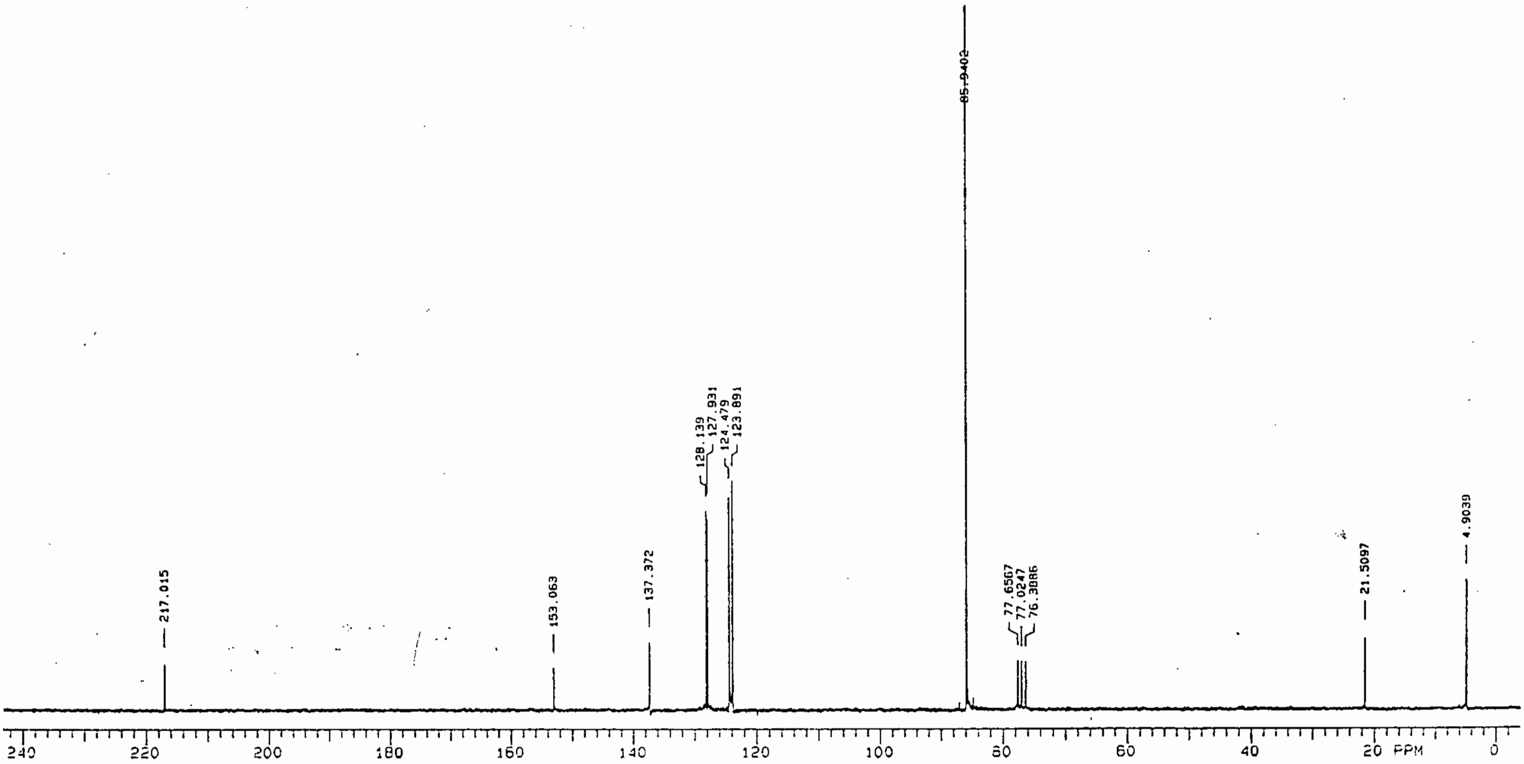


Figure 5 $^{13}$C NMR Spectrum of $[CpFe(CH_2C_6H_4\text{-m-}CH_3)(CO)_2]$ (X=solvent($CDCl_3$))

## $^1$H NMR

As was the case with the analogous [Mn($CH_2C_6H_4X$)$(CO)_5$] compounds, the $^1$H NMR spectra in the aromatic region are fairly complicated. However, the same discussion applies ie for the para derivatives an AA$'$BB$'$ spin system is present, whereas the ortho and meta derivatives exhibit an ABCD spin system which is sometimes not resolved. The methylene and cyclopentadienyl resonances are at the expected positions (*ca.* $\delta$ = 2.6ppm and $\delta$ = 4.7ppm, respectively). Our results and assignments are in good agreement with those given for [CpFe($CH_2C_6H_5$)$(CO)_2$][2] ($\delta$ = 2.77 $CH_2$, $\delta$ = 4.69 Cp and $\delta$ = 7.2 ArH), [CpFe($CH_2C_6H_4$-o-CN)$(CO)_2$][3] ($\delta$ = 2.86 $CH_2$, $\delta$= 5.17 Cp and $\delta$ = 2.74 ArH) and [CpFe($CH_2CH_2C_6H_5$)$(CO)_2$][37] ($\delta$ = 2.11 $CH_2CH_2$, $\delta$ = 4.75 Cp and $\delta$ = 7.20 ArH).

## $^{13}$C NMR

The $^{13}$C NMR data are given in Table 5.7. No variation in the carbonyl or aromatic carbon resonances could be seen upon changing X. However, the methylene ($CH_2$) resonance did move to slightly higher field upon changing the nature of X from electron-withdrawing to electron-donating. The change was in the order of 0.8ppm. As was the case with the analogous manganese compounds, the para-carbon atom of the benzene ring could only be assigned, on the basis of relative intensities, when the substituent was in the para position. In all other cases, only the $CH_2$-substituted ipso carbon atom of the benzene ring could be assigned unambiguously.

## MASS SPECTRA

The mass spectra of 8-20 are given in Table 5.8. They are all similar, with the predominant fragmentation pathway being loss of the carbonyl ligands followed by loss of the

## Table 5.6

## $^1$H NMR Data for $[CpFe(CH_2C_6H_4X)(CO)_2]$ and $[CpFe\{(CH_2)_nC_6H_5\}(CO)_2]^a$

| X | n | Cmpd No | $FeCH_2$ | $FeCH_2CH_2$ | $FeCH_2CH_2CH_2$ | ArH$^b$ | Cp | $CH_3$ |
|---|---|---|---|---|---|---|---|---|
| H | 1 | 9 | 2.65(s,2H) | - | - | 7.08(c,5H) | 4.58(s,5H) | - |
| o-$CH_3$ | 1 | 10 | 2.60(s,2H) | - | - | 6.93(d,1H,$H_6$);7.21(c,3H, $H_3$,$H_4$,$H_5$) | 4.76(s,5H) | 2.23(s,3H) |
| m-$CH_3$ | 1 | 11 | 2.68(s,2H) | - | - | 6.80(d,1H,$H_2$);6.98(c,3H, $H_4$,$H_5$,$H_6$) | 4.64(s,5H) | 2.29(s,3H) |
| p-$CH_3$ | 1 | 12 | 2.66(s,2H) | - | - | 6.94(br,4H,$H_2$,$H_3$,$H_5$,$H_6$) | 4.58(s,5H) | 2.20(s,3H) |
| o-Cl | 1 | 13 | 2.70(s,2H) | - | - | 6.84(tr,1H,$H_6$);6.99(tr,1H, $H_3$);7.15(c,2H,$H_4$,$H_5$) | 4.73(s,5H) | - |
| m-Cl | 1 | 14 | 2.60(s,2H) | - | - | 7.01(c,3H,$H_4$,$H_5$,$H_6$);7.10 (s,1H,$H_2$) | 4.65(s,5H) | - |
| p-Cl | 1 | 15 | 2.59(s,2H) | - | - | 7.02(br,4H,$H_2$,$H_3$,$H_5$,$H_6$) | 4.59(s,5H) | - |
| o-Br | 1 | 16 | 2.76(s,2H) | - | - | 6.80(c,1H,$H_6$);7.06(c,1H, $H_3$);7.21,7.39(both c,1H,$H_4$,$H_5$) | 4.79(s,5H) | - |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| m-Br | 1 | 17 | 2.56(s,2H) | - | - | 6.96(c,3H,$H_4$,$H_5$,$H_6$);7.20 (s,1H,$H_2$) | 4.61(s,5H) | - |
| p-Br | 1 | 18 | 2.60(s,2H) | - | - | 6.96(ud,2H,$H_3$,$H_5$);7.21 (ud,2H,$H_2$,$H_6$) | 4.62(s,5H) | - |
| H | 2 | 19 | 2.64(S,2H) | 1.65(tr,2H) | - | 7.18(c,5H,$H_2$,$H_3$,$H_4$,$H_5$, $H_6$) | 4.68(s,5H) | - |
| H | 3 | 20 | 2.68(s,2H) | 1.55(c,4H) | 1.55(c,4H) | 7.21(c,5H,$H_2$,$H_3$,$H_4$,$H_5$, $H_6$) | 4.73(s,5H) | - |

a:in $CDCl_3$, relative to TMS ($\delta$ = 0.00ppm), s = singlet, d = doublet, ud = unsymmetrical doublet
tr = triplet, c = complex signal, br = broad signal
b:see Fig 3 for numbering system

Table 5.7

$^{13}C$ NMR Data for $[CpFe(CH_2C_6H_4X)(CO)_2]$ and $[CpFe\{(CH_2)_nC_6H_5\}(CO)_2]^a$

| X | n | Cmpd No | $Fe\underline{C}H_2$ | $FeCH_2\underline{C}H_2$ | $FeCH_2CH_2\underline{C}H_2$ | CO | $ArH^b$ | Cp | $CH_3$ |
|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 9 | 4.95 | - | - | 219.96 | 153.20($C_1$);128.04,127.32($C_3$,$C_5$);122.97($C_4$)$^c$ | 85.91 | - |
| o-$CH_3$ | 1 | 10 | 0.93 | - | - | 216.73 | 151.16($C_1$);133.31,130.07,128.22,125.77,123.20($C_2C_3$,$C_4$, $C_5$,$C_6$) | 85.47 | 19.86 |
| m-$CH_3$ | 1 | 11 | 4.90 | - | - | 217.02 | 153.06($C_1$);137.37,128.14,127.93,124.48,123.89($C_2C_3$,$C_4$, $C_5$,$C_6$) | 85.94 | 21.51 |
| p-$CH_3$ | 1 | 12 | 4.81 | - | - | 217.08 | 149.79($C_1$);132.34($C_4$)$^c$;128.79,127.27($C_2$,$C_3$,$C_5$,$C_6$) | 85.96 | 20.99 |
| o-Cl | 1 | 13 | 0.41 | - | - | 216.48 | 151.41($C_1$),128.43($C_4$,$C_5$)$^c$;126.55,124.10($C_2$,$C_3$,$C_6$) | 85.46 | - |
| m-Cl | 1 | 14 | 4.07 | - | - | 216.65 | 155.87($C_1$);133.56,129.26,126.96,125.45,123.02($C_2C_3$,$C_4$, $C_5$,$C_6$) | 85.87 | - |
| p-Cl | 1 | 15 | 4.03 | - | - | 216.71 | 151.90($C_1$);128.42,128.04($C_2$,$C_3$,$C_5$,$C_6$);116.72($C_4$)$^c$ | 85.83 | - |
| o-Br | 1 | 16 | 4.08 | - | - | 217.11 | 154.18($C_1$),133.36,129.91,127.86,124.95,122.38($C_2$,$C_3$,$C_4$, $C_5$,$C_6$) | 86.10 | - |
| m-Br | 1 | 17 | 3.98 | - | - | 216.6 | 156.20($C_1$);129.84,129.56,125.85,109.71($C_2$,$C_3$,$C_4$,$C_5$,$C_6$) | 85.83 | - |
| p-Br | 1 | 18 | 4.13 | - | - | 216.74 | 152.52($C_1$);131.02,128.93($C_2$,$C_3$,$C_5$,$C_6$);115.99($C_4$)$^c$ | 85.89 | - |
| H | 2 | 19 | 5.40 | 44.05 | - | 217.43 | 145.65($C_1$);128.29,127.82($C_2$,$C_3$,$C_5$,$C_6$);125.36($C_4$)$^c$ | 85.32 | - |
| H | 3 | 20 | 3.02 | 41.14 | 40.30 | 217.50 | 142.75($C_1$);128.37,128.13($C_2$,$C_3$,$C_5$,$C_6$);125.39($C_4$)$^c$ | 85.25 | - |

a:in $CDCl_3$, relative to TMS ($\delta$ = 0.00ppm)
b:see Fig 3 for numbering system
c:assigned on the basis of relative intensities

Table 5.8

**Mass Spectral Data for $[CpFe(CH_2C_6H_4X)(CO)_2]$ and $[CpFe\{(CH_2)_nC_6H_5\}(CO)_2]$**

| Possible Assignments[a] | Cmpd No | | | | | | Relative Peak Intensities[b] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| [M] | 2 | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 |
| [M–CO][c] | 23 | 20 | 21 | 3 | 25 | 41 | 37 | 27 | 24 | 22 | 0 | 0 |
| [M–2CO][c] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 90 | 100 | 70 | 100 | 100 |
| [M–2CO–Cp][c] | 11 | 0 | 0 | 11 | 3 | 10 | 4 | 0 | 4 | 6 | 42 | 49 |
| [M–2CO–X] | 3 | 0 | 0 | 0 | 23 | 43 | 90 | 0 | 22 | 32 | 60 | 33 |
| $[M-CH_2C_6H_4X]$ | 2 | 0 | 0 | 8 | 7 | 0 | 8 | 0 | 9 | 6 | 0 | 4[d] |
| [M–2CO–Cp–X] | 8 | 0 | 0 | 12 | 10 | 22 | 92 | 100 | 21 | 100 | 4 | 0 |
| $[CH_2C_6H_4X]$[c] | 21 | 12 | 14 | 20 | 4 | 0 | 10 | 0 | 0 | 50 | 9[d] | 20[d] |
| [CpFe] | 53 | 35 | 37 | 31 | 51 | 41 | 40 | 42 | 43 | 24 | 38 | 71 |
| [Cp] | 8 | 0 | 2 | 7 | 6 | 0 | 5 | 0 | 6 | 17 | 0 | 0 |
| [Fe] | 24 | 17 | 16 | 17 | 38 | 27 | 30 | 31 | 28 | 20 | 52 | 40 |
| [CO] | 28 | 9 | 31 | 23 | 0 | 0 | 0 | 0 | 83 | 100 | 0 | 0 |

a:all peaks have a single positive charge

b:peak intensities relative to base peak for $[M-2CO]^+$ or $[M-2CO-Cp-X]^+$

c:these peaks exhibited doublets for $^{79}Br$ and $^{81}Br$ for compounds **16**, **17** and **18**

d:for compounds **19** and **20**, these assignments refer to $[M-(CH_2)nC_6H_4X]^+$ and $[(CH_2)nC_6H_4X]^+$

cyclopentadienyl ligand and then loss of the substituent on the aromatic ring. The initial loss of the benzylic fragment is a second, minor pathway.

## 5.2.3 MANGANESEPENTACARBONYL BENZYL DERIVATIVES, $[Mn(CH_2C_6H_4X)(CO)_5]$ (X=H, o-Br, m-Br, p-Br, o-$NO_2$, m-$NO_2$) - REACTIVITY

Cotton and co-workers, in a series of papers, have reported some reactivity studies on this metal-ligand system with various substituents [5,6,8-10]. They did not however, investigate the reactions of the bromo and nitro derivatives. We now report reactions for these compounds and discuss them. We also compare our results with those reported by Cotton *et al.*

The reaction studied was the triphenylphosphine-induced carbonyl insertion as shown in equation 5.

$$[Mn(CH_2C_6H_4X)(CO)_5] + PPh_3 \xrightarrow[30.0°C]{CH_3CN} cis\text{-}[Mn(COCH_2C_6H_4X)(CO)_4(PPh_3)] \quad (5)$$

The same experimental conditions used by Cotton and co-workers were employed for our reactivity studies *i.e.* the reactions were performed in a Schlenk tube under nitrogen in acetonitrile at 30.0°C using a *ca.* 15-fold molar excess of $PPh_3$. Since acetonitrile is a solvent of fairly strong coordinating ability, reaction by pathway (a) (see Introduction of this chapter) is anticipated, *i.e.* the reaction proceeds *via* a solvent-coordinated acyl species. Because triphenylphosphine is present in such a large excess, the reaction is pseudo first-order and the observed rate constant, $k_{OBS}$, approximates to $k_1$. The reactions were followed by infrared spectroscopy, monitoring the disappearance of the highest energy ($A_1$) carbonyl band at ca. 2112cm$^{-1}$. A plot of ln(I∞-It) versus time (see Appendix 2 for an example) then yielded $k_{OBS}$ (I∞ = intensity of band at time = ∞; It = intensity of band at time = t). The results are given in Table 5.9. A number of attempts were made to study the reaction of the p-$NO_2$ derivative with $PPh_3$, however, this compound decomposed rapidly to a non-carbonyl-containing product on dissolution. This also proved a problem when obtaining the $^1H$ and $^{13}C$ NMR spectra. Thus, we did not obtain kinetic data for [Mn($CH_2C_6H_4$-p-$NO_2$)$(CO)_5$].

In order to test whether a linear free energy relationship (LFER) existed for our compounds (as was found in the compounds studied by Cotton et al) a Hammett plot (log $(k_x/k_H)$ versus σ, the substituent constant) was made and is given in Fig. 6. However, the benzyl compounds with X=o-Br and o-$NO_2$ were not included on the plot since ortho substituents are virtually never included on a Hammett plot as the values of σ are always unreliable. The σ value is a measure of electron-donating/electron-withdrawing ability of a group and when this group is in the ortho position on a benzene ring, steric factors (which are assumed to be negligible in the meta and para positions) come to the fore. The effect that an ortho substituent may have on a reaction is thus due to both steric and electronic factors, whereas for the meta and para positions, it is assumed that the effect is purely electronic [39]. Cotton et al [8] have recently reported that they have calculated a set of σ values for ortho substituents in the series of compounds [M($CH_2C_6H_4X$)$(CO)_5$], (M = Mn, Re) based on spectroscopic data. However, we find that for the complexes [Mn($CH_2C_6H_4X$)$(CO)_5$] (X=o-,m-,p-Br and o-,m-$NO_2$) spectroscopic data varies very little upon changing the position of X.

A good correlation was found from our Hammett plot for the m-Br, p-Br, m-$NO_2$ and unsubstituted benzyl derivatives and $\rho$, the sensitivity parameter (given by equation 6) was found to be -0.95

$$\log\left(\frac{k_x}{k_H}\right) = \rho\sigma \qquad (6)$$

Our value of -0.95 is in good agreement with the value of -1.1 found by Cotton and Markwell [6]. For comparison, Figure 7 shows our Hammett plot (points denoted by ■ ) superimposed on the Hammett plot obtained by Cotton and

**Table 5.9**

**Data for Reaction of $[Mn(CH_2C_6H_4X)(CO)_5]$ with $PPh_3$**

| X | Hammett $\sigma$ value[a] | $k_{OBS}$ ($\times 10^5 sec^{-1}$) | $\log\left(\frac{k_x}{k_H}\right)$ | $t_{\frac{1}{2}}$[b] (min) |
|---|---|---|---|---|
| H | 0 | 26.39 | 0 | 43.8 |
| o-Br | - | 1.51 | -1.24 | 765.1 |
| m-Br | 0.39 | 11.20 | -0.37 | 103.1 |
| p-Br | 0.23 | 15.54 | -0.23 | 74.3 |
| o-$NO_2$ | - | 2.02 | -1.12 | 571.9 |
| m-$NO_2$ | 0.71 | 5.91 | -0.65 | 195.5 |

a: taken from reference 39

b: given by $\frac{\ln 2}{k_{OBS}}$

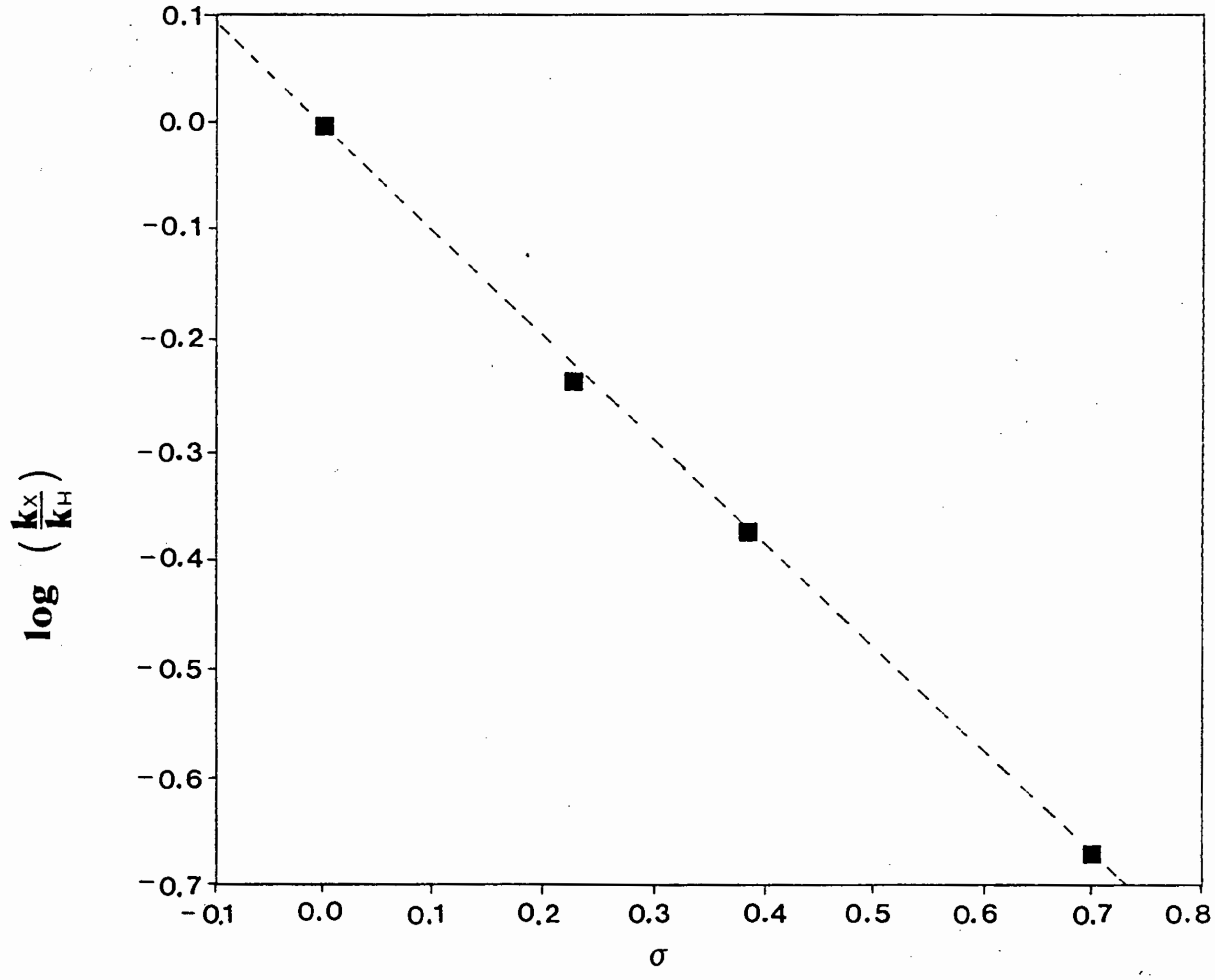


Fig. 6 Hammett Plot for [$Mn(CH_2C_6H_4X)(CO)_5$] (where X = m-Br, p-Br, m-$NO_2$, H)

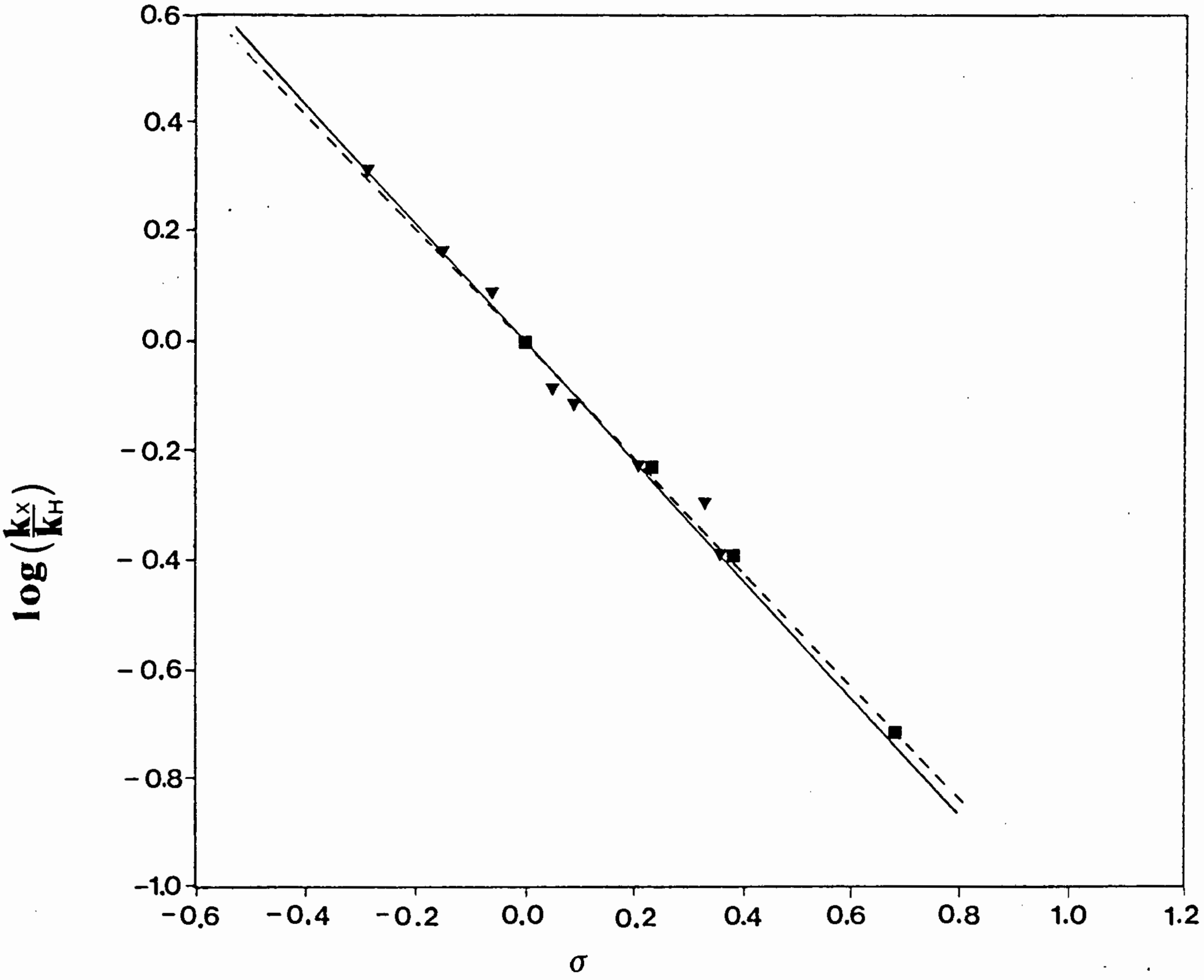


Figure 7 Hammett Plot for $[Mn(CH_2C_6H_4X)(CO)_5]$ ( ■ )[this work] including values measured by J. D. Cotton and R. D. Markwell ( ▼ ) [6].

Markwell (points denoted by ▼ ) for X = m-$CH_3$,p-$CH_3$,m-Cl,p-Cl,m-F,p-F,m-$OCH_3$ and p-$OCH_3$. As a point of reference the $k_x$ and $\sigma$ values used by Cotton and Markwell are given in Table 5.10. The new results that we have obtained in this work provide more data points and show good agreement with Cotton and Markwell's results.

Our value of -0.95 for the sensitivity parameter, $\rho$ (and Cotton and Markwell's value of -1.1) is much lower in magnitude than that of -8.7 obtained by Cawse et al for the carbonylation reaction of [Mn($CH_2R$)$(CO)_5$] compounds [21]. This is presumably because, in the benzyl complexes, the substituent in question is much further removed from the reaction centre than it is in the [Mn($CH_2R$)$(CO)_5$] system and thus electronic effects are not as strongly felt as they are in [Mn($CH_2R$)$(CO)_5$] compounds.

The negative sign of $\rho$ and its modest value imply that in the transition state of the first ($k_1$) step of pathway (a), there is electron demand at a reaction centre situated beyond the benzylic carbon atom. Thus, our results are in excellent agreement with those of Cotton et al [5,6,8,9,10], namely that electron-withdrawing substituents tend to retard the carbonyl insertion reaction. The $NO_2$ group is more electron-withdrawing than the bromo substituent, as is seen by the larger $\sigma$ values (see Table 5.9) for the $NO_2$ substituents. The reactions of those compounds containing the $NO_2$ substituent are consequently slower. This was as predicted on the basis of our IR data.

In the reactions studied by us, the following reactivity orders were observed: p-Br>m-Br>>o-Br and m-$NO_2$>o-$NO_2$. These orders are, as was also observed by Cotton and Markwell [6], incompatible with the steric enhancement that has been observed in other metal-ligand systems. It can, as suggested by Cotton and Markwell, be explained by the concept of two opposing steric effects. One effect will increase the rate of reaction as the steric bulk increases, due to non-bonded interactions in the starting material which will weaken the metal-benzylic $CH_2$ bond in the ground state. However, retardation of the rate of reaction can also result from steric interactions in the transition state when the benzyl group migrates to an adjacent carbonyl carbon atom. The overall effect of these two opposing factors is to create a "steric window" within which, reactivity is enhanced [6]. For the two substituents studied by us (Br and $NO_2$), the second steric effect overrides the first. The difference in rate between the o-$NO_2$ and m-$NO_2$ derivatives is smaller than that between the o-Br and m-Br derivatives. This could be taken to mean that, because the $NO_2$ group is larger than the Br group, the first (rate enhancing) steric effect plays a larger role for the $NO_2$ derivatives than for the Br derivatives, *i.e.* steric interactions in the ground state are starting to become more important for the $NO_2$ derivatives.

**Table 5.10**

**Data for Reaction of $[Mn(CH_2C_6H_4X)(CO)_5]$ with $PPh_3$[a]**

| X | Hammett σ Value | $k_{OBS}$ ($\times 10^5 sec^{-1}$) | $\log\left(\frac{k_x}{k_H}\right)$ |
|---|---|---|---|
| H | 0 | 29.0 | 0 |
| m-$CH_3$ | -0.06 | 36.0 | 0.09 |
| p-$CH_3$ | -0.14 | 43.2 | 0.17 |
| m-Cl | 0.37 | 12.1 | -0.39 |
| p-Cl | 0.22 | 17.3 | -0.23 |
| m-F | 0.34 | 12.0 | -0.39 |
| p-F | 0.06 | 34.2 | 0.07 |
| m-$OCH_3$ | 0.10 | 22.9 | -0.11 |
| p-$OCH_3$ | -0.28 | 60.2 | 0.31 |

a:taken from reference 6

## 5.2.4 CYCLOPENTADIENYLIRONDICARBONYL BENZYL DERIVATIVES - REACTIVITY

An identical procedure to that used for the $[Mn(CH_2C_6H_4X)(CO)_5]$ compounds was employed here. Typically, a 0.008M acetonitrile solution of the benzyl complex, $[CpFe\{(CH_2)_nC_6H_4X\}(CO)_2]$ was reacted with a *ca.* 15-molar excess of $PPh_3$ at 32°C and the reactions were monitored by infrared spectroscopy, following the disappearance of the highest energy carbonyl vibration at *ca.* 2012cm$^{-1}$. The same rate expressions as used for the manganese system will apply. However, after attempting to follow the reactions it was observed that only compounds **19** and **20**, the phenylethyl and phenylpropyl derivatives *i.e.* $[CpFe\{(CH_2)_nC_6H_5\}(CO)_2]$ (n = 2,3) reacted under these conditions, to give the phosphine-substituted acyl products as indicated in equation 7.

$$[CpFe\{(CH_2)_nC_6H_5\}(CO)_2] + PPh_3 \longrightarrow [CpFe\{CO(CH_2)_nC_6H_5\}(CO)(PPh_3)]\ (n = 2,3) \qquad (7)$$

The kinetic data for these two reactions are given in Table 5.11. The rate constants that we obtained are in the same range as those obtained by other workers for similar reactions [17,26].

In an attempt to induce the reactions of the benzyl derivatives to occur the reaction temperature was increased first to 50°C, and then to 80°C. However, no reaction occured, even at these increased temperatures. An oxidant, silver tetrafluoroborate, which is known to induce the alkyl migration reaction to occur in these cyclopentadienyl iron derivatives [39], was added to the benzyl, para-methyl and ortho-chloro derivatives. Again, no reaction occurred and it was concluded that the $[CpFe(CH_2C_6H_4X)(CO)_2]$ system must be extremely reluctant to undergo alkyl migration.

Table 5.11

**Kinetic Data for the Reaction of [CpFe{$(CH_2)_nC_6H_5$}$(CO)_2$] with $PPh_3$**

| n | k<br>(x$10^5$sec$^{-1}$) | log k | t½<br>(min) |
|---|---|---|---|
| 2 | 16.50 | -3.78 | 70.0 |
| 3 | 22.10 | -3.66 | 52.3 |

This has been noted before [26] with the benzyl and para-methoxy derivatives. This reluctance could be due to the distribution of charge within the molecule. If one considers that the charge in the molecule can be distributed as follows:

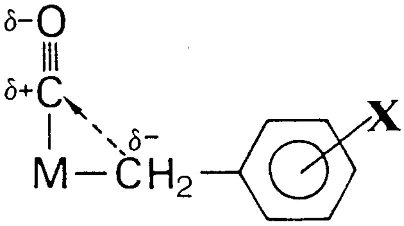


Figure 8

then one can see that electron-donating substituents should increase the rate of reaction since they will increase the charge density on the benzylic $CH_2$ fragment which will make the migration process more favourable. Conversely, if one can determine that the charge density on the benzylic $CH_2$ is reduced, then it follows that the alkyl migration process will be slower, or may not even take place at all. One can get an idea of the charge density that exists on the benzylic $CH_2$ of the iron system relative to that of the manganese system by comparison of $^1H$ NMR data. Comparison of $^{13}C$ NMR data would be somewhat complicated since $^{13}C$ chemical shifts do not depend only on the charge distribution within the molecule [35]. Thus, when one compares the $^1H$ NMR data for these two systems (see Table

5.12) one can see that there is indeed significantly less charge density on the benzylic $CH_2$ fragment of the iron system than that of the manganese system. This should result in the alkyl migration process in $[CpFe(CH_2C_6H_4X)(CO)_2]$ compounds being more difficult, as is observed.

The phenylpropyl derivative, $[CpFe(CH_2CH_2CH_2C_6H_5)(CO)_2]$ reacts faster than the phenylethyl derivative, $[CpFe(CH_2CH_2C_6H_5)(CO)_2]$. This may be due to the phenylpropyl group behaving more like an n-alkyl than a benzyl group.

**Table 5.12**

**Comparison of $^1$H NMR Data for $[Mn(CH_2C_6H_4X)(CO)_5]$ and $[CpFe(CH_2C_6H_4X)(CO)_2]^a$**

| X | $FeCH_2$ | $MnCH_2$ | $\Delta(\delta)^b$ |
|---|---|---|---|
| H | 2.65 | 2.38 | 0.27 |
| p-$CH_3$ | 2.66 | 2.39 | 0.27 |
| o-Br | 2.76 | 2.30 | 0.46 |
| m-Br | 2.56 | 2.58 | -0.02 |
| p-Br | 2.60 | 2.39 | 0.21 |

a:in $CDCl_3$, relative to TMS ($\delta$ = 0.00)
b:given by $\delta(FeCH_2)-\delta(MnCH_2)$

n-Alkyl derivatives of $[CpFe(CO)_2]$ are known to undergo alkyl migration more readily [17,23,26] than the benzyl derivative [26].

## 5.3 CONCLUSIONS

Several new benzyl compounds of the types [Mn($CH_2C_6H_4X$)($CO)_5$] and [CpFe($CH_2C_6H_4X$)($CO)_2$] have been synthesized for the first time.

We have shown that manganesepentacarbonyl benzyl derivatives, [Mn($CH_2C_6H_4X$)($CO)_5$] (X = H,o-Br,m-Br,p-Br,o-$NO_2$, m-$NO_2$), undergo alkyl migration to form *cis*-tetracarbonyl acyl compounds of the type *cis*-[Mn($COCH_2C_6H_4X$)($CO)_4$($PPh_3$)]. The rate constants and $\rho$ , the sensitivity parameter, for these reactions are in excellent agreement with those obtained by other workers in this field [6,9] for similar reactions. The cyclopentadienylirondicarbonyl derivatives were observed to be much less reactive, which can be explained on the basis of reduced negative charge on the benzylic $CH_2$ group, as indicated by $^1H$ NMR data. This lack of reactivity was not entirely unexpected however, since it has been observed previously in similar systems [26]. It was hoped that at elevated temperatures or by addition of an oxidant that the reaction could be observed. The phenylethyl and phenylpropyl derivatives, [CpFe($CH_2CH_2C_6H_5$)($CO)_2$] and [CpFe($CH_2CH_2CH_2C_6H_5$)($CO)_2$] did however, react readily to give $PPh_3$-substituted acyl products and gave rate constants in the expected range.

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# CHAPTER 6

# SYNTHESIS, STRUCTURE AND REACTIVITY OF SOME DIMANGANESE NONACARBONYL CYCLIC CARBENE COMPLEXES

## 6.1 INTRODUCTION

### 6.1.1 Perspective

An isomer of the 1,4-butanediyl complex, $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$, discussed in Chapter 2 is a dimanganese cyclic carbene complex containing the 2-oxacyclopentylidene ligand *viz.* $[Mn_2(CO)_9(=\overline{CCH_2CH_2CH_2O})]$. Transition metal carbene complexes are those which contain a derivative of divalent carbon, $CR_2$, bonded to a transition metal where the metal to carbene carbon bond may approach a double bond, as shown in Fig. 1.

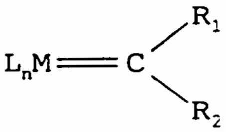
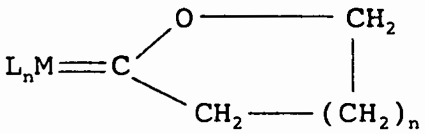


Fig. 1

Such species are important in metal-catalyzed reactions such as polymerization of alkenes [1], alkene cyclopropanation [2], the Fischer-Tropsch synthesis [3] and olefin metathesis [4], as well as in reactions leading to carbon-carbon bond formation in organic synthesis [5]. One of the most important properties of transition metals is their ability to stabilize short-lived species as ligands in co-ordination compounds. Classical sources of carbenes (*viz.*:$CR_1R_2$) are diazo compounds and ketenes [6-8] which readily undergo thermal, photolytic or metal-induced cleavage. Traditionally, free carbenes are only to be expected in gas phase reactions, for example by thermolysis or photolysis of ketenes, although Arduengo *et al.* [9a] have recently laid claim to the first isolation of a free carbene under ambient conditions. Their claim was however, disputed [9b] and Bertrand and co-workers claimed to have published the first report concerning the synthesis and isolation of the first free "bottle-able" carbene [9c]. Thus, carbene complexes contain metal-stabilized carbenes and extensive interest has been generated in the properties and reactivity of this prominent class of compounds.

Initially, carbene complexes attracted a great deal of attention as a potential source of free carbenes. However, there is now ample evidence against this premise, for example Casey's observation [10] that thermolysis of (2-oxacyclopentylidene)pentacarbonylchromium(0) gives mainly the dimer of 2-oxacyclopentylidene not cyclobutanone. Cyclobutanone was identified, in a separate experiment, as the product arising from the free 2-oxacyclopentylidene carbene species. In no instance has a compelling case for the intervention of a free carbene been made. This is not really suprising since a free carbene is a high energy species and should be reluctant to leave the coordination sphere of the metal. Thus, from a synthetic viewpoint, a metal carbene complex should be regarded as a functional group which can be synthesized and modified rather than as a source of free carbenes. In the area of organic synthesis, 2-oxacycloalkylidene ligands (Fig. 2) are attractive due to ease of ligand formation [11], modification [12] and subsequent removal of the metal [13].

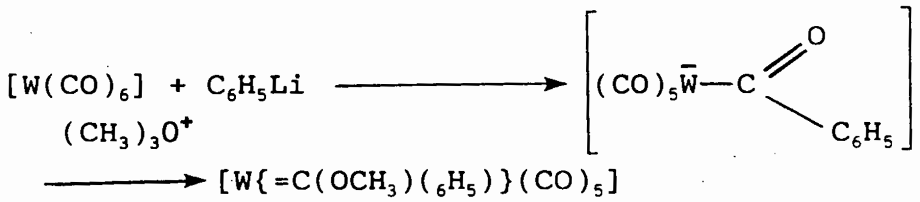


(n = 1 or 2)

Fig. 2

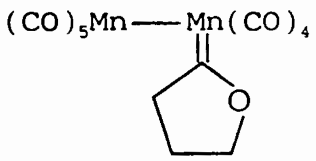
With respect to carbene modification, the isolobal analogy of alkoxycarbene complexes and esters has been a useful guide for the development of carbene reactions [14].

The first stable transition metal carbene complex was synthesized and characterized by Fischer and Maasböl in 1964 (equation 1) [15].



(1)

The first complex containing the 2-oxacyclopentylidene ligand, $[Mn_2(CO)_9(=\overline{CCH_2CH_2CH_2O})]$, 1, was reported in 1963 [16] but was not recognized as such until seven years later [17]. Since that time, intramolecular cyclization reactions have given rise to a host of transition metal cyclic carbene complexes.



1

Traditionally, transition metal carbene complexes have been divided into two classes: the Fischer-type [18] and the Schrock-type [19], named after their discoverers. Fischer-type compounds traditionally contain a metal from groups VI to VIII, in a low oxidation state, which is stabilized by a series of other ligands with pronounced acceptor properties *e.g.* carbon monoxide. The carbene ligand is electrophilic. Complexes of the Schrock type are characterized by an early transition metal and the carbene ligand is nucleophilic. Thus, traditionally, electrophilic reactivity at the carbene carbon atom has been attributed to late transition metal carbene complexes and nucleophilic reactivity, to the early transition metals. However, the complexes on which these comparisons have been based often differ greatly, either in the molecular charge or the substituents on the carbene carbon. There is now evidence which affirms that the nucleophilicity or electrophilicity of a carbene ligand is more dependent upon the groups on the carbene carbon and the ligands on the metal centre than upon the position of the metal in the periodic table [20]. Specifically, only complexes of the type $L_nM=C(R_1)(R_2)$ will be discussed by us.

## 6.1.2 SYNTHESIS

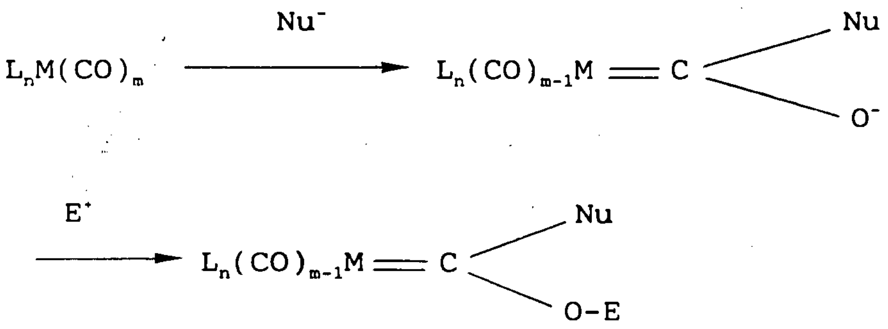
Since the synthesis of the first carbene complex by Fischer and Maasböl in 1964 [15], a large number of synthetic pathways to carbene complexes have been developed, resulting in the formation of hundreds of compounds involving nearly all the transition metals in the periodic table.

New carbene complexes may be obtained from non-carbene complex precursors as well as by modification of pre-existing carbene complexes. The synthesis from non-carbene complex precursors can involve

(a) transformation of a non-carbene ligand into a carbene ligand (the carbene carbon atom is already attached to the metal in the precursor complex), or

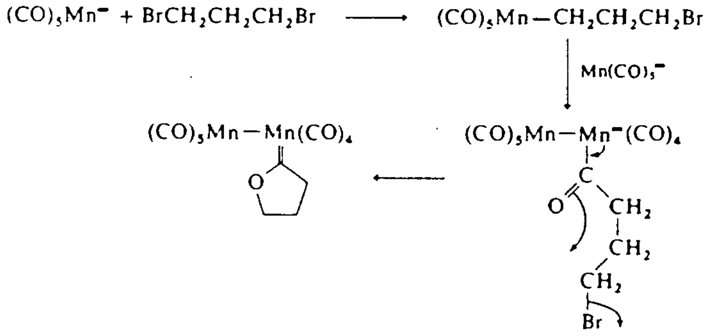
(b) addition of a carbene ligand precursor to a metal complex with concomitant transformation of the latter into a carbene complex. The carbene carbon atom is added to the metal in the course of the reaction.

Route (a) is the most widely used partly because of the commercial availability of the metal carbonyl starting materials. In this method, a carbonyl ligand is converted into an alkoxy- or aryloxycarbene ligand by successive addition of a nucleophile and an electrophile (Scheme 1). Organolithium reagents are used extensively as nucleophiles. The acyl metallates (Scheme 1) are alkylated with oxonium salts or fluoroalkanesulfonates.



Scheme 1

For example, $[Cr\{=C(OCH_3)Ph\}(CO)_5]$ has been prepared by this method [21]. An adaptation of this method (the conversion of a carbonyl ligand to a carbene ligand) is used to synthesize the dimanganese cyclic carbene complex, $[(CO)_5MnMn(CO)_4(=\overline{CCH_2CH_2CH_2O})]$, 1 [16,17]. This is formed from the reaction of $Na[Mn(CO)_5]$ with 1,3-dibromopropane *via* intramolecular alkylation of an intermediate acyl complex (Scheme 2). Several $[CpMo(CO)_2(L)(=\overline{CCH_2CH_2CH_2O})]$ complexes have been prepared by an extension of this latter procedure (Scheme 3) [22-25].

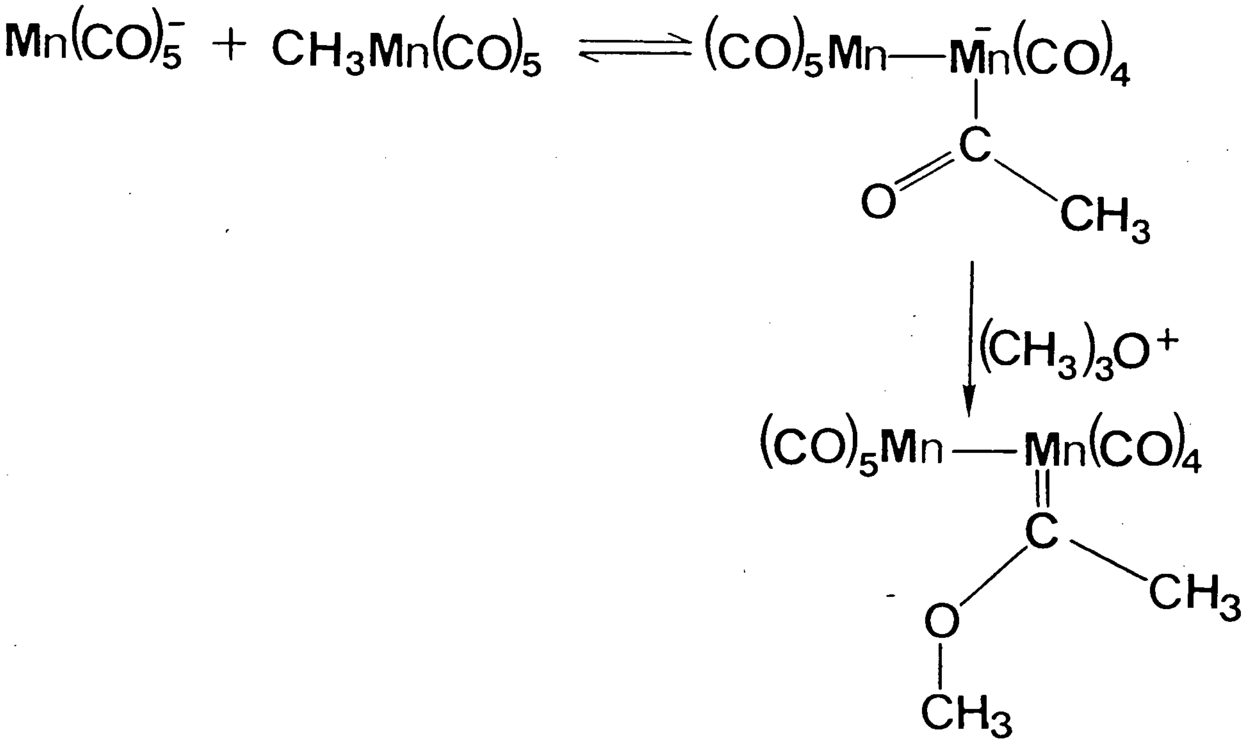


Scheme 2

$$Na[CpMo(CO)_3] + Br(CH_2)_3Br \longrightarrow [CpMo(CO)_3\{(CH_2)_3Br\}]$$
$$[CpMo(CO)_3\{(CH_2)_3Br\}] + L \longrightarrow [CpMo(CO)_2(L)(=\overline{CCH_2CH_2CH_2O})]$$

Scheme 3

Studies on the reaction of $[Mn(CH_3)(CO)_5]$ with $[Mn(CO)_5]^-$ indicate that these two species are in equilibrium with an anionic acyl species which, when alkylated at oxygen, gives a carbene complex (Scheme 4) [10].



Scheme 4

Nucleophilic attack on isocyanide or thiocarbonyl complexes gives carbene ligands with nitrogen or sulfur, respectively, as the heteroatom in the carbene ligand [26].

### 6.1.3 STRUCTURE

A prerequisite for understanding carbene complexes and their reactions, both stoichiometric and catalytic, is to understand the nature of the metal-carbene carbon bond in these complexes and how this bond is influenced by the remainder of the molecule.

Carbene complexes may be viewed as metallated carbenium ions (Fig. 3), *i.e.* a carbenium ion in which one of the substituents is a metal complex moiety, $ML_n$ [27]. The empty p orbital at the carbene carbon atom is perpendicular to the plane of the three σ-bonds of the carbene carbon ("carbene plane"). By π-interaction between the carbene carbon atom and its substituents, electron delocalization over the heteroatom can occur. In principle, only one π-donating substituent ($R_1$, $R_2$ or $L_nM$ in Fig. 3) is necessary to form stable compounds. However, most commonly two or all of the substituents bonded to the carbene carbon have π-donor properties and will compete with each other for π-bonding with the carbene carbon. Thus, the bond order between the carbene carbon and a particular substituent is determined not only by the π-donor ability of the substituent in question, but also by the π-donor abilities of the other carbene substituents.

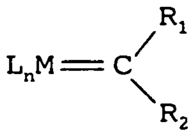
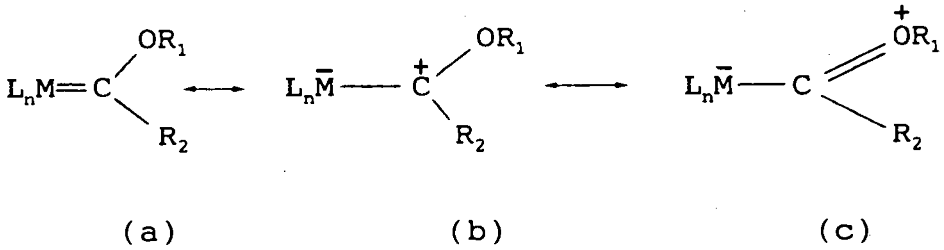


Fig. 3

There are three important resonance structures for Fischer-type carbene complexes (a-c) which are useful in understanding structure and reactivity.



### 6.1.3.1 INFRARED STUDIES

The ν(CO) bands of vibrational spectra can enable one to gain an understanding of the bonding in carbene complexes [28,29]. Carbonyl ligands donate electron density to vacant orbitals on the metal atom which leads to an increase of electron density on the metal. This is reduced somewhat by back-donation of charge density from the metal to the carbonyl group *via* a dπ-pπ back-bond. Thus, carbonyl ligands have both acceptor and donor properties. The σ-donor/π-acceptor ratio of the carbonyl ligand in a complex may be considered a probe of the electronic nature of the other ligands in the complex. For example, carbon monoxide as a ligand can be compared to methoxy(phenyl)-carbene in complexes of the type $[Cr(CO)_5(L)]$ (L = CO or $C(OCH_3)Ph$) by considering ν(CO) absorptions [30]. While the symmetric $A_1$ ν(CO) stretching frequency in $[Cr(CO)_6]$ appears at 2108 $cm^{-1}$ [31], the absorption of the CO group *trans* to the carbene ligand is shifted to 1953 $cm^{-1}$ ($A_1$) in $[Cr\{=C(OCH_3)(Ph)\}(CO)_5]$[32]. This implies that the carbene ligand is a better σ-donor and a weaker π-acceptor than CO[30].

### 6.1.3.2 NMR STUDIES

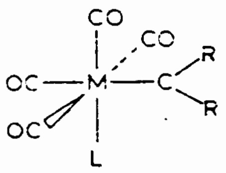
The most useful diagnostic tool for the presence of a carbene ligand is $^{13}C$ NMR spectroscopy. The position of the carbene carbon atom resonance varies greatly with the nature of the attached groups. NMR studies have indicated the partial double bond nature of the carbene carbon-heteroatom bond in the metal carbene complexes represented in resonance form (c) (page 274)[26]. For carbene ligands containing a heteroatom, the nature of the heteroatom is important; alkoxy groups resonate in the range 310 - 365 ppm while most amine groups resonate in the 250 - 290 ppm range [33]. This is probably due to the greater π-donor ability of $NR_2$ over OR. In either case however, the carbene carbon resonance is at very low field and can be used as a diagnostic indicator for carbene ligands.

### 6.1.3.3 MASS SPECTRAL STUDIES

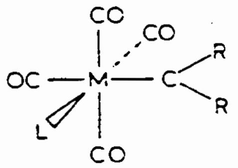
Electron impact mass spectra of many carbonyl carbene complexes $[M\{=C(X)Y\}(CO)_n]$ have, in most instances, indicated the presence of the molecular ion followed by a successive loss of carbonyl groups [34-36]. Further fragmentation will depend on the metal, the nature of X and Y and upon the other ligands. For example, the mass spectrum of $[Cr\{=C(OCH_3)(CH_3)\}(CO)_5]$ indicates that the carbene ligand is bound more tightly to the metal than are the carbonyl ligands [34].

### 6.1.3.4 X-RAY CRYSTAL STRUCTURES

Each crystal structure contains information about the electronic structure of a compound. This information may be obscured by the limitations of the method of structure determination and also by superimposed crystal packing effects [37]. However, by comparison of a number of structures of chemically related compounds, systematic trends for relevant structural parameters can be determined. Burgi and Dunitz [38] have shown that such systematic analyses of crystal data can be a powerful research technique for a variety of stereochemical and structural problems. In closely related complexes, bond lengths between the carbene carbon and its substituents should correlate with bond orders. Thus, a comparison of bond lengths should provide information about bonding. For example, in [Cr{=C($OCH_3$)(Ph)}$(CO)_5$], the methoxy group and the metal fragment act as π-donating substituents [39]. Thus the Cr-Cα (2.043 Å) and Cα-O (1.332Å) bond lengths are shorter than expected for single bond distances. The phenyl group is not involved in any π-bonding with the carbene carbon atom [40]. π-bonds between the carbene carbon and its substituents are only possible if the orbitals concerned have the correct symmetry and orientation to provide sufficient overlap. A prerequisite is the correct orientation of each π-interacting substituent relative to the carbene plane. On the other hand, the orientation of these substituents will provide information about their π-interaction with the carbene carbon atom. In alkoxycarbene complexes, the oxygen atom is $sp^2$-hybridized with a filled p orbital perpendicular to the C(carbene)-O-C(alkyl) plane. For π-interaction to occur between the filled orbital on oxygen and the vacant Cα p orbital, the alkoxy plane has to be coplanar with the carbene plane, *i.e.* the σ-bonds between the oxygen atom and its substituents must be located within the carbene plane [37]. If large torsion angles are observed instead, it can be concluded that there is no, or at least only a very weak, π-bond between the carbene carbon atom and the relevant substituent. The steric influence of the carbene substituents is also reflected in the bond angles at the carbene carbon atom. In octahedral alkoxycarbene complexes, the mean M-Cα-O bond angle is 118° [37]. This will, however, change where the alkoxycarbene ligand is cyclic. In *cis*-[M(L)$(CO)_4$(carbene)] complexes, in which L has different electronic properties to CO, the carbene plane should be eclipsed with the *cis* ligands. Depending on the σ- and π-bonding capacities of L relative to CO, L will be either within the carbene plane (A) or perpendicular to it (B).



(A)



(B)

In octahedral complexes, the best agreement between theoretical and real structures is found in *cis*-$[(CO)_5M-M(CO)_4(carbene)]$ complexes (M = Mn,Re) [41-45] which all adopt the less sterically demanding conformation B. In these complexes, the *cis* ligand ($M(CO)_5$) is electronically different to CO.

Table 6.1 gives selected bond lengths and angles of selected 2-oxyacyclopentylidene and related complexes upon which X-ray analyses have been performed [24,25,41,46-55].

Mention should be made of a recent molecular orbital study on a carbene complex containing the 2-oxyacyclopentylidene ligand, *viz.* $[CpFe(I)(CO)(=\overline{CCH_2CH_2CH_2O})]$ [55]. A simple molecular mechanics approach, MMI [56,57], was used to investigate steric factors and Fenske-Hall calculations [58] were used to probe electronic factors. The MMI approach permitted a fairly broad range of orientations for the carbene ring about the $Fe{=}C\alpha$ bond. The Fenske-Hall calculations were performed by generating the frontier molecular orbitals of the [CpFe(I)(CO)] fragment and then examining their compatibility with those of the $(=\overline{CCH_2CH_2CH_2O})$ ring. It was found that there were just two molecular orbitals on the $(=\overline{CCH_2CH_2CH_2O})$ fragment which were relevant to interfragment interaction. These were the LUMO and the HOMO, as represented in Fig. 4.

Fig. 4

**Table 6.1** Structural Data for Selected 2-oxacyclopentylidene and Related Carbene Complexes of the Type $ML_n$ (carbene)

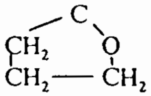
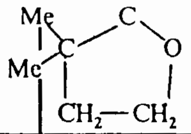
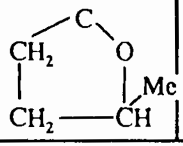
| $ML_n$ | Carbene Ligand | M-Cα (Å) | Cα-C (Å) | Cα-O (Å) | M-Cα-O (deg) | M-Cα-C (deg) | O-Cα-C (deg) | Conformation of Ring | Ref |
|---|---|---|---|---|---|---|---|---|---|
| $(CO)_5Mn-Mn(CO)_4$ (two molecules per unit cell) |  | 1.948<br>(1.952) | 1.498<br>(1.496) | 1.312<br>(1.309) | 122.4<br>(123.7) | 129.5<br>(127.1) | 107.5<br>(108.7) | Ring adopts envelope conformation | 41 |
| $CpMo(CO)_3-(\mu-PPh_2)(\mu-H)\{Pt(PCy)_3\}$ | " | 1.950 | 1.44 | 1.32 | 119 | 130 | 111 | Ring approaches planarity | 49 |
| CpFe(I)(CO) |  | 1.903 | 1.483 | 1.349 | 113.9 | 136.2 | 109.7 | Ring adopts envelope conformation; central $CH_2$ out of plane | 55 |
| $(CO)_5Mn-Mn(CO)_4$ |  | 1.95 | 1.504 | 1.299 | 123.3 | 128.6 | 107.9 | Ring approaches planarity | 41 |

Table 6.1 (.... continued)

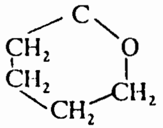
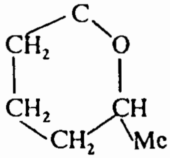
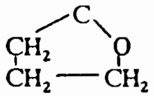
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $(CO)_5Mn-Mn(CO)_4$ |  | 1.971 | 1.396 | 1.384 | 118.5 | 125.3 | 116.1 | Ring fairly puckered; central $CH_2$ groups out of plane | 42 |
| $(CO)_5Mn-Mn(CO)_4$ |  | 1.982 | 1.493 | 1.299 | 118.5 | 126.4 | 115.0 | Ring adopts envelope conformation | 42 |
| $Mn(Cl)(CO)_4$ |  | 1.96 | 1.33<br>(Cα-0) | 1.31 | Not Given | Not Given | 110°<br>(0-Cα-0) | Not given | 50 |
| $CpMo(CO)_2(I)$ | " | 2.086 | 1.453 | 1.337 | 123.7 | 128.2 | 108.1 | Central $CH_2$ out of plane by 0.41Å | 24 |
| $\{(CpMo(CO)_3\}-W(CO)_2Cp$ | " | 1.977 | 1.46 | 1.32 | 124.1 | 126.0 | 109.9 | Central $CH_2$ out of plane by 0.41Å | 25 |
| $CpMo(CO)_2(I)$<br>(*trans*) | " | 2.040 | 1.530 | 1.325 | 123.8 | 129.8 | 106.1 | Ring adopts envelope conformation | 46 |

Table 6.1 (.... continued)

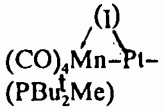
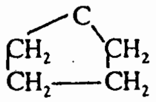
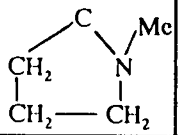
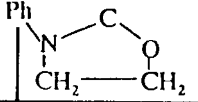
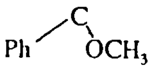
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| CpMo(CO)$_2$(I)<br>(*cis*) | " | 2.105 | 1.527 | 1.245 | 124.5 | 130.2 | 105.0 | Ring adopts envelope conformation | 46 |
| Pt(CH$_3$)(PPhMe$_2$) | " | 2.00 | 1.53 | 1.26 | 122.0 | 125.0 | 112.0 | Central CH$_2$ out of plane by 0.13Å | 47 |
|  $(CO)_4Mn{-}Pt{-}(PBu^t_2Me)$ | " | 1.885 | 1.46 | 1.32 | 123.0 | 127.8 | 109.2 | Ring approaches planarity | 48 |
| CpFe(I)(CO)<br>(two molecules per unit cell) | " | 1.867<br>(1.860) | 1.473<br>(1.458) | 1.311<br>(1.314) | 121.3<br>(122.7) | 129.3<br>(128.9) | 109.3<br>(108.4) | Ring approaches planarity (ring adopts slight envelope conformation) | 55 |
| [Pt(H)(PPh$_3$)$_2$]$^+$ | " | 2.012 | 1.301<br>(Cα-0) | 1.301 | 123.9 | Not given<br>(M-Cα-0) | 112.2<br>(0-Cα-0) | Ring approaches planarity | 51 |
| [W(Br)$_2$(OCH$_2$-t-Bu)$_2$]$^+$ |  | 1.890 | 1.505 | 1.561<br>(Cα-C) | Not Given | Not Given | Not Given | Ring is puckered; two central CH$_2$ fragments out of plane by 0.14Å and -0.44Å | 52 |

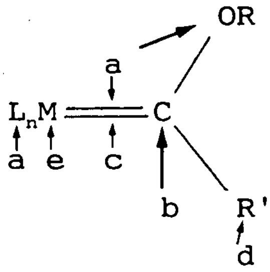
Table 6.1 (.... continued)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| [W(Br)(OCH$_2$-t--Bu)$_2$] | " | 1.896 | 1.514 | 1.518<br>(Cα–C) | Not Given | Not Given | Not Given | Ring is puckered; two central CH$_2$ fragments out of plane by 0.14Å and –0.44Å | 52 |
| *cis*–CpMo(I)(CO)$_2$ (two molecules per unit cell) |  | 2.141<br>(2.147) | 1.499<br>(1.524) | 1.280<br>(1.288)<br>(Cα–N) | 133.1<br>(131.4)<br>(M–Cα–N) | 121.0<br>(122.3) | 105.9<br>(106.2)<br>(N–Cα–C) | Ring adopts an envelope conformation; Central C out of plane | 53 |
| [Pt(Br)-(PPh$_3$)$_2$]$^+$ |  | 1.98 | 1.30<br>(Cα–N) | 1.33 | 115.0 | 133.0<br>(M–Cα–N) | 111.0<br>(0–Cα–N) | Ring is strictly planar | 54 |
| (CO)$_5$Mn–Mn(CO)$_4$ |  | 1.950 | 1.483 | 1.315 | 119.4 | 125.0 | 115.5 | – | 43 |

The HOMO is the carbene lone pair which interacts with the symmetric LUMO of the [CpFe(I)(CO)] fragment. This is the typical carbene-metal donor interaction. The LUMO of the carbene ring allowed for back-bonding from the metal to the carbene ligand. It was concluded from the Fenske-Hall calculations that electronic effects were important in determining the stable conformations of the carbene ring [55].

## 6.1.4 REACTIVITY

Transition metal carbene complexes are becoming increasingly important as starting materials for the synthesis of organic compounds or as precursors for new organometallic species. Fischer-type alkoxycarbene complexes may, in principle, react in several different ways, as indicated in Scheme 5.



Scheme 5 a = substitution; b = nucleophilic addition; c = insertion of a molecule; d = reaction at the carbene side chain; e = oxidation or reduction of the metal.

A consequence of the electrophilic nature of the carbene carbon atom in Fischer-type alkoxy(alkyl) carbene complexes is that the protons on the carbon atom adjacent to the carbene carbon tend to be fairly acidic. Kreiter [59] first demonstrated, by $^1$H NMR spectroscopic studies, the acidity of these hydrogen atoms. In $CH_3OD$ solution, in the presence of catalytic amounts of sodium methoxide, methoxy(methyl)carbene chromiumpentacarbonyl exchanges all the hydrogen atoms of the methyl group bonded to the carbene carbon atom (equation 2).

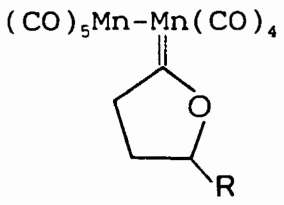
$$[Cr\{=C(OCH_3)(CH_3)\}(CO)_5] + 3CH_3OD \xrightarrow{CH_3ONa} [Cr\{=C(OCH_3)(CD_3)\}(CO)_5] + 3CH_3OH \quad (2)$$

Deuterium exchange processes in alkoxycarbene complexes are now fairly well known [12,17,30,59-62]. The acidity of these hydrogen atoms also facilitates anion formation at the carbon atom adjacent to the carbene carbon atom [12,60,63,64].

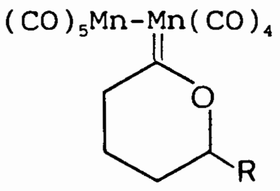
## 6.2 SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF THE TYPE *eq*-$[(CO)_5MnMn(CO)_4(L)]$ WHERE L IS A CYCLIC CARBENE LIGAND WITH A FIVE- OR SIX-MEMBERED RING

### 6.2.1 SYNTHESIS

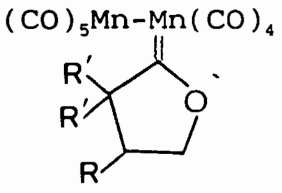
We have prepared six nonacarbonyldimanganese complexes containing 2-oxyacycloalkylidene ligands (**1**-**6**).



1, R = H
2, R = $CH_3$



**3**, R = H
**4**, R = $CH_3$



**5**, R = $CH_3$; R′ = H
**6**, R = H; R′ = $CH_3$

In all cases the cyclic carbene ligand occupied an equatorial position. Although there have been many reports of cyclic carbene complexes with five-membered rings [see, for example, 17,22-26,46-55,59,61-63,66-75], there are relatively few known with six-membered rings [23,53,62,73,77]. We have recently reported the first structural analysis of this type of compound [42]. We carried out our study to determine what effect changes in the carbene ring size would have on the properties, both physical and chemical, of these complexes. Compounds **1-3** have been synthesized previously [16], although the structures assigned to them (an unusual ring structure containing a manganese-hydrogen bond) were incorrect [16]. It was 7 years later that Casey [17] correctly assigned a cyclic carbene structure to 1. The structures of these compounds have not, as far as we know, been discussed further. We report improved yields and crystal structures of **1-4** which prove conclusively that these compounds are indeed cyclic carbene complexes [41,42].

Compounds **1-4** were synthesized by known procedures involving the reaction of THF solutions of $Na[Mn(CO)_5]$ with the appropriate dibromoalkanes [16], as shown in equation 3 (for **4**).

$$Na[Mn(CO)_5] + BrCH_2CH_2CH_2CH(CH_3)Br \xrightarrow[Na[Mn(CO)_5]]{THF}$$

$$[Mn\{CH_2CH_2CH_2CH(CH_3)Br\}(CO)_5] \longrightarrow$$

$$\mathit{eq}\text{–}[(CO)_5MnMn(CO)_4\{=\overline{CCH_2CH_2CH_2CH(CH_3)O}\}] \qquad (3)$$

**4**

Compound **5** was similarly prepared by the reaction of a THF solution of $Na[Mn(CO)_5]$ with 1-bromo-3-chloro-2-methylpropane. Compound **6** was prepared by exchange of the two acidic hydrogens on the carbene ring of **1** for two methyl groups (equation 4).

$$eq\text{-}[(CO)_5MnMn(CO)_4(=\overline{CCH_2CH_2CH_2O})] \xrightarrow[\text{ii) } CH_3I]{\text{i) } Na/Hg/THF}$$

$$eq\text{-}[(CO)_5MnMn(CO)_4\{=\overline{CC(CH_3)_2CH_2CH_2O}\}] \qquad (4)$$

It is interesting to note that the methyl group of the substituted dibromoalkane directs the attack of the first $[Mn(CO)_5]^-$ moiety, *i.e.* the regioselectivity observed in the alkylation reaction probably reflects the different reactivity of the two halide functions (primary versus secondary). **1-6** were all obtained in moderate yield as yellow-orange crystalline solids. They are stable in air for several days, except for **4**, which was mildly air- and light-sensitive. They are generally stable in solution under nitrogen at room temperature, but decompose to unidentified products when exposed to air and to $[Mn_2(CO)_{10}]$ and an unidentified organic compound when heated. They were all soluble in most organic solvents, including hexane. Yields, microanalysis, IR and melting points are given in Table 6.2. Details of the synthetic procedures are given in Chapter 7.

## 6.2.2 CHARACTERIZATION

### IR

The IR spectra in the $\nu(CO)$ region for **1-6** all show eight bands (the band at 1994cm$^{-1}$ for compound **6** is a combination of two unresolved bands) consistent with the compounds all being of the type $eq$-$[Mn_2(CO)_9(L)]$ rather than *ax*-

Table 6.2

Data for *eq*-[$(CO)_5MnMn(CO)_4(L)$]

| L | Yield (%) | mp (°C) | IR ν(CO) (cm$^{-1}$)$^a$ | Elemental Analysis C:found(calcd) | Elemental Analysis H:found(calcd) |
|---|---|---|---|---|---|
| $\overline{CCH_2CH_2CH_2O}$ | 40 | 68-69 | 2089(mw),2024(s),2008(mw)<br>1999(s),1987(s),1971(m)<br>1957(m),1951(m) | 36.15(36.14) | 1.6(1.40) |
| $\overline{CCH_2CH_2CH(CH_3)O}$ | 35 | 72-73 | 2089(mw),2023(s),2007(mw)<br>1999(s),1987(s),1970(m)<br>1956(m),1950(m) | 37.90(37.69) | 1.9(1.81) |
| $\overline{CCH_2CH_2CH_2CH_2O}$ | 23 | 98-101 | 2088(mw),2022(s),2009(m)<br>1996(s),1985(s),1969(m)<br>1954(mw),1948(m) | 37.60(37.69) | 1.8(1.81) |
| $\overline{CCH_2CH_2CH_2CH(CH_3)O}$ | 23 | 56-58 | 2087(mw),2021(s),2006(m)<br>1996(s),1985(s),1968(m)<br>1953(mw),1947(m) | 39.14(39.16) | 2.25(2.19) |
| $\overline{CCH_2CH(CH_3)CH_2O}$ | 27 | 79-80 | 2089(w),2024(s),2008(m)<br>1998(s),1987(s),1971(m)<br>1957(w),1950(w) | 37.80(37.69) | 1.9(1.81) |
| $\overline{CC(CH_3)_2CH_2CH_2O}$ | 20 | 80-82 | 2089(m),2020(s),2014(m)<br>1994(s,br),1971(m)<br>1955(m),1945(m) | 39.20(39.16) | 2.1(2.19) |

a:in hexane, mw = medium/weak, s = strong, m = medium, w = weak, br = broad

[$Mn_2(CO)_9(L)$]; *ax*-[$Mn_2(CO)_9(L)$] species have $C_{4v}$ symmetry and should give rise to five IR active carbonyl stretching modes [78]. However, *eq*-[$Mn_2(CO)_9(L)$] has a lower overall symmetry and as many as nine $\nu$(CO) bands have been resolved for these species [79].

### $^1$H and $^{13}$C NMR

Assignments of the $^1$H and $^{13}$NMR spectra were made by using COSY and HETCOR experiments, as well as by comparison of all the NMR data for **1-6** with the literature values for related molybdenum [24,25], iron [55], ruthenium and osmium [62] 2-oxacyclopentylidene complexes. As an example of the results obtained, the $^1$H, $^{13}$C, $^{13}$C ($^1$H coupled), COSY and HETCOR spectra of **2** are shown in Figures 6-10.

### $^1$H NMR

The $^1$H NMR data for **1-6** are shown in Table 6.3. In compound **1**, the protons of the carbene ring give rise to an apparently first order pattern of two triplets and a quintet. The latter, found at $\delta$ = 1.97ppm, is readily assigned to the protons attached to C4, coupled to the two methylene groups at C3 and C5. The triplet at $\delta$ = 4.87ppm was assigned to the protons attached to C3 since it is adjacent to the electronegative oxygen atom. The peak at $\delta$ = 3.68ppm can then be assigned to the protons attached to C5. These assignments agree with those of Casey [17]. The $^1$H NMR spectrum of **2**, the methyl-substituted 2-oxacyclopentylidene compound, was more complex (Figure 6). It contains, in addition to the methyl doublet at $\delta$ = 1.54ppm, multiplets at $\delta$ = 1.49, 2.10, 3.40, 3.95 and 5.16ppm. The sextet at $\delta$ = 5.16ppm was assigned to the single proton attached to C3 (Ha in Figure 5).
The presence of the methyl group and the rigidity of the carbene ring cause the protons of each of the two methylene groups, C4 and C5,to be inequivalent, giving rise to four

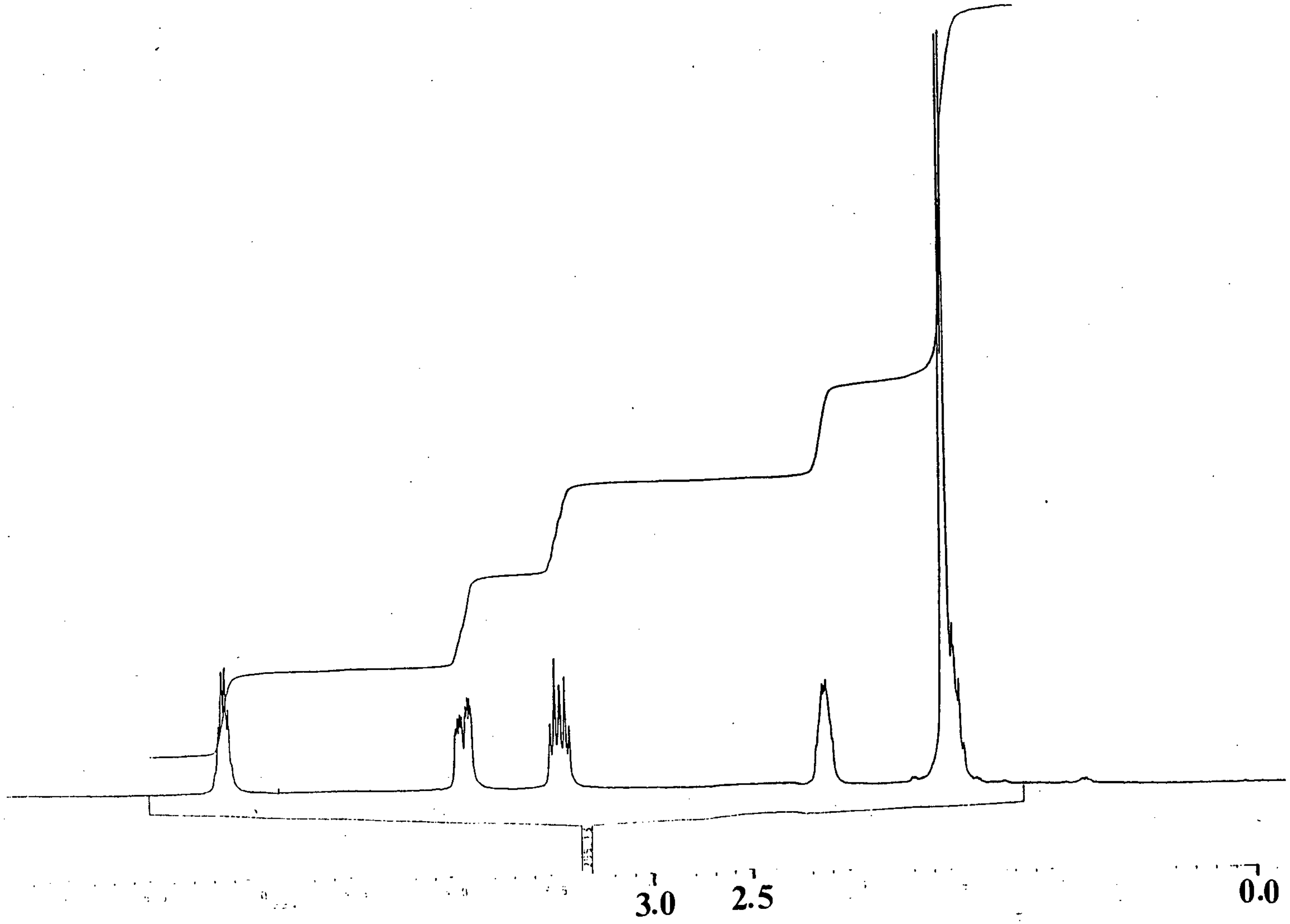


Fig. 6 $^{1}$H NMR Spectrum of *eq*-[$Mn_2(CO)_9\{=\overline{CCH_2CH_2CH(CH_3)O}\}$]

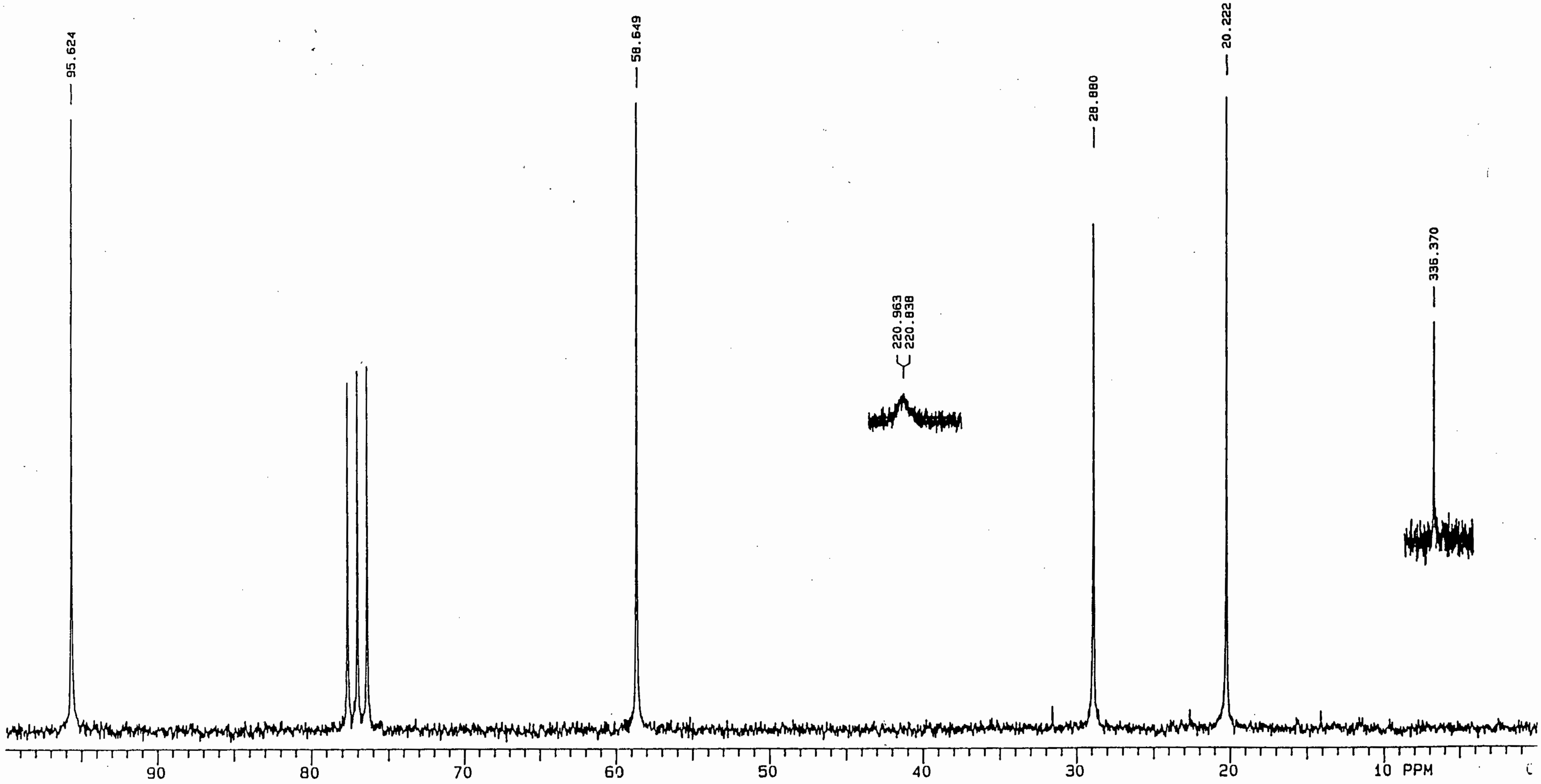


Fig. 7 $^{13}$C NMR Spectrum of *eq*-$[\mathrm{Mn_2(CO)_9}\{=\overline{\mathrm{CCH_2CH_2CH(CH_3)O}}\}]$

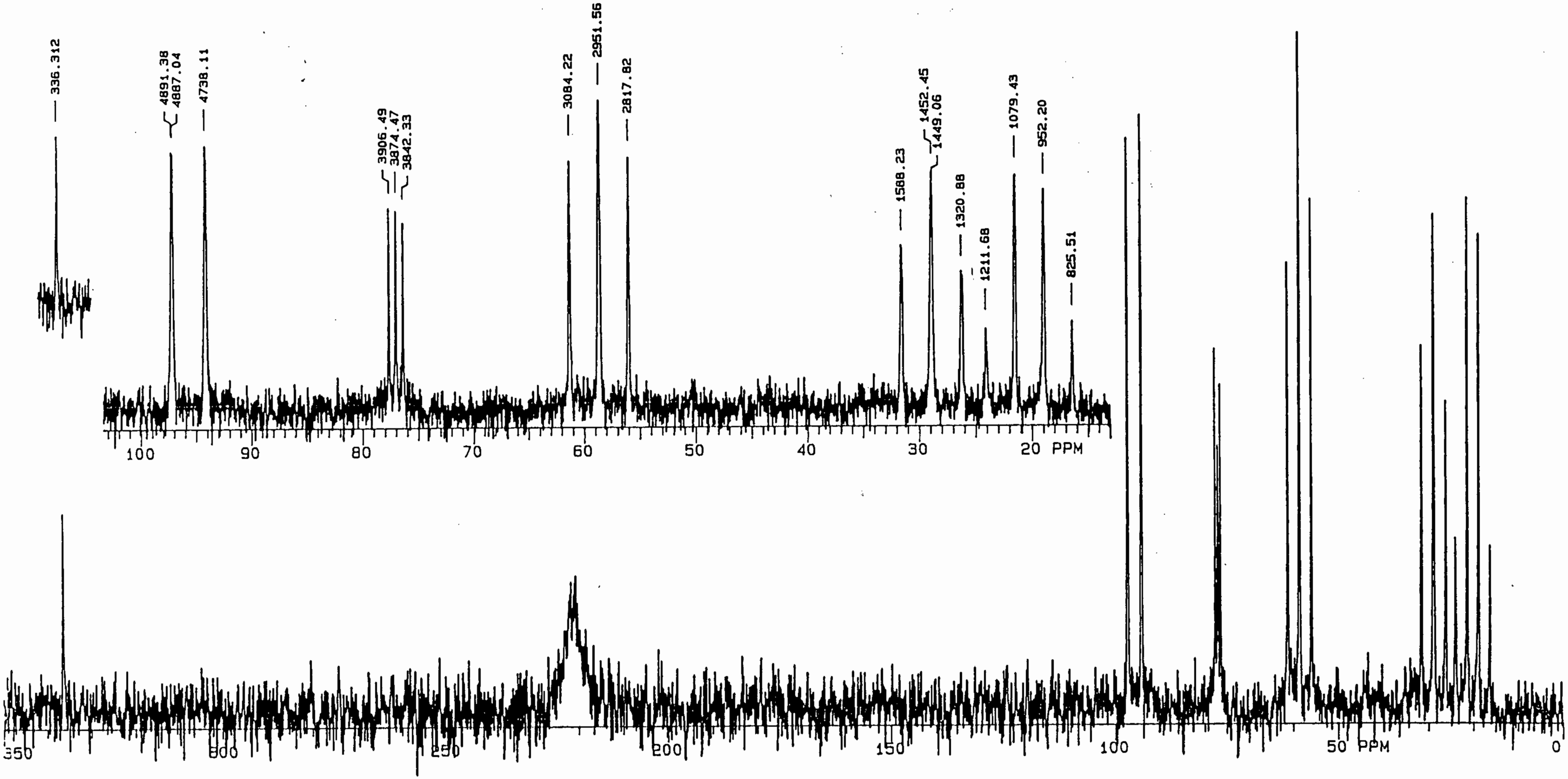


Fig. 8 $^{13}$C ($^{1}$H coupled) NMR Spectrum of *eq*-$[\mathrm{Mn_2(CO)_9\{=\overline{CCH_2CH_2CH(CH_3)O}\}}]$

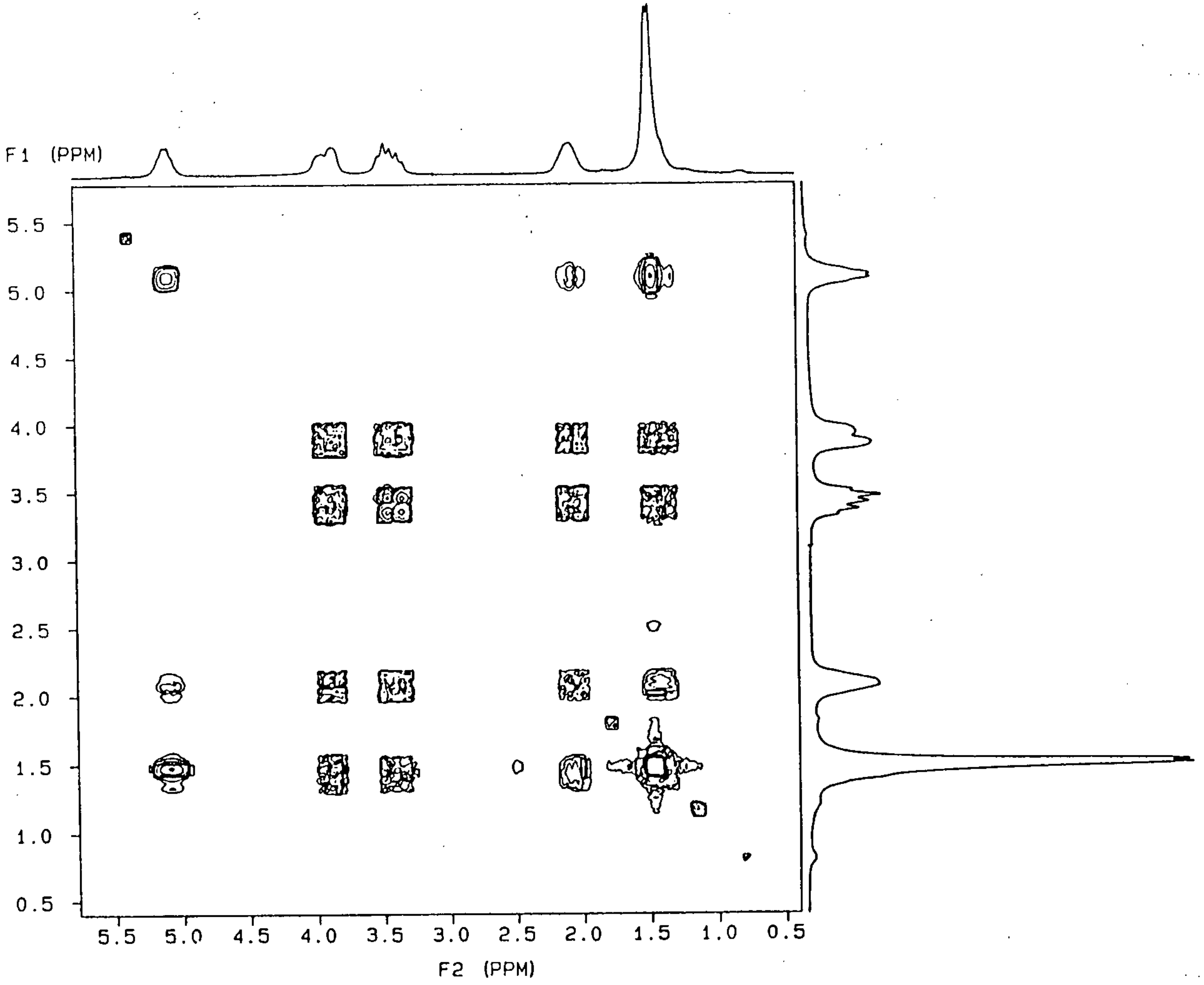


Fig. 9 COSY OF *eq*-$[Mn_2(CO)_9\{=\overline{CCH_2CH_2CH(CH_3)O}\}]$

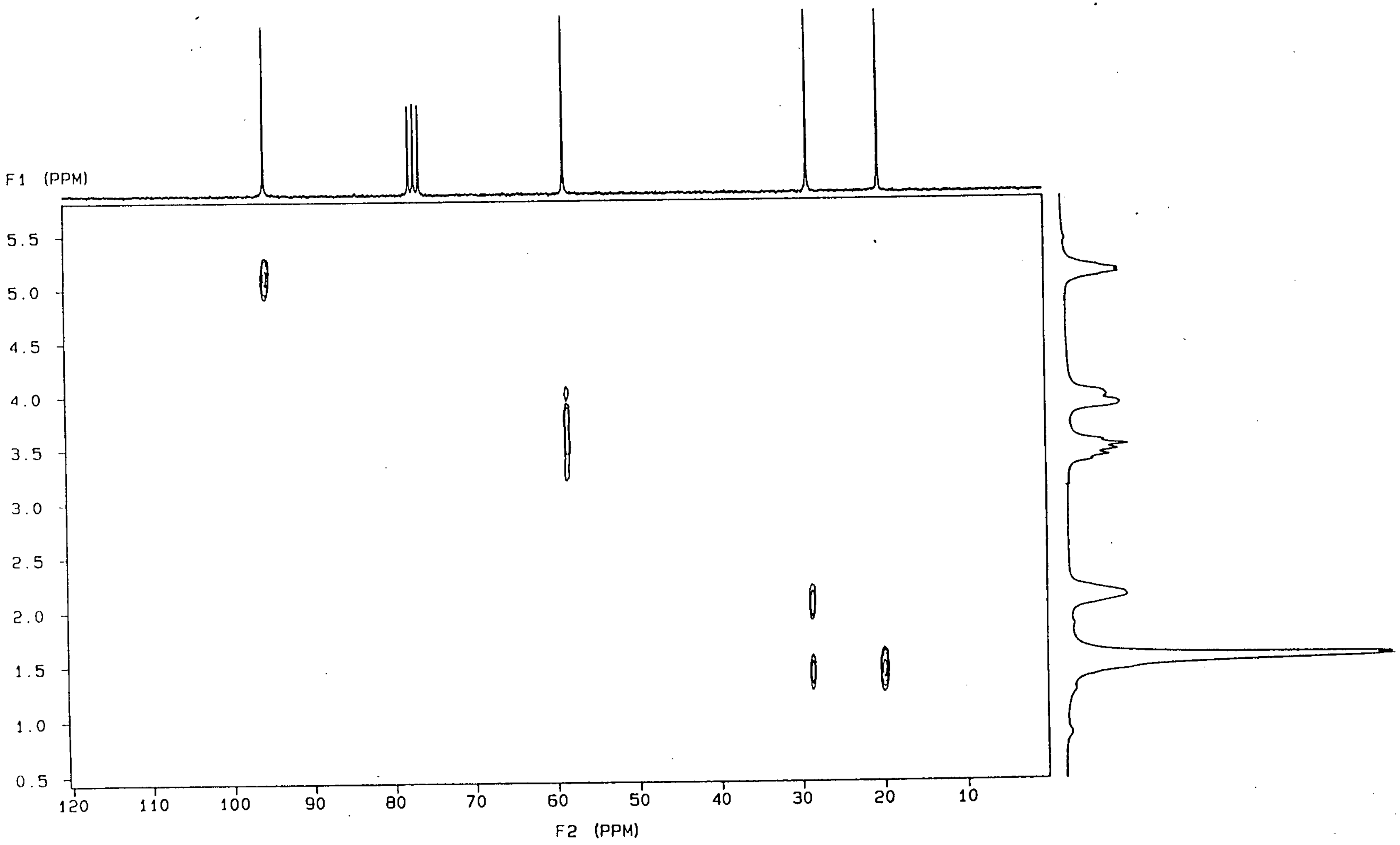


**Fig. 10** HETCOR of *eq*-[$Mn_2(CO)_9\{=\overline{CCH_2CH_2CH(CH_3)O}\}$]

Table 6.3

$^{1}$H and $^{13}$C NMR Parameters for Compounds 1-6$^{a,b,c}$

| cmpd | nucleus | C1 | C3 | C4 | C5 | C6 | Me |
|---|---|---|---|---|---|---|---|
| 1 | $^{1}$H | - | 4.87t | 1.97qu | 3.68t | - | - |
| | $^{13}$C | 338.1 | 85.1 | 21.6 | 55.1 | - | - |
| 2 | $^{1}$H$^{d}$ | - | 5.16se | 1.49,<br>2.10 | 3.40,<br>3.95 | - | 1.54d |
| | $^{13}$C | 336.1 | 95.6 | 28.9 | 58.7 | - | 20.2 |
| 3 | $^{1}$H | - | 4.61t | 1.80m | 1.80m | 3.51tr | - |
| | $^{13}$C | 351.3 | 76.4 | 17.1 | 21.8 | 51.2 | - |
| 4$^{e}$ | $^{1}$H | - | 3.43dt | 1.02m | 2.54m | 3.60m | 0.91m |
| | $^{13}$C | 349.9 | 83.7 | 27.9 | 19.8 | 50.9 | 16.3 |
| 5 | $^{1}$H | - | 4.70dt | 2.46m | 3.57qd | - | 1.07d |
| | $^{13}$C | 339.6 | 90.6 | 30.0 | 65.9 | - | 17.6 |
| 6 | $^{1}$H | - | 4.78t | 1.80m | - | - | 1.38s<br>1.41s |
| | $^{13}$C | 349.0 | 81.7 | 36.7 | 66.5 | - | 25.1,<br>25.3 |

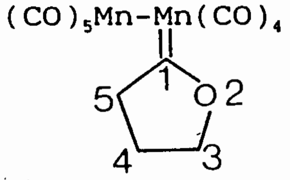
a: in $CDCl_3$, relative to TMS ($\delta$ = 0.00 ppm), s = singlet, d = doublet, t = triplet, qu = quintet, se = sextet, m = multiplet, dt = doublet of triplets, qd = quartet of doublets

b: see Fig. 5 for atomic numbering

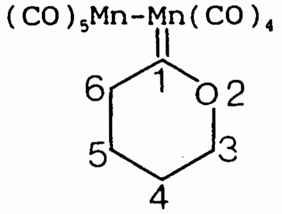
c: broad, weak peaks were observed in the region 217-220ppm due to the CO groups

d: recorded on a Bruker AM 400MHz spectrometer

e: in $C_6D_6$



or



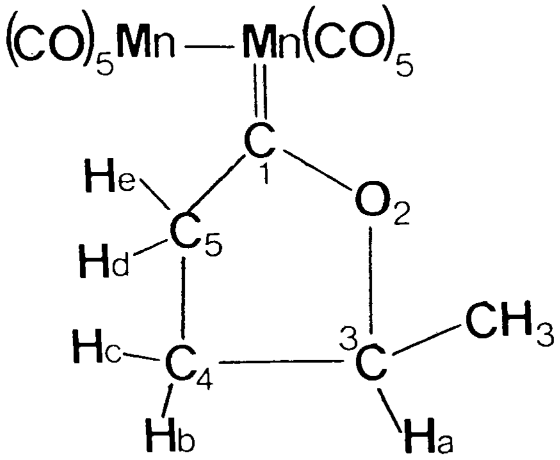


Fig. 5

sets of multiplets in a complex pattern. A quartet of doublets centred at δ = 3.95 ppm is observed

for one of the protons attached to C5 (He), while the other proton attached to C5 (Hd) resonates as a doublet of triplets centred at δ = 3.40 ppm. Here, the vicinal and geminal coupling constants have similar values. A complex, unresolvable multiplet centred at δ = 2.10 ppm is observed for one of the protons attached to C4 (Hc), while the other proton (Hb) resonates at 1.49ppm, again as a complex signal. COSY and HETCOR spectra (Figures 9 and 10) helped confirm these assignments in that the COSY enabled us to judge conclusively which protons were engaging in first order coupling to each other and the HETCOR enabled us to determine which protons were attached to which carbon atom (the $^{13}$C NMR spectrum was relatively easy to assign). The $^{1}$H NMR spectrum of compound **3** was relatively simple and assignments were in agreement with those reported for [CpRu(PPh$_3$)$_2$(=$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}}$)] [62]. The assignment of the $^{1}$H NMR spectrum of **4** was made by comparison with those of **2** and **3**; a COSY spectrum also proved useful. The $^{1}$H NMR spectrum of **5** also showed many peaks. The peaks at δ = 1.07 and 2.46ppm were readily assignable to the methyl protons and the lone proton attached to C4, respectively. A quartet of doublets centred at δ = 3.57 ppm was observed for the protons attached to C5. These protons are inequivalent and couple to each other and then to the lone proton on the adjacent carbon atom, *i.e.* an ABX spin system that appears as a quartet of doublets. Similarly, a doublet of triplets centred at δ = 4.70 ppm was observed for the protons attached to C3; here, the vicinal and geminal coupling constants again have similar values. The $^1$H NMR spectrum of 6 was relatively simple and assignments were in agreement with those reported for the related compounds $[\mathrm{CpFe(CO)_2\{=\overline{CC(CH_3)_2CH_2CH_2O}\}}]$ [55] and $[\mathrm{CpRu(PPh_3)_2\text{-}\{=\overline{CC(CH_3)_2CH_2CH_2O}\}}]$ [62].

## $^{13}$C NMR

$^{13}$C NMR data for compounds 1-6 are given in Table 6.3. The characteristic carbene carbon resonance (ranging from δ = 336.1 ppm in 2 to δ = 351.3 ppm in 3) was observed in all cases. The chemical shift for the carbene carbon atom in the six-membered carbene rings was observed to be *ca.* 10ppm higher than in the five-membered rings (except for 6). The chemical shift of C3 (adjacent to the ring oxygen atom) was observed to be lower in the six-membered rings than in the five-membered rings (again, 6 was the exception). The central methylene groups in all the rings resonated at positions typical for methylene groups. The methyl group resonances were also observed at expected positions.

## MASS SPECTRA

The mass spectra of 1-6 are reported in Table 6.4. They are all similar and all show weak parent molecular ions with the predominant fragmentation pathway being sequential loss of CO. This is indicative of the carbene ligand being bonded to the manganese atom more strongly than the other ligands, including the second manganese atom (under mass

**Table 6.4**
**Mass Spectral Data for 1-6**

| Suggested Assignment | Relative Peak Intensity[a] Compound 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $[M]^+$ | 15 | 19 | 6 | 7 | 13 | 8 |
| $[M\text{-}4CO]^+$ | 10 | 12 | 3 | 4 | 9 | 10 |
| $[M\text{-}5CO]^+$ | 20 | 27 | 7 | 9 | 21 | 21 |
| $[M\text{-}6CO]^+$ | 32 | 26 | 4 | 8 | 21 | 30 |
| $[M\text{-}7CO]^+$ | 30 | 32 | 23 | 44 | 31 | 53 |
| $[M\text{-}8CO]^+$ | 29 | 39 | 35 | 46 | 36 | 46 |
| $[M\text{-}9CO]^+$ | 40 | 41 | 36 | 52 | 42 | 48 |
| $[M\text{-}8CO\text{-}Mn]^+$ | 24 | 32 | 20 | 33 | 32 | 46 |
| $[M\text{-}9CO\text{-}Mn]^+$ | 56 | 77 | 42 | 59 | 70 | 100 |
| $[M\text{-}9CO\text{-}2Mn]^+$ | 12 | 3 | 2 | 8 | 12 | 9 |
| $[M\text{-}9CO\text{-}Mn(C_3H_6)^+$ | 12 | 15 | 10 | 15 | 8 | 9 |
| $[Mn(CO)_5]^+$ | 2 | 32 | 21 | 4 | 28 | 2 |
| $[Mn(CO)_4]^+$ | 2 | 32 | 20 | 3 | 32 | 3 |
| $[Mn]^+$ | 100 | 100 | 100 | 100 | 100 | 100 |
| $[C_3H_6]^+$ | 3 | 3 | 1 | 20 | 0 | 5 |
| $[CO]^+$ or $[C_2H_4]^+$ | 100 | 100 | 100 | 100 | 19 | 100 |

a:measured as a % of the base peak

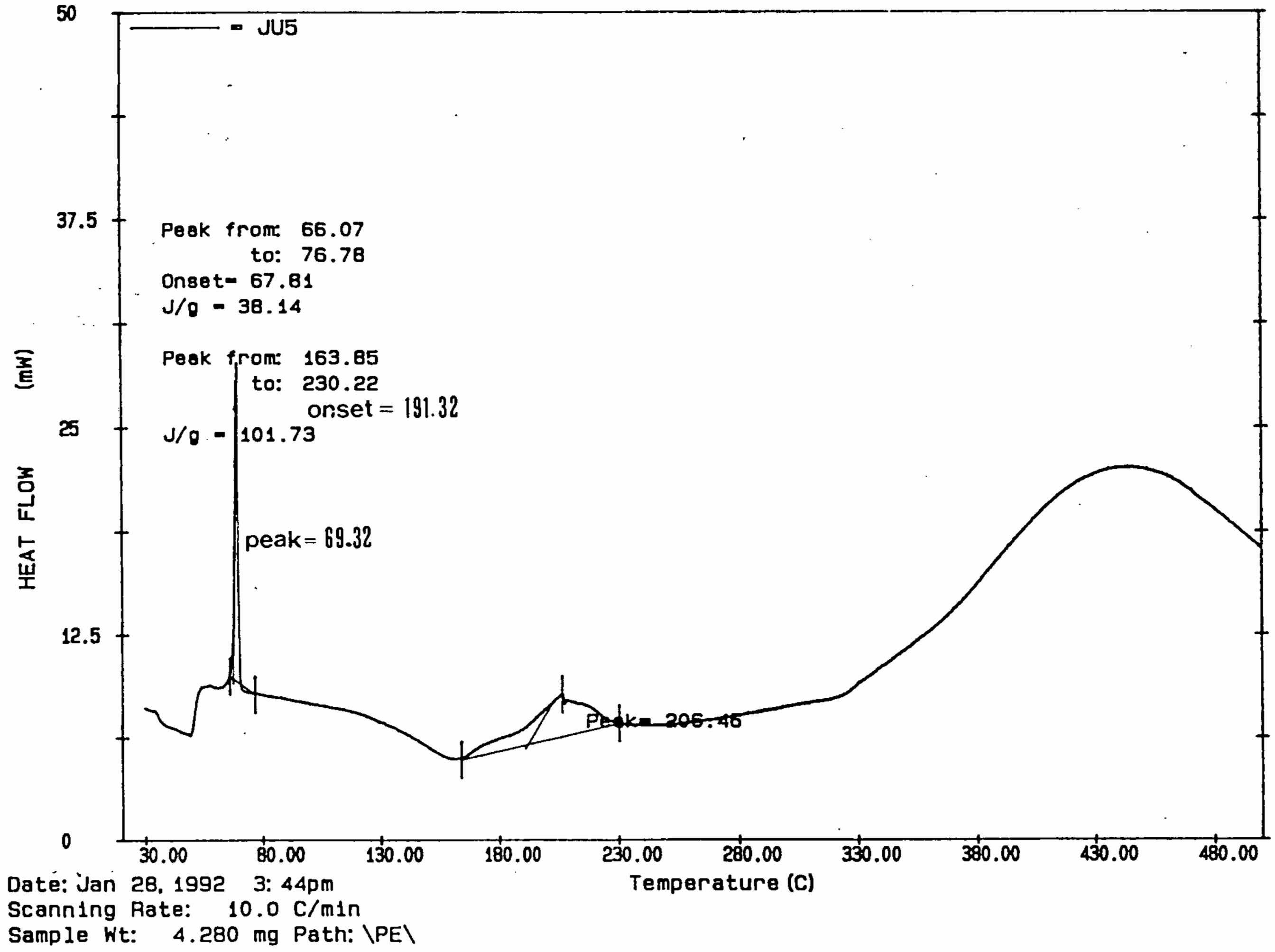
spectral conditions). Indeed, the most intense peak (besides the base peaks) in the mass spectra of **1-6** is due to the $[Mn{=}carbene]^+$ species. The conclusion that the carbene ligand is bonded to the metal more firmly than the other ligands is in agreement with conclusions reached by other workers in this field [26,80].

## THERMAL ANALYSIS

DSC traces and TGAs of **1-6** were obtained in order to probe their thermal stabilities.

### Differential Scanning Calorimetry

The DSC traces for **1-6** were all recorded over the range 30-480°C. The DSC trace of 1 is shown in Fig. 11. All traces showed a sharp endothermic peak in temperature ranges which correspond to their melting ranges measured by conventional means (Kofler hot stage microscope).



Date: Jan 28, 1992 3: 44pm
Scanning Rate: 10.0 C/min
Sample Wt: 4.280 mg Path: \PE\

Fig. 11 DSC Trace of 1, *eq*-[(CO)$_5$MnMn(CO)$_4$(=$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$)]

Table 6.5 lists the onset temperatures, Ti, and Tmax, obtained from thermograms of each sample compound and ΔHendo, the enthalpies of melting. Another weak, endothermic peak was observed for **1-6** at *ca.* 200°C, which probably corresponds to decomposition of the samples as was observed in the TGAs. Compounds **3**, **4** and **6** also gave rise to sharp endothermic peaks at *ca.* 450°C.

**Table 6.5**

**Melting Ranges and DSC Results for Compounds 1-6**

| Compound | Melting Range (°C)[a] | Ti (°C)[b] | Tmax (°C)[c] | ΔHendo[d] (kJ.mol$^{-1}$) |
|---|---|---|---|---|
| 1 | 68 - 69 | 62 | 68 | 19.49 |
| 2 | 72 - 73 | 62 | 74 | 21.71 |
| 3 | 98 - 101 | 93 | 103 | 23.08 |
| 4 | 56 - 58 | 46 | 61 | 22.88 |
| 5 | 79 - 80 | 74 | 79 | 24.01 |
| 6 | 80 - 82 | 73 | 83 | 25.30 |

a:determined on a Kofler hot stage microscope
b:temperature corresponding to onset of peak
c:temperature corresponding to peak maximum
d:calculated by Perkin Elmer PC Series DS7 machine (in J.g$^{-1}$)

## Thermogravimetry

The TGA's of compounds **1-6** all show only one very sharp loss in mass over the temperature range 130-200°C which may correspond to elimination of [$Mn_2(CO)_{10}$]. This was not unexpected since **1-6** all decompose to [$Mn_2(CO)_{10}$] at high temperatures. No peak was observed for the loss of the carbene ligand;

Thus, compounds 1-6 all show similar thermal behaviour and relatively high thermal stability.

## 6.3 CRYSTAL STRUCTURES OF 1-4

Single crystals of **1**, **2**, **3** and **4** were obtained from slow crystallization of dilute hexane solutions at 0°C. A suitable single crystal of each compound was selected and subjected to an X-ray diffraction study. The structures of the five-membered ring compounds, 1 and **2**, will be discussed first. The structures were solved by direct methods. Least-squares anisotropic refinement of the non-hydrogen atom positions were straightforward with the exception of the atomic positions for the $(CH_2)_3O$ moiety in the carbene ring of molecule II in compound 1 which was disordered. For compound 1, there were two molecules per unit cell, differing only in their Mn-Mn and Mn-C(carbene) bond lengths. The refinement of the atomic positions of the carbene ring for molecule II of compound 1 was completed as follows: (i) the bond lengths in both models were constrained to have the same values as corresponding bond lengths in molecule 1; (ii) all hydrogen atoms were placed in fixed calculated positions; (iii) the site occupation factors were refined. The ratio of occupancy of the model containing C(A2), C(A3), C(A4) and O(A5) to that containing O(B2), C(B3), C(B4) and C(B5) is 0.754:(1-0.754). The positions of C(A2) and O(B2) are virtually superimposed, as is also the case for the positions of O(A5) and C(B5) *i.e.* unequal occupation of the set of positions by enantiomers. This disorder is thought to be of the type observed by Adams *et al.* [55] in similar cyclic carbene complexes. Further details of the data collection, structure solution and refinement are given in Table 6.6. Bond lengths are given in Table 6.7 and bond angles and torsion angles for the carbene rings are given in Table 6.8. Views of a molecule of **1** and a molecule of **2** are shown in Figures 12 and 13a and 13b respectively.

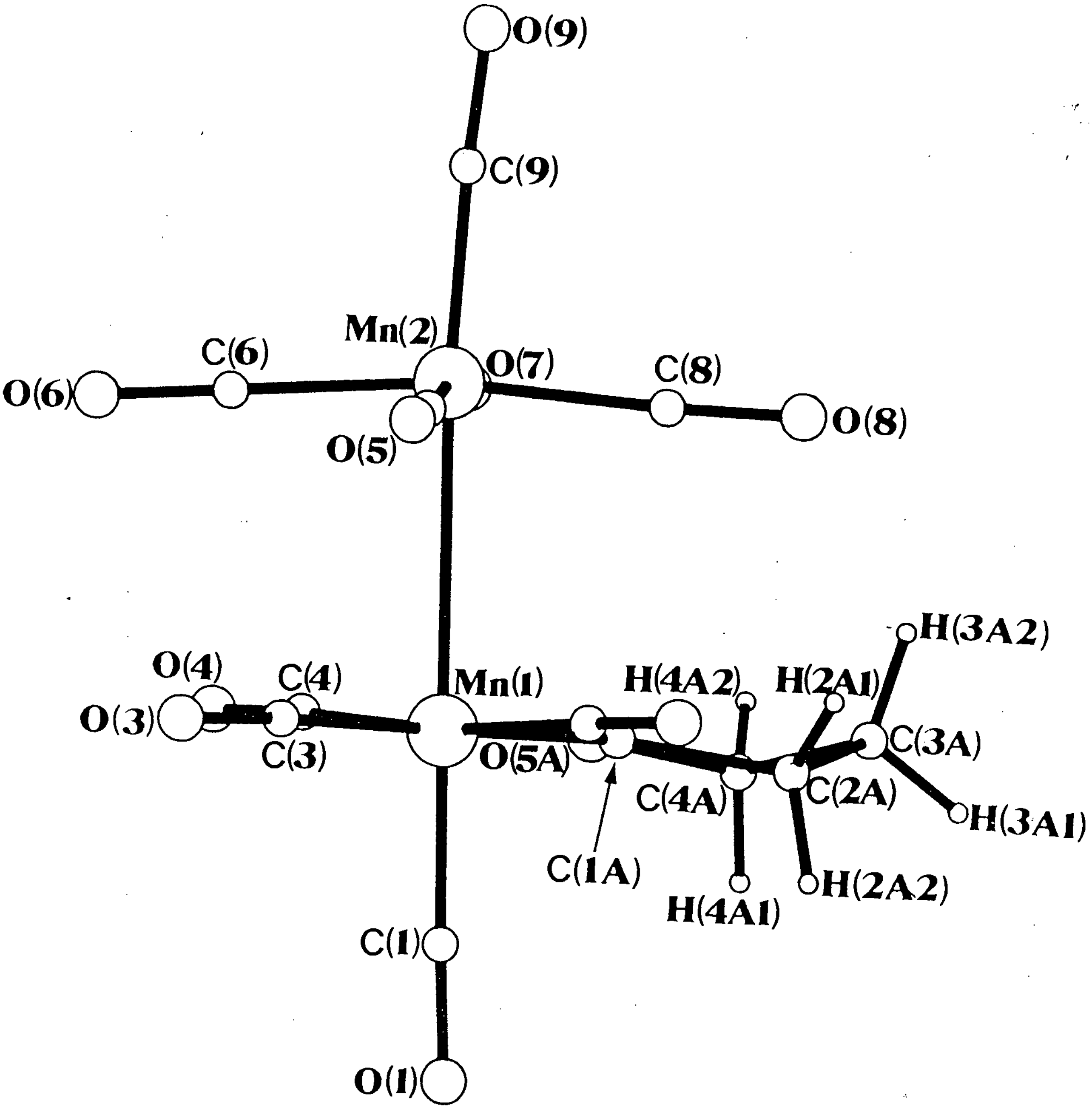


Fig. 12 View of the Structure of Compound 1 (Molecule 1)

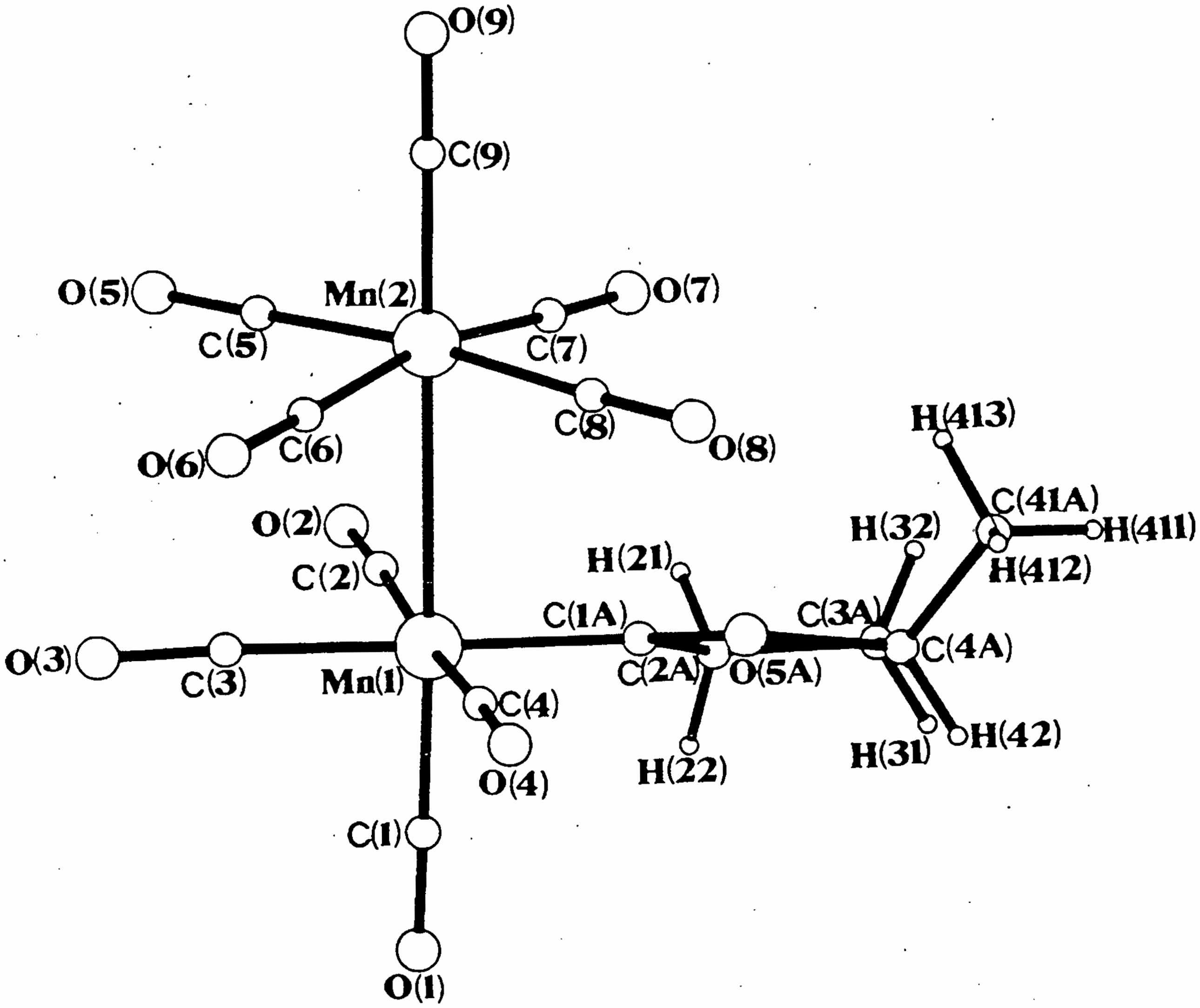


Fig. 13a View of the Structure of Compound 2

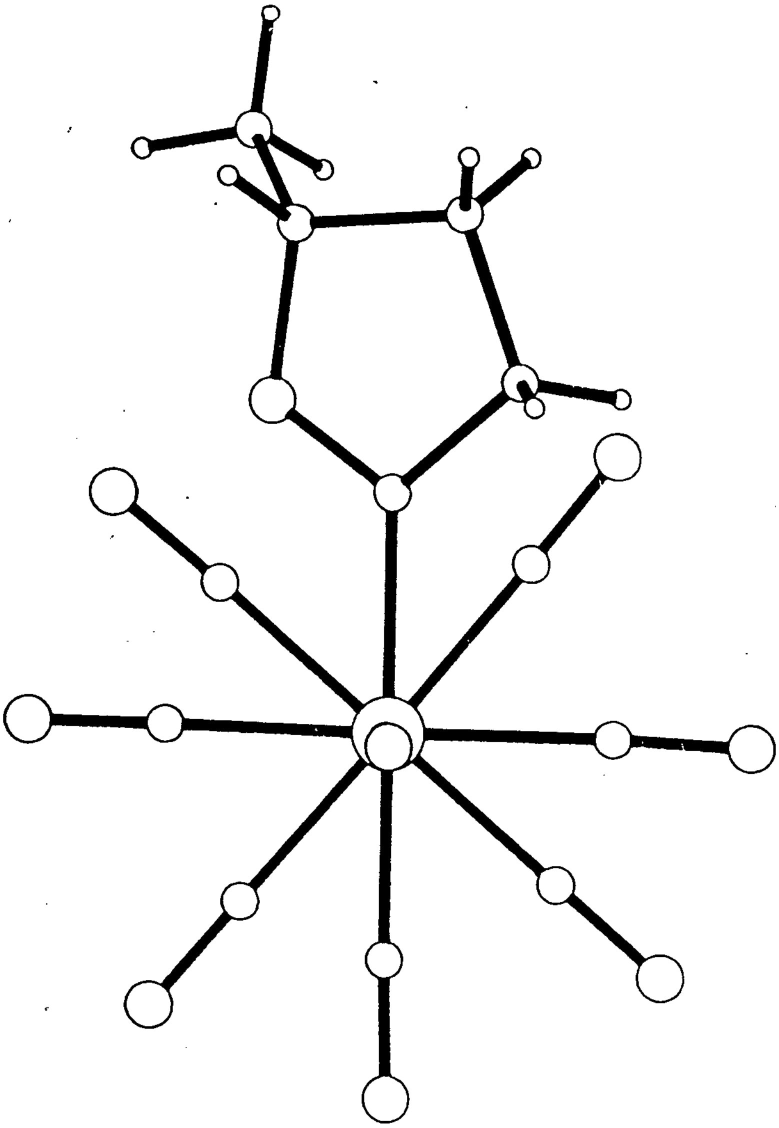


**Fig. 13b** View of the Structure of Compound 2, Showing the Staggered Conformation of the Carbonyl Groups

**Table 6.6**

**Crystal and X-ray Diffraction Data for 1 and 2**

| | 1 | 2 |
|---|---|---|
| formula | $C_{13}H_6O_{10}Mn_2$ | $C_{14}H_8O_{10}Mn_2$ |
| cryst colour | orange | orange |
| cryst habit | plates | plates |
| cryst syst | triclinic | monoclinic |
| space group | P1 | P21/*n* |
| a, Å | 8.902(6) | 8.342(1) |
| b, Å | 12.796(6) | 13.444(3) |
| c, Å | 15.428(5) | 16.494(2) |
| α, deg | 107.21(3) | 90 |
| β, deg | 97.30(5) | 104.50(1) |
| γ, deg | 91.01(5) | 90 |
| V, $Å^3$ | 1662(1) | 1790.9(5) |
| Z | 4 | 4 |
| D(calcd), $g.cm^{-3}$ | 1.73 | 1.65 |
| cryst dimens, mm | 0.50x0.53x0.56 | 0.47x0.53x0.56 |
| temp, °C | room temp | room temp |
| μ (MoKα), $cm^{-1}$ | 15.06 | 14.01 |
| radiatn | graphite monochromated MoKα (λ = 0.71069Å) | |
| scan mode | $\omega/2\theta$ | $\omega/2\theta$ |
| scan width, deg | $0.90+0.35\tan\theta$ | $0.90+0.35\tan\theta$ |
| aperture width, mm | 4 | 4 |
| stability of std refln, % | 1.3 | 1.3 |
| $2\theta$ range, deg | 1-25 | 1-25 |
| no of collected data | 6088 | 3401 |
| no of unique data | 5453 | 2953 |
| no of unique data with I>2σ(I) | 4873 | 2718 |
| weighting scheme | $1/[\sigma^2(Fo)+0.001539Fo]$ | $1/[\sigma_2(Fo)+0.000219Fo]$ |
| R | 0.034 | 0.034 |
| Rw | 0.041 | 0.039 |
| S | 1.2 | 4.2 |

The crystal structures of 1 and 2 confirmed Casey's proposal [17] that the cyclic carbene ligand occupies an equatorial position. The equatorial CO groups all adopt a staggered conformation (see Figure 13b), thereby minimizing their steric interactions. The metal atoms are approximately octahedrally coordinated with one position occupied by the second manganese atom. The structure of 2 is very similar to that of 1. The presence of the methyl

**Table 6.7**

**Bond Lengths (Å) with e.s.d.'s in parentheses for Compounds 1 and 2**

| | 1(I) | 1(II) | 2 |
|---|---|---|---|
| Mn(1)-Mn(2) | 2.903(1) | 2.914(1) | 2.903(1) |
| Mn(1)-C(1A) | 1.948(3) | 1.952(3) | 1.948(3) |
| Mn(1)-C(1) | 1.779(4) | 1.792(4) | 1.787(3) |
| Mn(1)-C(2) | 1.851(4) | 1.853(3) | 1.838(3) |
| Mn(1)-C(3) | 1.838(3) | 1.844(3) | 1.836(3) |
| Mn(1)-C(4) | 1.827(3) | 1.846(3) | 1.855(3) |
| Mn(2)-C(5) | 1.846(3) | 1.851(3) | 1.845(3) |
| Mn(2)-C(6) | 1.836(3) | 1.851(3) | 1.837(3) |
| Mn(2)-C(7) | 1.851(4) | 1.822(3) | 1.833(4) |
| Mn(2)-C(8) | 1.830(3) | 1.842(3) | 1.852(3) |
| Mn(2)-C(9) | 1.808(4) | 1.805(4) | 1.804(3) |
| C(1)-O(1) | 1.151(5) | 1.147(5) | 1.147(4) |
| C(2)-O(2) | 1.130(5) | 1.125(4) | 1.137(4) |
| C(3)-O(3) | 1.149(4) | 1.129(4) | 1.140(5) |
| C(4)-O(4) | 1.135(4) | 1.132(4) | 1.124(4) |
| C(5)-O(5) | 1.130(4) | 1.131(4) | 1.133(4) |
| C(6)-O(6) | 1.131(4) | 1.130(4) | 1.128(4) |
| C(7)-O(7) | 1.125(5) | 1.150(4) | 1.134(4) |
| C(8)-O(8) | 1.142(4) | 1.126(4) | 1.134(4) |
| C(9)-O(9) | 1.142(5) | 1.133(6) | 1.133(4) |
| C(1A)-C(2A) | 1.498(4) | 1.498(6) | 1.504(5) |
| C(2A)-C(3A) | 1.503(4) | 1.500(10) | 1.463(8) |
| C(3A)-C(4A) | 1.481(5) | 1.481(11) | 1.481(7) |
| C(4A)-O(5A) | 1.475(3) | 1.481(6) | 1.486(5) |
| O(5A)-C(1A) | 1.312(3) | 1.309(4) | 1.299(3) |
| C(4A)-C(41A) | - | - | 1.452(6) |

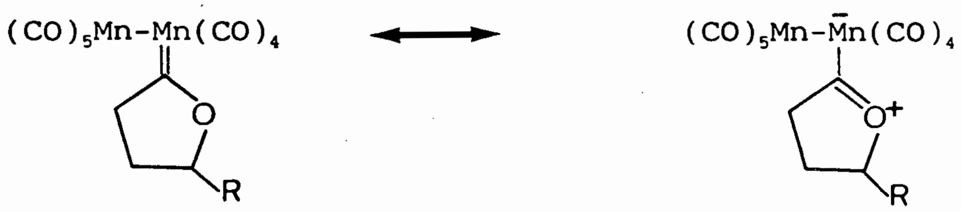
group appears to have little effect on the structure of the molecule, although it does point towards the second manganese atom not away from it as might have been expected on steric grounds. The carbene ring is approximately perpendicular to the Mn-Mn bond direction in 1 but is twisted somewhat further out of this plane in 2. This configuration may occur to maximize the π-back-bonding and is probably not a consequence of the cyclic carbene ligands since it is also observed in *eq*-[$\mathrm{Mn_2(CO)_9\{=C(OCH_3)Ph\}}$] [43]. The Mn-C(carbene) bond lengths in 1 and 2 of 1.948Å, 1.952Å and 1.948Å agree with the corresponding distance of 1.950Å found in the acyclic Fischer-type carbene complex

**Table 6.8**

**Bond Angles (deg) and Torsion Angles (deg) with e.s.d.'s in parentheses for the Carbene Ring in Compounds 1 and 2**

| | 1(I) | 1(II) | 2 |
|---|---|---|---|
| Mn(1)-C(1A)-C(2A) | 129.5(2) | 127.2(4) | 128.6(2) |
| Mn(1)-C(1A)-O(5A) | 122.4(2) | 123.7(4) | 123.3(2) |
| O(5A)-C(1A)-C(2A) | 107.5(3) | 108.7(5) | 107.9(2) |
| C(1A)-C(2A)-C(3A) | 105.1(3) | 106.8(5) | 106.6(4) |
| C(2A)-C(3A)-C(4A) | 102.9(3) | 105.5(6) | 107.1(5) |
| C(3A)-C(4A)-O(5A) | 103.8(3) | 105.7(6) | 103.5(4) |
| C(4A)-O(5A)-C(1A) | 112.7(3) | 113.0(4) | 114.1(2) |
| C(3A)-C(4A)-C(41A) | - | - | 118.0(5) |
| O(5A)-C(4A)-C(41A) | - | - | 108.2(4) |
| Mn(2)-Mn(1)-C(1A) | 92.2(1) | 92.2(1) | 92.7(1) |
| Mn(2)-Mn(1)-C(1A)-C(2A) | 100.3(3) | -94.5(5) | 117.9(3) |
| Mn(2)-Mn(1)-C(1A)-O(5A) | -89.3(3) | 93.4(4) | 69.0(2) |
| Mn(1)-C(1A)-O(5A)-C(4A) | 171.2(3) | 177.7(4) | 173.2(2) |
| Mn(1)-C(1A)-C(2A)-C(3A) | 172.0(3) | 174.0(5) | 178.7(2) |
| C(2A)-C(3A)-C(4A)-O(5A) | 26.9(4) | 4.9(6) | -9.0(5) |

*eq*-$[Mn_2(CO)_9\{=C(OCH_3)Ph\}]$ [43], suggesting delocalization of electron density over Mn-C(carbene)-O in all of these complexes. The structure of the $Mn_2(CO)_9$ skeleton in **1** and **2** is virtually identical to that described for $[Mn_2(CO)_{10}]$ [81]. The Mn-Mn bond lengths in 1 and 2 (2.903Å, 2.914Å and 2.902Å) are in good agreement with the value of 2.904Å found for *ax*-$[Mn_2(CO)_9(PPhMe_2)]$ [82] and 2.909Å for *eq*-$[Mn_2(CO)_9\{=C(OCH_3)Ph\}]$[43]. They are also very close to the value of 2.904Å found for $[Mn_2(CO)_{10}]$ [81]. These results indicate that if L (in $[Mn_2(CO)_9(L)]$) is changed from CO to various other ligands, this has very little effect on the Mn-Mn bond length. This was also found by Churchill and Holladay [83]. The structure of the carbene rings in **1** and **2** have been compared to other compounds having a similar or identical carbene ligand (see Table 6.1). For example, in $[CpMo(CO)_2(I)(=\overline{CCH_2CH_2CH_2O})]$ [24], the carbene ligand is bonded to the molybdenum atom *via* a partial double bond which is longer than those to the carbonyl carbon atoms, suggesting some delocalization of electron density over the carbene carbon-oxygen bond which is intermediate in length between single and double. In 1 and 2 the carbene ligand is bonded to the manganese atom by a bond which has some multiple bond character. Some delocalization over C(carbene)-O is indicated by virtue of the fact that the carbene carbon-oxygen bond lengths are relatively short, approaching that of a double bond (1.20Å). The values of 1.312Å, 1.309Å and 1.299Å for this bond length in 1 and 2 are slightly shorter than most of those in Table 6.1, suggesting a greater degree of electron delocalization than occurs in most of the carbene compounds in Table 6.1. This could imply a greater contribution from a Zwitterionic form, as shown in Fig. 14.



$(R = H, CH_3)$
**Fig. 14**

The same was also suggested for $[CpMoCO)_2(I)-\{=\overline{CCH_2CH_2CH_2N}(CH_3))\}]$[53].

An interesting point to note is that the carbene ring in 1 is puckered. It adopts an envelope conformation (see Fig. 15) with C(3A) lying out of the plane of the carbene ring (with which the manganese atom (Mn(1)) is coplanar).

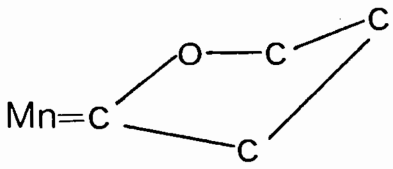


**Fig. 15**

Such puckering effects are also present in most of the compounds listed in Table 6.1. The existence of this coplanarity over most of the carbene fragment is further evidence for electron delocalization over the ring. However, compound 2, which differs from 1 only by a methyl substituent on the carbene ligand, shows far less puckering in the carbene ring, although delocalization is still taking place, as indicated by the bond lengths. That the out-of-plane deviations for the carbene ring are only observed for C(3A) could be due to an effort to optimize conjugation.

The structures of **3** and **4** were solved by similar means to 1 and 2 *i.e.* by direct methods and refined by least-squares techniques. High temperature factors in the ring atoms indicate conformational flexibility and associated disorder in the carbene ring, with the disorder in 3 being greater than in 4. This disorder appears to be of the type observed for 1 and 2, and for other similar transition metal carbene complexes [46,55]. This is suspected mainly because in **3**, the C(carbene)-C(ring) bond is remarkably short, a fact which can be explained if the positions C(29) and O(25) are each assumed to be composites of carbon and oxygen electron density. This situation arises through rotation of the Mn-C(carbene) bond by 180°. The $\alpha$-carbon (ring) (C(29)) and oxygen (O(25)) positions were thus modelled as 50:50 C:O mixtures. The space group being P21/*c* however, did not allow any further resolution of the two rotamers. All hydrogen atoms were placed in calculated positions. Detailed mapping of the ring electron density in 3 showed that the observed positions for C(26), C(27) and C(28) are fairly well defined, with only slight blurring around the mean positions. This is to be expected, since the observed half-chair ring conformation has a pseudo-$C_2$ axis aligned with the Mn-C(carbene) axis. Further details of the data collection, structure solution and refinement are given in Table 6.9. Bond lengths are

**Table 6.9**

**Crystal and X-ray Diffraction Data for 3 and 4**

| | **3** | **4** |
|---|---|---|
| formula | $C_{14}H_8O_{10}Mn_2$ | $C_{15}H_{10}O_{10}Mn_2$ |
| cryst colour | orange | orange |
| cryst habit | plates | plates |
| cryst syst | monoclinic | monoclinic |
| space group | P21/*c* | P21/*n* |
| a, Å | 9.669(2) | 10.495(1) |
| b, Å | 11.828(2) | 11.724(1) |
| c, Å | 16.027(2) | 15.832(1) |
| α, deg | 90 | 90 |
| ß, deg | 105.36(2) | 106.19(1) |
| γ, deg | 90 | 90 |
| V, $Å^3$ | 1761.0(6) | 1871.0(6) |
| Z | 4 | 4 |
| D(calcd), $g.cm^{-3}$ | 1.68 | 1.63 |
| cryst dimens, mm | 0.30x0.40x0.50 | 0.19x0.31x0.41 |
| temp, °C | room temp | room temp |
| μ (MoKα), $cm^{-1}$ | 14.196 | 13.434 |
| radiatn | graphite monochromated MoKα<br>( λ = 0.71069Å) | |
| scan mode | $\omega$-$2\theta$ | $\omega$-$2\theta$ |
| scan width, deg | $0.90+0.35\tan\theta$ | $0.90+0.35\tan\theta$ |
| aperture width, mm | 4 | 4 |
| stability of std refln, | 2.6 | 2.8 |
| $2\theta$ range, deg | 1-25 | 1-25 |
| no of collected data | 3860 | 3596 |
| no of unique data | 2489 | 2860 |
| no of unique data with I>2σ(I) | 1829 | 2350 |
| weighting scheme | $(\sigma^2F)^{-1}$ | $(\sigma_2F)^{-1}$ |
| R | 0.042 | 0.056 |
| Rw | 0.038 | 0.053 |
| S | 2.31 | 6.08 |

given in Table 6.10 and bond angles and torsion angles for the carbene ring are given in Table 6.11. Views of a molecule of 3 and a molecule of 4 are shown in Figures 16a, 16b and 17, respectively.

The crystal structures of 3 and 4 confirm the proposal that the six-membered cyclic carbene ligands occupy equatorial positions on one of the manganese atoms. Apart from ring details the structures of 3 and 4 do not vary significantly from 1 and 2. The equatorial CO groups adopt the usual

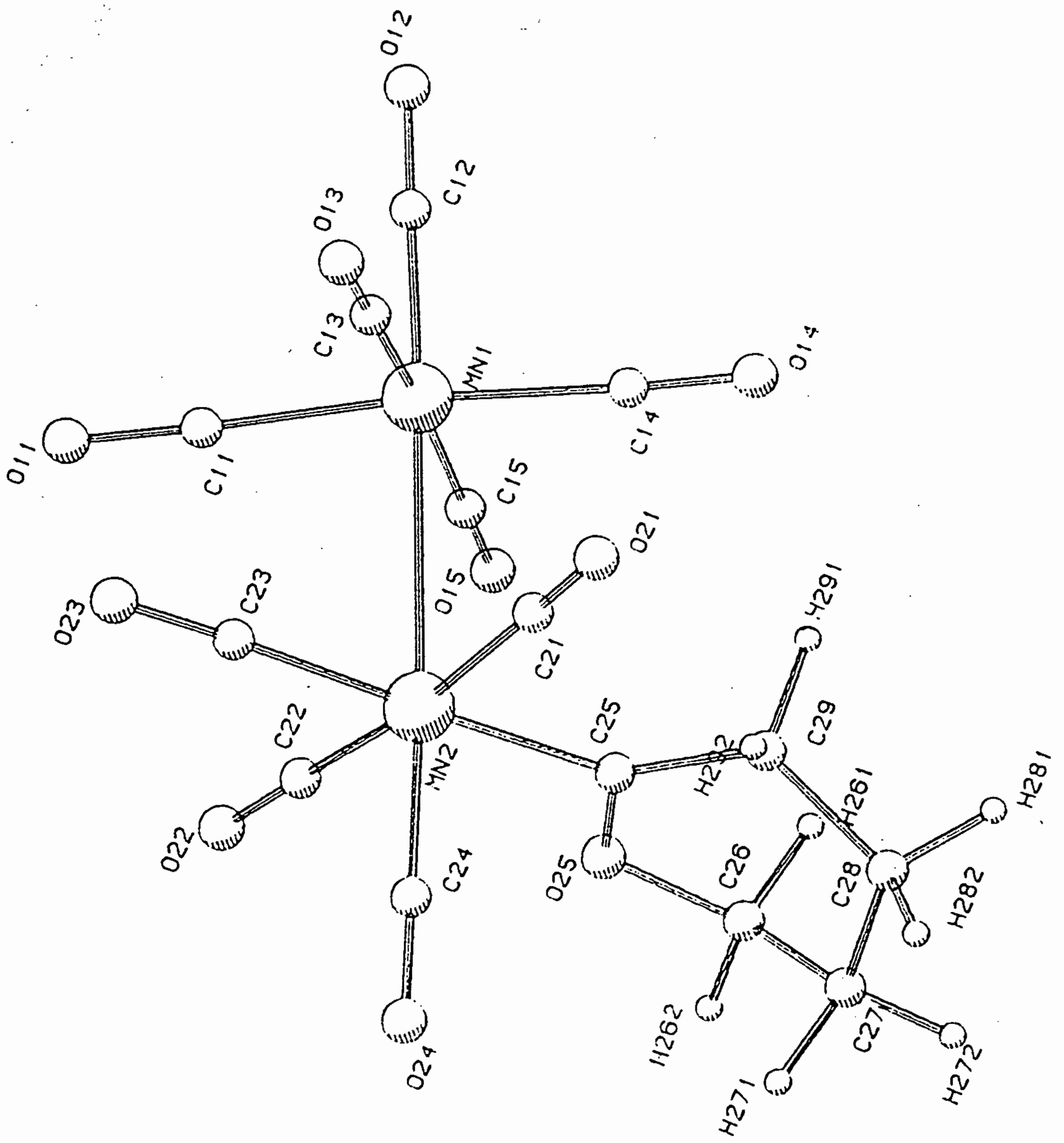


Fig. 16a View of the Structure of Compound 3

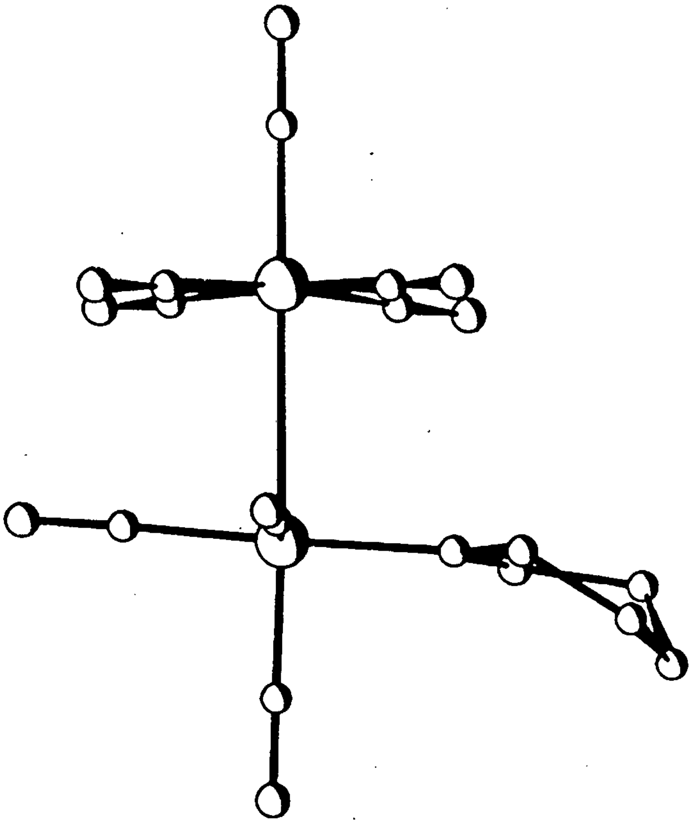


**Fig. 16b** View of the Structure of Compound 3, Showing the Puckering in the Carbene Ring

staggered conformation. As shown in Figures 16a, 16b and 17, the carbene ring exists in a twist conformation, the conformational restriction being the $sp^2$ hybridized carbene carbon atom (C(25)). The out-of-plane bending for the ring appears to be confined to C(27) and C(28). This is presumably in order to maximize orbital overlap.

Both rings bend away from the other manganese atom in order to minimize unfavourable steric interactions. In **4** the methyl group points away from the second manganese atom, as would be expected on steric grounds. As in **1** and **2**, the carbene rings in both **3** and **4** are twisted out of the plane of the Mn-Mn bond direction. Presumably, as in **1** and **2**, this occurs in order

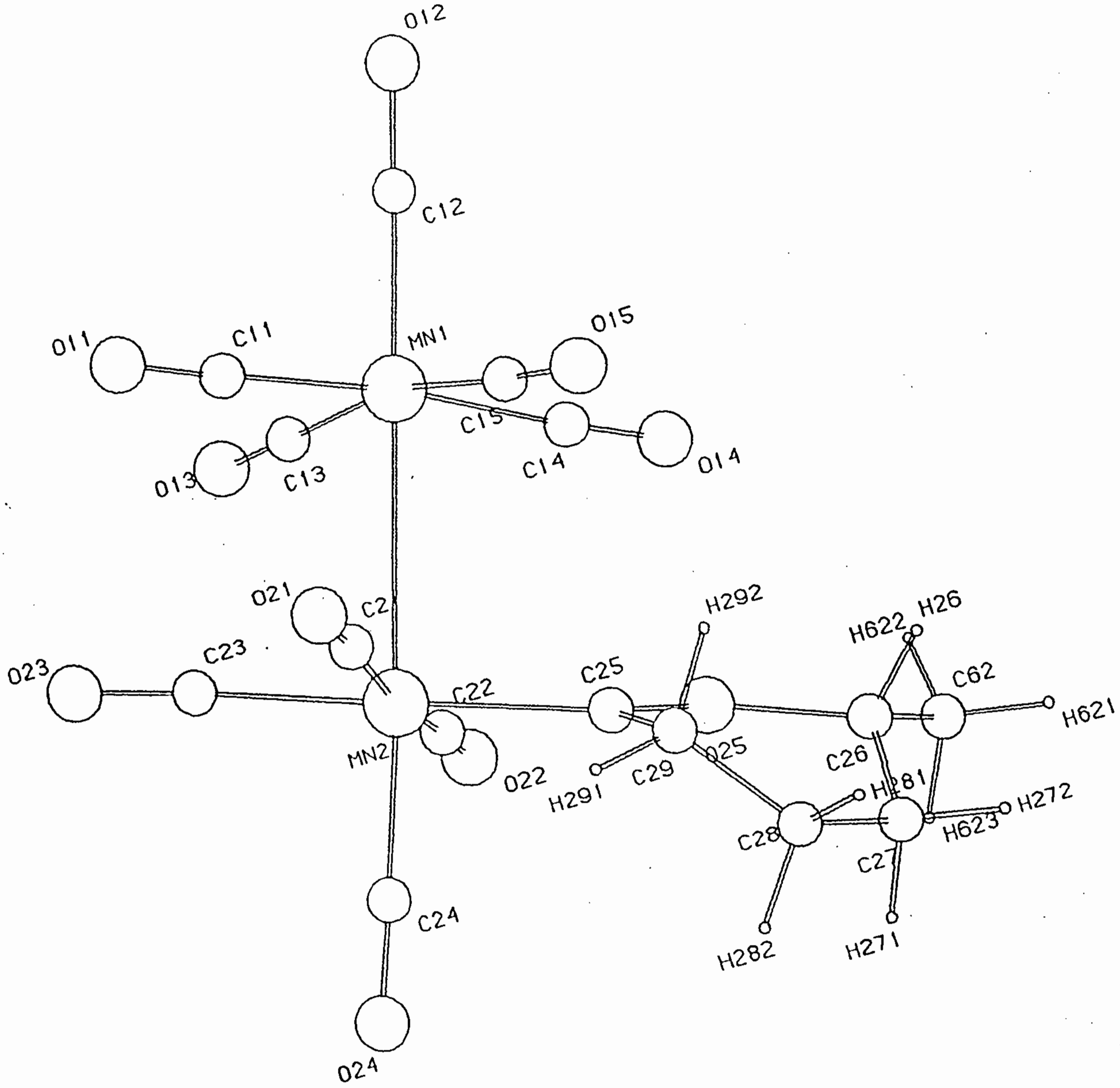


Fig. 17 View of the Structure of Compound 4

to maximize the π-back-bonding. The C(29)-C(25)-O(25)-C(26) and Mn(2)-C(25)-O(25)-C(26) fragments are almost entirely planar, as can be seen from the very low torsion angles (Table 6.11). The presence of the methyl group in **4** has a significant effect on the structure of the carbene ring; it lengthens the C(25)-C(29) bond but shortens the C(25)-O(25) bond. This may be as a result of only one rotamer being present. The C(25)-C(29) bond in **3** is unusually short, approaching a double bond in length. This very short bond length may, as mentioned previously, be a consequence of the C(29) and O(25) positions each being composites of carbon and oxygen electron density. However, a similar phenomenon is also observed in **1** and **2**, where the C(carbene)-C(ring) bond length is not unusually short, so the very short C(25)-C(29) bond length in **3** MAY be a real consequence of the bonding in **3**. The C(carbene)-O bond length in **4** is also very short, again approaching a double bond in length; this may then result in the C(carbene)-C(ring) bond being longer in **4** than in **3**. The C(carbene)-O bond is also very short in **2**; this may then be as a result of the presence of the methyl substituent in **2** and **4**.

Thus in **3**, there appears to be greater electron delocalization over the C(29)-C(25)-O(25) fragment than in **4**. The carbene ring in **3** is more puckered than in **4**, as can be seen by the larger C(26)-C(27)-C(28)-C(29) torsion angle in **3**. A similar effect was observed in **1** and **2**, *viz.* the substituted ring was less puckered than the unsubstituted ring.

The Mn-C(carbene) bond length is singificantly longer for the six-membered ring complexes than for the five-membered ring complexes. This indicates increased delocalization of electron density in the carbene rings for the six-membered ring complexes and less electron delocalization over the Mn-C(carbene) bond than for the five-membered ring complexes. The longer Mn-C(carbene) bonds in **3** and **4** and the increased puckering of the carbene ring could both occur as a result of

**Table 6.10**

**Bond Lenths (Å) with e.s.d.'s in parentheses for Compounds 3 and 4.**

| | 3 | 4 |
|---|---|---|
| Mn(1)-Mn(2) | 2.892(2) | 2.898(2) |
| Mn(1)-C(11) | 1.849(9) | 1.864(7) |
| Mn(1)-C(12) | 1.807(8) | 1.785(8) |
| Mn(1)-C(13) | 1.865(8) | 1.806(8) |
| Mn(1)-C(14) | 1.850(9) | 1.887(9) |
| Mn(1)-C(15) | 1.870(8) | 1.820(8) |
| Mn(2)-C(21) | 1.843(7) | 1.833(7) |
| Mn(2)-C(24) | 1.780(8) | 1.782(8) |
| Mn(2)-C(23) | 1.836(8) | 1.876(8) |
| Mn(2)-C(22) | 1.853(8) | 1.851(7) |
| Mn(2)-C(25) | 1.971(7) | 1.982(7) |
| C(11)-0(11) | 1.120(11) | 1.116(9) |
| C(12)-0(12) | 1.152(9) | 1.114(9) |
| C(13)-0(13) | 1.123(10) | 1.158(11) |
| C(14)-0(14) | 1.123(11) | 1.109(10) |
| C(15)-0(15) | 1.123(10) | 1.157(10) |
| C(21)-0(21) | 1.126(10) | 1.145(9) |
| C(24)-0(24) | 1.147(10) | 1.152(10) |
| C(23)-0(23) | 1.147(9) | 1.122(10) |
| C(22)-0(22) | 1.153(9) | 1.138(9) |
| C(25)-0(25) | 1.384(11) | 1.299(7) |
| C(25)-C(29) | 1.396(12) | 1.493(11) |
| 0(25)-C(26) | 1.468(14) | 1.497(10) |
| C(26)-C(62) | - | 1.460(11) |
| C(26)-C(27) | 1.405(20) | 1.355(12) |
| C(27)-C(28) | 1.476(25) | 1.464(14) |
| C(28)-C(29) | 1.461(14) | 1.391(15) |

strain within the ring caused by steric factors.

Thus, in 1, 2, 3 and 4 the following bonding scheme may apply

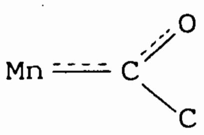
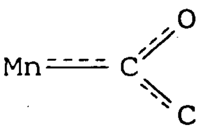


**Table 6.11**

**Bond Angles (deg) and Torsion Angles (deg) with e.s.d.'s in parentheses for the Carbene Ring in Compounds 3 and 4**

| | 3 | 4 |
|---|---|---|
| Mn(2)-C(25)-C(29) | 125.3(6) | 126.4(5) |
| Mn(2)-C(25)-O(25) | 118.5(5) | 118.5(5) |
| O(25)-C(25)-C(29) | 116.1(7) | 115.0(6) |
| C(25)-O(25)-C(26) | 120.7(8) | 120.1(6) |
| O(25)-C(26)-C(27) | 109.2(12) | 112.3(7) |
| O(25)-C(26)-C(62) | - | 104.9(7) |
| C(62)-C(26)-C(27) | - | 123.8(8) |
| C(26)-C(27)-C(28) | 111.4(14) | 117.5(8) |
| C(27)-C(28)-C(29) | 116.8(11) | 115.0(9) |
| C(27)-C(29)-C(28) | 118.0(9) | 116.6(8) |
| Mn(1)-Mn(2)-C(25) | 93.9(2) | 94.5(2) |
| Mn(1)-Mn(2)-C(25)-O(25) | -93.7(6) | -71.9(5) |
| Mn(1)-Mn(2)-C(25)-C(29) | 90.7(7) | 112.1(6) |
| Mn(2)-C(25)-C(29)-C(28) | 147.9(9) | 139.7(8) |
| Mn(2)-C(25)-O(25)-C(26) | -175.0(8) | -177.2(5) |
| O(25)-C(25)-C(29)-C(28) | -27.8(12) | -36.4(11) |
| C(29)-C(25)-O(25)-C(26) | 1.0(12) | -0.8(9) |
| C(25)-O(25)-C(26)-C(62) | — | 176.7(6) |
| C(25)-O(25)-C(26)-C(27) | 42.5(15) | 39.8(10) |
| O(25)-C(26)-C(27)-C(28) | -56.8(16) | -41.6(12) |
| C(62)-C(26)-C(27)-C(28) | — | -169.3(10) |
| C(26)-C(27)-C(28)-C(29) | 32.9(19) | 7.0(15) |
| C(27)-C(28)-C(29)-C(25) | 11.0(9) | 33.3(13) |

and in 3 a contribution from the following scheme could occur



This proposed bonding scheme for **3** may be a function of a six-membered carbene ring but is not seen in **4** because of the methyl substituent. This bonding scheme (for **3**) would impose a greater steric rigidity, causing the rest of the carbene ring to become more puckered (to preserve optimum conjugation), as is observed.

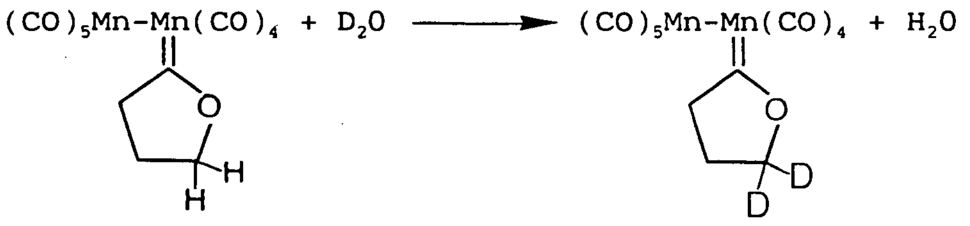
## 6.4 REACTIVITY OF 1-6

In order to probe the relative acidities of the protons attached to the *α*-carbon atom of the carbene ring (*i.e.* the carbon atom adjacent to the carbene carbon atom) in 1-6, deuterium exchange studies were carried out. These were performed in 1:5 $D_2O : (CD_3)_2CO$ (with no added catalyst) at 40.0°C and were interpreted on the basis of the following scheme (equation 5).

$$X\text{-}H + \tfrac{1}{2} D_2O \longrightarrow X\text{-}D + \tfrac{1}{2} H_2O \qquad (5)$$

(X = carbene complex)

For example, the reaction for **1** is shown in equation 6



(6)

The two protons exchange simultaneously.

The reaction is irreversible and the rate data are therefore assessed only in terms of the forward reaction. Under the pseudo-first-order conditions imposed by a very large concentration of $D_2O$ relative to the carbene complex, the rate is given by:

$$\frac{-d[XH]}{dt} = k_{OBS}[XH] \qquad (7)$$

Only the carbene complexes with unsubstituted rings (1 and 3) underwent deuterium exchange. The results are given in Table 6.12. No exchange reaction occurred with compounds **2**,**4**,**5** or **6**. This shows how the electron-donating effect of the substituent methyl group can be transmitted through the carbene ring to positions several carbon atoms away. This lends credence to the suggestion that there may be considerable electron delocalization in these carbene rings. The results for the five-membered rings were not surprising, since in **2** the methyl group is only two carbon atoms away from the $\alpha$-protons and in **5** it is only one carbon atom away. The fact that **4** did not undergo a deuterium exchange reaction (the methyl group is three carbon atoms away from the $\alpha$-protons) was somewhat surprising. Compound **3** reacts approximately twice as fast as compound **1**, indicating that the $\alpha$-$CH_2$ protons on the six-membered rings are more acidic than those on the five-membered rings. The half-life of 21 minutes for the deuterium exchange reaction of **1** is in good agreement with the value of 23 minutes obtained by Casey [17] for the same reaction for complex **1**.

**Table 6.12**

**Results of Deuterium Exchange Experiments**

| Compound | $k_{OBS}$ ($sec^{-1}$) | $t_{1/2}{}^a$ (min) |
|---|---|---|
| 1 | $5.476 \times 10^{-4}$ | 21.09 |
| 3 | $1.110 \times 10^{-3}$ | 10.41 |

a: given by $\frac{\ln 2}{k_{OBS}}$

Reaction of **1**-**6** with tertiary phosphines ($PPh_3$ or $PPh_2Me$) at 100°C leads only to the formation of the phosphine-substituted dimers, $[Mn_2(CO)_8(PR_3)_2]$, in high yield. At lower temperatures, no reaction at all occurred. The same product has been obtained previously [84] from the reaction of **1** with $PPh_3$, although the product was then, we believe, incorrectly identified as $[(CH_2)_3\{Mn(CO)_4(PPh_3)\}_2]$ [84]. The characterization data given for this compound (infrared, molecular weight, elemental analysis and melting point) all agreed with that given for $[Mn_2(CO)_8(PPh_3)_2]$ [85]. The fact that **1-6** all gave $[Mn_2(CO)_8(PR_3)_2]$ on reaction with tertiary phosphines was not surprising since **1-6** all decompose to $[Mn_2(CO)_{10}]$ at high temperatures in solution [86], which could then react with the phosphine to give the phosphine-substituted dimer [85].

## 6.5 CONCLUSIONS

We have synthesized, in moderate yield, a series of dimanganese cyclic carbene complexes **1-6**. Thermal analysis indicates relatively high thermal stability, although compound **4** was observed to be slightly less stable than the others. The NMR data and crystal structure analyses (of 1-4) indicate some delocalization of electron density over the carbene rings, and multiple bond character in the Mn-C(carbene) bond. The structures of the six-membered rings are different from the structures of the five-membered rings. This could be due to packing effects, strain within the carbene rings (caused by steric factors), or some disorder within the rings.

Deuterium exchange experiments show that electronic effects can be transmitted through the carbene ring and that the protons attached to the α-carbon atom of the six-membered carbene ring in **3** are more acidic than those attached to the carbene ring in **1**.

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# CHAPTER 7

# EXPERIMENTAL

## 7.1 GENERAL

All reactions were carried out under an atmosphere of high purity nitrogen using standard Schlenk tube techniques unless stated otherwise.

The solvents used were generally analytical grade and were purified as follows: tetrahydrofuran (THF), toluene and hexane were dried by distilling under a nitrogen atmosphere over sodium/benzophenone, dichloromethane ($CH_2Cl_2$) was distilled over anhydrous $CaCl_2$, while acetonitrile was distilled over $P_2O_5$. Nitrogen was bubbled through the solvents for *ca.* 10 minutes prior to use.

Triphenylphosphine (Merck) was used without further purification. The compounds $Br(CH_2)_nCH_3$, $Br(CH_2)_nBr$, $BrCH(R)(CH_2)_nBr$, $ClCO(CH_2)_nCH_3$, $ClCO(CH_2)_nCOCl$, $BrCH_2CH(CH_3)CH_2Cl$, triphenylcarbenium hexafluorophosphate, $Ph_3CPF_6$, and silver tetrafluoroborate, $AgBF_4$, were obtained from Aldrich Chemical Corporation and were used without further purification. All the substituted benzyl halides used were also obtained from Aldrich, and were used without further purification. $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$ and $[CpFe(CO)_2]_2$ were purchased from Strem Chemicals Inc., and were used without further purification. Deuterium oxide, $D_2O$, and acetone-$d_6$ were obtained from Aldrich.

Column chromatography was carried out using neutral aluminium oxide (BDH, active neutral, Brockman grade I) which was deactivated as follows: a 50% slurry of the aluminium oxide in distilled water was prepared and allowed to stand for 4h at room temperature. The water was then decanted and the alumina allowed to dry in the oven (120°C) for *ca.* 18h.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer in solution cells with NaCl windows or between NaCl plates as neat films or Nujol mulls. The following abbreviations are used in the description of infrared spectra: w = weak, mw = medium weak, m = medium, s = strong, sh = shoulder and br = broad.

$^1$H NMR spectra were recorded on a Varian EM360 60MHz, Brücker WH90 90Mhz, Varian XR200 200MHz or a Varian EM400 400MHz spectrometer. $^{13}$C NMR spectra were recorded on a Varian XR200 200MHz spectrometer. In all cases, tetramethylsilane (TMS) was used as an internal reference standard and chemical shifts are reported in ppm, downfield of TMS ($\delta$ = 0.00 ppm).

Low resolution mass spectra were recorded with a VG Micromass 16F spectrometer operated at 70eV ionizing voltage and using an accelerating voltage of 4 kV. The source temperature was initially 20-30°C and was raised to *ca.* 200°C during data collection. The data were analyzed on a VG 200 Digital data system.

Melting points were determined on a Kofler hotstage microscope (Reichert Thermovar) and are uncorrected. Differential scanning calorimetry (DSC) traces were recorded on a Perkin-Elmer PC Series 7 instrument under a nitrogen atmosphere with a heating rate of 20°C per minute. High pressure gas reactions were carried out in a 250ml Berghof autoclave.

The removal of solvents under reduced pressure implies the use of a rotary evaporator, unless otherwise stated.

The X-ray analyses were carried out on an Enraf-Nonius CAD4 diffractometer using MoKα ( $\lambda$ = 0.710Å) radiation. Cell parameters were obtained from least-squares analysis of the setting angles of 24 reflections in the range $16° < \theta < 17°$. During data collection, the intensities of three reference reflections were monitored every hour and recentering was checked after every 100 measured reflections. Data were corrected for Lorentz-polarization effects and an empirical absorption correction was applied [1]. The structures were solved by direct methods and refined by full matrix least-squares techniques (SHELX [2,3]). Complex neutral atom scattering factors were used for hydrogen [4] and for all other atom types [5]; dispersion corrections were taken from Cromer and Liberman [6]. PLUTO produced the drawings [7]. All calculations were performed at the University of Cape Town on a Univac 1100/81 computer.

## 7.2 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 2

### 7.2.1 General Synthetic Route to the Compounds $[Mn(COR)(CO)_5]$ (R = $CH_3$ to n-$_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

$[Mn_2(CO)_{10}]$ (2.00g; 5.13mmol) in tetrahydrofuran (30ml) was stirred over a sodium amalgam (0.4g Na in 4ml Hg), for 2h at room temperature. The resulting solution of $Na[Mn(CO)_5]$ (10.26 mmol) was then transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the acyl chloride, RCOCl (10.26 mmol). The reaction mixture was stirred for 2h at room temperature. After this time the solvent was removed under reduced pressure, leaving a yellow/brown oily residue. This was extracted with $CH_2Cl_2$ (2 x 30ml) and centrifuged at maximum speed for *ca.* 10 mins. The solvent was removed from the liquid portion under reduced pressure to give a yellow oily residue. This was extracted with hexane (*ca.* 15ml) and filtered. Chromatography on an alumina column (1.5cm x 14cm) with hexane as eluent gave a yellow band ([$Mn_2(CO)_{10}$]) followed immediately by a second, virtually colourless band. The solvent was removed from the second band under reduced pressure to give a pale yellow crystalline solid. This was recrystallized from hexane at -78°C. All of the products are pale yellow solids. The yields and characterization data are given in Tables 2.1 - 2.4 (see Chapter 2).

### 7.2.2 General Synthetic Route to the Compounds [$(CO)_5MnCO(CH_2)_nCOMn(CO)_5$] (n = 4-8;10)

The above compounds were prepared using a modified literature procedure [8].

[$Mn_2(CO)_{10}$] (2.00g; 5.13mmol) in tetrahydrofuran (30ml) was stirred over a sodium amalgam (0.4g Na in 4ml Hg) for 2h at room temperature. The resulting solution of Na[$Mn(CO)_5$] (10.26 mmol) was then transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the diacyl dichloride, $ClCO(CH_2)_nCOCl$ (5.13 mmol). The reaction mixture was stirred for 4½h at room temperature, after which time the solvent was removed under reduced pressure to give a yellow oily residue. This was extracted with warm chloroform (*ca.* 40ml) and filtered. The filtrate was reduced to *ca.* 10ml and hexane was added until the solution went cloudy. Cooling to -15°C resulted in crystallization of the product. All the products were creamy coloured solids. The yields and characterization data are given in Tables 2.5 - 2.8 (see Chapter 2).

### 7.2.3 General Synthetic Route to the Compounds [$Mn(R)(CO)_5$] (R = $C_2H_5$ to n-$C_9H_{10}$; n-$C_{11}H_{23}$, n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

[$Mn(COR)(CO)_5$] (0.70g) was dissolved in hexane (20ml) and the solution refluxed for 1h under $N_2$. The reaction can be followed by IR spectroscopy, by monitoring the disappearance of the acyl band at around 1650cm$^{-1}$ . After this time the solvent was removed under reduced pressure to give a yellow oil. This was extracted with hexane (*ca.* 15ml) and filtered. Chromatagraphy on an alumina column (1.5cm x 9cm) with hexane as eluent gave two overlapping yellow bands which were collected as two separate fractions. The first, bright yellow fraction contained [$Mn_2(CO)_{10}$] and the second, pale yellow fraction contained only the required product from which the solvent was removed under reduced pressure to give a yellow oil. The product was recrystallized from hexane at -78°C, although most products were yellow oils at room temperature. The yields and characterization data are given in Tables 2.9 - 2.12 (see Chapter 2).

### 7.2.4 General Synthetic Route to the Compounds [$Mn(R)(CO)_5$] (R = n-$C_{12}H_{25}$; n-$C_{14}H_{29}$; n-$C_{16}H_{33}$; n-$C_{18}H_{37}$)

[$Mn_2(CO)_{10}$] (0.75g; 1.92 mmol) in tetrahydrofuran (20ml) was stirred over a sodium amalgam (0.3g Na in 3 ml Hg) for 2h at room temperature. The resulting solution of Na[$Mn(CO)_5$] (3.84 mmol) was then transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the bromoalkane, RBr (3.84 mmol). The reaction mixture was stirred at room temperature for 5-7 days. After this time, the solvent was removed under reduced pressure to give a yellow/brown oily residue. This was extracted with $CH_2Cl_2$ (2 x 20ml) and centrifuged at maximum speed for *ca.* 10 mins. The solvent was removed from the liquid portion under reduced pressure to give a yellow/brown oil. This was extracted with hexane (*ca.* 10ml) and filtered. Chromatography on an alumina column (1.5cm x 8cm) with hexane as eluent gave two overlapping yellow bands which were collected as two separate portions. The first, bright yellow fraction contained [$Mn_2(CO)_{10}$] and the second, pale yellow fraction contained the required product. The solvent was removed from this second fraction under reduced pressure to give a yellow oil. The product was recrystalized from hexane at -78°C. The yields and characterization data are given in Tables 2.9 - 2.12 (see chapter 2).

### 7.2.5 Synthesis of [Mn($CH_3$)($CO)_5$]

Because of its high volatility [Mn($CH_3$)($CO)_5$] could not be prepared by either of the above methods used for the other [Mn(R)($CO)_5$] compounds. We found that it was best synthesized by the method of Closson *et al.* [9]. Typically, [$Mn_2(CO)_{10}$] (1.00g; 2.56 mmol) in tetrahydrofuran (20ml) was stirred over a sodium amalgam (0.2g Na in 3ml Hg) for 2h at room temperature. The resulting solution of Na[Mn($CO)_5$] (5.12 mmol) was transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing methyl iodide, $CH_3I$ (5.12 mmol). The reaction mixture was stirred at room temperature for 2h. After this time the solvent was removed (cautiously) under reduced pressure (water pump) over thirty mins. giving a pale yellow residue. The solvent was removed cautiously at a low temperature (*ca.* 10°C) to minimize loss of product due to volatilization. This solid, pale yellow residue was then extracted with petroleum ether (30°-40°C) and filtered. The resultant pale yellow solution was cooled to -78°C to give pale yellow crystals of [Mn($CH_3$)($CO)_5$] which were purified by sublimation on a water cooled probe in a closed system to prevent loss of product. The product was stored under vacuum. The yield and characterization data are given in Tables 2.9 - 2.12 (see Chapter 2).

### 7.2.6 General Synthetic Route to the Compounds [($CO)_5Mn(CH_2)_nMn(CO)_5$] (n = 4-8;10)

The diacyl compounds, [($CO)_5MnCO(CH_2)_nCOMn(CO)_5$] (n = 4-8;10) were converted to the corresponding μ(1,n)-alkanediyl compounds by a simple thermal decarbonylation. Typically, *ca.* 1.00g of $[(CO)_5MnCO(CH_2)_nCOMn(CO)_5]$ was dissolved in hexane (100ml). The solution was then refluxed for 45 mins under nitrogen. The reaction can be followed by IR spectroscopy, by monitoring the disappearance of the acyl band at *ca.* 1625 $cm^{-1}$. Removal of the hexane under reduced pressure leaves a creamy coloured solid which can be recrystallized by dissolving in a minimum of chloroform and adding hexane. Cooling to -15°C results in the formation of a white, crystalline solid. Yields and characterization data are given in Tables 2.13 - 2.16 (see Chapter 2).

## 7.3 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 3

### 7.3.1 Decarbonylation of $[Mn(COR)(CO)_5]$ : Kinetic Studies

$$[Mn(COR)(CO)_5 \xrightarrow{k} [Mn(R)(CO)_5] + CO \qquad (1)$$

(R = $CH_3$ to $n\text{-}C_9H_{19}$; $n\text{-}C_{11}H_{23}$; $n\text{-}C_{13}H_{27}$; $n\text{-}C_{15}H_{31}$; $n\text{-}C_{17}H_{35}$)

The method outlined by Cotton and co-workers [10,11] was employed for these kinetic measurements. Kinetic data for the decarbonylation process were obtained by monitoring the decrease in intensity of the highest energy ($A_1$) carbonyl vibration (*ca.* 2112 $cm^{-1}$). A Schlenk tube containing 10ml hexane was placed in a constant temperature bath at 55.5°C, at which point the temperature dropped slightly. When the temperature had reached 55.5°C again, the manganese acyl complex (typically, sufficient complex to give a 0.04M solution) was added. Aliquots were then removed periodically and the infrared transmission measured using the attached ordinate data processing facility. The reaction was kept under nitrogen for the duration of the experiment and was degassed periodically in order to prevent CO buildup. The temperature remained constant to within 0.5°C. A plot of ln ($I_\infty - I_t$) versus time yielded $k_{OBS}$.

($I\infty$ = intensity at time = $\infty$, It = intensity at time = t). The results were analyzed over *ca.* 75% of the reaction by linear regression. Errors in the $k_{OBS}$ values are generally around 4%. Reactions were followed for approximately three half-lives. Results are given in Table 3.1 (see Chapter 3).

The decarbonylations of $[(CO)_5MnCO(CH_2)_7COMn(CO)_5]$ and $[(CO)_5MnCO(CH_2)_{10}COMn(CO)_5]$ were also followed by this method and results for these two kinetic studies are given in Table 3.2 (see Chapter 3).

### 7.3.2 Reaction of $[Mn(R)(CO)_5]$ with Triphenylphosphine : Kinetic Studies

$$[Mn(R)(CO)_5] + PPh_3 \xrightarrow{k} cis\text{-}[Mn(COR)(CO)_4(PPh_3)] \quad (2)$$

(R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$; n-$C_{18}H_{37}$)

The method outlined by Cotton and co-workers [10,11] was again employed for these kinetic measurements. Kinetic data for the CO insertion (alkyl migration) process was obtained by monitoring the decrease in intensity of the highest energy ($A_1$) carbonyl vibration (*ca.* 2105cm$^{-1}$). A solution of the manganese alkyl complex in hexane (10ml of *ca.* 0.07M solution) was placed in a Schlenk tube in a constant temperature bath at 32.0°C. An infrared spectrum was run, corresponding to time = 0. The triphenylphosphine (typically a 9-molar excess) was then added to the solution in the Schlenk tube. Time = 0 was taken at the point when half of the $PPh_3$ had been added. Aliquots were then removed periodically and the infrared transmission measured using the attached ordinate data processing facility. The reaction was kept under nitrogen for the duration of the experiment. The temperature remained constant to within

0.5°C. A plot of ln (I∞/It) versus time yielded $k_{OBS}$ (I∞ = intensity at time = ∞, It = intensity at time = t). The results were analyzed over *ca.* 75% of the reaction by linear regression. Errors in the $k_{OBS}$ values are generally around 5%. Reactions were followed over approximately three half-lives. Results are given in Table 3.3 (see Chapter 3).

The reaction of $PPh_3$ with $[(CO)_5Mn(CH_2)_8Mn(CO)_5]$ and $[(CO)_5Mn(CH_2)_{10}Mn(CO)_5]$ was also followed by this method and results for these two kinetic studies are given in table 3.4 (see Chapter 3).

In order to confirm the validity of this method, the following reactions were also followed by $^1H$ NMR spectroscopy, by monitoring the decrease in the $MnCOCH_2$ resonance (for equation 3) and by monitoring the decrease in the $MnCH_3$ resonance (for equation 4):

$$[(CO)_5MnCO(CH_2)_{10}COMn(CO)_5] \longrightarrow [(CO)_5Mn(CH_2)_{10}Mn(CO)_5] + 2CO \qquad (3)$$

$$[Mn(CH_3)(CO)_5] + PPh_3 \longrightarrow cis\text{-}[Mn(COCH_3)(CO)_4(PPh_3)] \qquad (4)$$

Reaction 3 was performed in $CDCl_3$ at 55.5°C and Reaction 4 was performed in $CDCl_3$ at 32.0°C. A good correlation with the results obtained by infrared spectroscopy was found. Results are given in Tables 3.2 and 3.3 (see Chapter 3).

### 7.3.3 Reaction of $[Mn\{(CH_2)_{14}CH_3\}(CO)_5]$ and $[Mn\{(CH_2)_{16}CH_3\}(CO)_5]$ with Trityl Salt

Typically, 0.170g of manganese alkyl complex was dissolved in 5ml $CH_2Cl_2$ in a Schlenk tube with stirring under nitrogen. This solution was then transferred by syringe to another Schlenk tube containing 0.160g of $Ph_3CPF_6$ in 10ml

$CH_2Cl_2$. The reaction mixture was stirred under nitrogen at room temperature for 12h, after which time the solution was filtered and diethyl ether was added. However, after 24h no crystals had formed at -15°C so the solvent was removed under reduced pressure, leaving a yellow residue. This was extracted with hexane (*ca.* 8ml), filtered and recrystallized at -78°C. The resulting pale yellow microcrystalline solid was filtered off to give *ca.* 40% of the acyl products, $[Mn\{CO(CH_2)_{14}CH_3\}(CO)_5]$ and $[Mn\{CO(CH_2)_{16}CH_3\}(CO)_5]$. Characterization data are given in Table 3.5 (see Chapter 3).

### 7.3.4 Reaction of $[Mn\{(CH_2)_8CH_3\}(CO)_5]$ with Synthesis Gas in THF

The method outlined by Mapolie and Moss [8] was employed for this reaction; thus, the reaction was carried out in an autoclave which was charged with $[Mn\{(CH_2)_8CH_3\}(CO)_5]$ (0.630g; 1.955 mmol) and tetrahydrofuran (10ml). The autoclave was sealed and then pressurized with synthesis gas (1:1 $CO/H_2$) until a pressure of 40 atm.was reached. The mixture was then heated at 55°C for 2½h. During this time, the pressure rose rapidly to 94 atm., at which point it then remained fairly constant. The autoclave was allowed to cool down to room temperature and then the gases were vented. A dark brown mixture was obtained which yielded a yellow filtrate. The solvent was removed from this filtrate, leaving a pale yellow oil An IR spectrum (neat film) of the oily residue showed it to be a mixture of $CH_3(CH_2)_9OH$ and $[Mn_2(CO)_{10}]$, with the alcohol being the major component. The oil was dissolved in a minimum of a 1:1 mixture of $CH_2Cl_2$/hexane. This solution was then run through a short (1.2cm x 5cm) alumina column made up with hexane. Two bands were observed on the column, a faint yellow (almost colourless) band and a bright yellow band. The pale yellow band was eluted with 10% $CH_2Cl_2$/hexane and on evaporation of the solvent gave a pale yellow oil. This was identified as $CH_3(CH_2)_9OH$ on the basis of its IR [12] and $^1H$ NMR [13] spectra (46% yield). The second yellow band was eluted with $CH_2Cl_2$ and removal of the solvent under reduced pressure gave a yellow solid, the IR spectrum of which was identical to that of $[Mn_2(CO)_{10}]$ (14% yield).

### 7.3.5 Reaction of $[Mn_2(CO)_{10}]$ with 1-hexene and Synthesis Gas (in Tetrahydrofuran)

The above reaction was carried out in an autoclave which was charged with $[Mn_2(CO)_{10}]$ (0.25g; 1.282 mmol), tetrahydrofuran (10ml) and 1-hexene (0.541g; 6.428 mmol). The autoclave was sealed and then pressurized with synthesis gas (1:1 $CO/H_2$) until a pressure of 40 atm. was reached. The mixture was then heated at 74°C for 8½h. The autoclave was allowed to cool down to room temperature and then the gases were vented. A dark brown mixture was obtained which was filtered to give a pale yellow filtrate. The solvent was removed from this filtrate under reduced pressure, leaving a pale yellow oil. An IR spectrum (neat film) of the oily residue showed it to be a mixture of $CH_3(CH_2)_6OH$ and $[Mn_2(CO)_{10}]$, with the alcohol being the major component. No aldehydic species were observed. The oil was dissolved in a minimum of a 1:1 mixture of $CH_2Cl_2$/hexane. The solution was then run through a short (1.2cm x 5cm) alumina column made up with hexane. Two bands were observed on the column, a faint yellow (almost colourless) band and a bright yellow band. The pale yellow band was eluted with 10% $CH_2Cl_2$/hexane, which, after removal of the solvent under reduced pressure, left a pale yellow oil. This was identified as $CH_3(CH_2)_6OH$ on the basis of its IR [12] and $^1H$ NMR [13] spectra (27% yield). The second yellow band was eluted with $CH_2Cl_2$ and removal of the solvent under reduced pressure gave a yellow solid, the IR spectrum of which was identical to $[Mn_2(CO)_{10}]$ (88% recovery).

### 7.3.6 Reaction of $[Mn\{(CH_2)_{12}CH_3\}(CO)_5]$ with Synthesis Gas in Hexane

The same general procedure as outlined by Mapolie and Moss [8] was used for this reaction. The reaction was carried out in an autoclave which was charged with $[Mn\{(CH_2)_{12}CH_3\}(CO)_5]$ (0.910g; 2.405 mmol) and hexane (15 ml). The autoclave was sealed and pressurized with $CO/H_2$ until a pressure of 40 atm.was reached. The mixture was then heated to 55°C for 2½h. During this time the pressure rose rapidly to *ca.* 70 atm. at which point it then remained fairly constant. At the end of 2½h, the autoclave was allowed to cool down to room temperature and then the gases were vented. A dark brown mixture was obtained which gave a yellow/brown filtrate. The solvent was removed from this filtrate, leaving a yellow/brown oil. An IR spectrum ($\nu$ (CO) in $CH_2Cl_2$) of the oil showed it to be a mixture of $[Mn_2(CO)_{10}]$ and the alkoxycarbonyl $[Mn\{CO(O)CH_2(CH_2)_{12}CH_3\}(CO)_5]$. The oil was dissolved in a 1:2 mixture of $CH_2Cl_2$/hexane and this solution was then run through a short (1.2cm x 3cm) alumina column made up with 1:2 $CH_2Cl_2$/hexane. Two bands separated on the column. The first was a bright yellow band which was subsequently (on the basis of its IR) shown to be $[Mn_2(CO)_{10}]$. The second band was virtually colourless and removal of the solvent gave the alkoxycarbonyl compound as an off-white solid, which was recrystallized from petroleum ether (bp 80°-100°C) at -78°C to give a yield of 32%. The product, $[Mn\{CO(O)CH_2(CH_2)_{12}CH_3\}(CO)_5]$, was characterized by IR ( $\nu$(CO) in $CH_2Cl_2$ : 2126cm$^{-1}$, 2029cm$^{-1}$, 2010 (shoulder)cm$^{-1}$ and 1657cm$^{-1}$), melting point (35°-37°C), $^1$H NMR (in $CDCl_3$; $\delta$ = 3.64ppm (triplet, 2H), $MnCO(O)CH_2$; 1.58ppm (multiplet, 2H), $MnCO(O)CH_2CH_2$; 1.26ppm (broad singlet, 22H), $(CH_2)_x$ and 0.88ppm (triplet, 3H), $CH_3$) and its mass spectrum ($M^+$ = 436).

## 7.4 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 4

### 7.4.1 General Synthetic Route to the Compounds $[Re(COR)(CO)_5]$ (R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

$[Re_2(CO)_{10}]$ (1.00g; 1.53 mmol) in tetrahydrofuran (25ml) was stirred over a sodium amalgam (0.3g Na in 4ml Hg) for 2h at room temperature. During this time the solution changed colour from green to orange. The resulting orange solution of $Na[Re(CO)_5]$ (3.06 mmol) was then transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the acyl chloride, RCOCl (3.05 mmol). The solution went cloudy almost immediately with a precipitate forming. The reaction mixture was stirred for 3h at room temperature. After this time, the solvent was removed under reduced pressure, leaving a pale yellow residue. This was extracted with $CH_2Cl_2$ (2 x 30ml) and centrifuged at maximum speed for *ca.* 10 mins. The solvent was removed from the liquid portion under reduced pressure to give a pale yellow solid, which was extracted with hexane (*ca.* 15ml), filtered and recrystallized at -78°C. All of the products were pale yellow solids. The yields and characterization data are given in Tables 4.1 - 4.5 (see Chapter 4).

### 7.4.2 General Synthetic Route to the Compounds $[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$(n = 4-8;10)

A slight variation on a previously reported method [14] was used for the above syntheses. $[Re_2(CO)_{10}]$ (1.20g; 1.84 mmol) in tetrahydrofuran (25ml) was stirred over a sodium amalgam (0.3g Na in 4ml Hg) for 2h at room temperature. The resulting orange solution of $Na[Re(CO)_5]$ (3.68 mmol) was transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the diacyl chloride $ClCO(CH_2)_nCOCl$, (1.84 mmol). The solution went cloudy almost immediately with a precipitate forming. The reaction mixture was stirred for 3h at room temperature. After this time the solvent was removed under reduced pressure, leaving a creamy coloured residue. This was extracted with $CH_2Cl_2$ (2 x 25ml) and centrifuged at maximum speed for *ca.* 10 mins. The solvent was removed from the liquid portion under reduced pressure to give a creamy coloured solid which was recrystallized from warm acetone at -15°C. All of the products were off-white microcrystalline solids. The yields and characterization data are given in Tables 4.6 - 4.10 (see Chapter 4).

### 7.4.3 General Synthetic Route to the Compounds [Re(R)(CO)$_5$] (R = $C_2H_5$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

[Re(COR)(CO)$_5$] (1.0g) was dissolved in toluene (50ml) and the solution refluxed for 4h under $N_2$. The solution was then cooled down to room temperature and the solvent removed under reduced pressure to give the product as a yellow oil or yellow solid, which was then recrystallized from hexane at -78°C. The yields and characterization data are given in Tables 4.11 - 4.14 (see Chapter 4).

### 7.4.4 General Synthetic Route to the Compounds [Re(R)(CO)$_5$] (R = n-$C_{10}H_{21}$; n-$C_{12}H_{25}$; n-$C_{14}H_{29}$; n-$C_{16}H_{33}$; n-$C_{18}H_{37}$)

[$Re_2(CO)_{10}$] (1.10g; 1.69 mmol) in tetrahydrofuran (20ml) was stirred over a sodium amalgam (0.3g Na in 4ml Hg) for 2h at room temperature. The resulting orange solution of Na[Re(CO)$_5$] (3.37 mmol) was transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the alkyl bromide, RBr (3.37 mmol). The solution rapidly went cloudy with a precipitate forming. The mixture was stirred for 7h at room temperature. After this time, the solvent was removed under reduced pressure, leaving a pale yellow residue. This was extracted with $CH_2Cl_2$ (2 x 30ml) and centrifuged at maximum speed for *ca.* 10 mins. The solvent was removed from the liquid portion under reduced pressure to give a pale yellow solid. This was extracted with hexane (*ca.* 20ml), filtered and recrystallized at -78°C. All of the products were cream/yellow solids. The yields and characterization data are given in Tables 4.11 - 4.14 (see Chapter 4).

### 7.4.5 General Synthetic Route to the Compounds $[(CO)_5Re(CH_2)_nRe(CO)_5]$ (n = 4-8;10)

$[(CO)_5ReCO(CH_2)_nCORe(CO)_5]$ (0.8g) was dissolved in toluene (80ml) and the solution was refluxed for 4h under $N_2$. The solution was filtered while hot and the filtrate reduced to *ca.* 20ml. This was then cooled to -15°C, resulting in the formation of off-white crystals, which were filtered off to give the product. Yields and characterization data are given in Tables 4.15 - 4.18 (see Chapter 4).

### 7.4.6 Synthesis of $[(CO)_5Re(CH_2)_9Re(CO)_5]$

$[Re_2(CO)_{10}]$ (1.0g; 1.53 mmol) in tetrahydrofuran (20ml) was stirred over a sodium amalgam (0.2g Na in 3ml Hg) for 2h at room temperature. The resulting orange solution of $Na[Re(CO)_5]$ (3.06 mmol) was added dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing 1,9-dibromononane (0.44g; 1.54 mmol). The solution rapidly went cloudy with a precipitate forming. The reaction mixture was stirred for 8h at room temperature. After this time, the solvent was removed under reduced pressure, giving a pale yellow residue. This was extracted with

$CH_2Cl_2$ (2 x 20ml) and centrifuged at maximum speed for 10 mins. The solvent was removed from the liquid portion under reduced pressure to give a pale yellow solid. This was extracted with warm hexane (*ca.* 15ml) and recrystallized at -78°C to give a cream/yellow microcrystalline solid. The yield and characterization data are given in Tables 4.15 - 4.18 (see Chapter 4).

### 7.4.7 Decarbonylation of [Re(COR)(CO)$_5$] : Kinetic Studies

$$[Re(COR)(CO)_5] \xrightarrow{k} [Re(R)(CO)_5] + CO \qquad (5)$$

(R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; n-$C_{15}H_{31}$; n-$C_{17}H_{35}$)

Attempts were made to follow the decarbonylation reactions of the complexes [Re(COR)(CO)$_5$] (R = $CH_3$ to n-$C_9H_{19}$; n-$C_{11}H_{23}$; n-$C_{13}H_{27}$; $C_{15}H_{31}$; n-$C_{17}H_{35}$) by infrared spectroscopy in order to obtain rate constants for the reactions. Typically, 5ml of a 0.05M toluene solution of the acyl complex was placed in a constant temperature bath at 94°C and the disappearance of the highest energy ($A_1$) carbonyl vibration (*ca.* 2130cm$^{-1}$) was followed. However, as was outlined in Chapter 4, although it was established that the reactions went to completion and that the alkyl complexes [Re(R)(CO)$_5$] were formed in good yield, reliable rate data were not obtained from the infrared spectra for this section as (a) the peaks being monitored were broad and (b) the reactions were slow, taking several hours to reach completion. These problems could presumably be overcome by using a high-boiling saturated hydrocarbon solvent (*e.g.* n-octane, boiling point = 125°C). Thus, further experiments need to be performed on this system in order to make reliable kinetic measurements.

### 7.4.8 Reaction of [Re(R)(CO)$_5$] with Triphenylphosphine: Kinetic Studies

$$[Re(R)(CO)_5] + PPh_3 \xrightarrow{k} cis\text{-}[Re(R)(CO)_4(PPh_3)] + CO \qquad (6)$$

(R = $C_2H_5$ to n-$C_{18}H_{37}$)

Again, attempts were made to follow the reactions of [Re(R)(CO)$_5$] (R = $C_2H_5$ to n-$C_{18}H_{37}$) with PPh$_3$ by infrared spectroscopy in order to measure rate constants for the reactions. However, as with the decarbonylation reactions, and as was outlined in Chapter 4, reliable rate data were not obtained due to (a) the reactions being slow, taking several hours for completion and (b) the peaks in the infrared spectra being broad. Again, these problems could presumably be overcome by the use of a saturated hydrocarbon solvent of high boiling point. Further experiments thus need to be performed on this system. Typically, 5ml of a 0.04M toluene solution of the alkyl complex, [Re(R)(CO)$_5$], was placed in a constant temperature bath at 94°C and a 9-fold molar excess of PPh$_3$ was added. The disappearance of the highest energy ($A_1$) carbonyl vibration was followed. It was, however, established that the reactions all went to completion and that the phosphine-substituted alkyl products, *cis*-[Re(R)(CO)$_4$(PPh$_3$)], were formed. These were all relatively high melting yellow solids which were characterized by IR ( $\nu$(CO) in $CH_2Cl_2$ at *ca.* 2023cm$^{-1}$ (weak), 1954cm$^{-1}$ (shoulder), 1927cm$^{-1}$ (strong)) and $^1$H NMR (in $CDCl_3$; $\delta$ = *ca.* 0.8ppm (broad triplet, 3H)CH$_3$; 0.9ppm (complex, 2H)ReCH$_2$; 1.25ppm (broad singlet)(CH$_2$)$_x$ and 7.4ppm (complex, 15H) PPh$_3$). This data agrees well with the characterization data reported for *cis, cis*-[(PPh$_3$)(CO)$_4$Re(CH$_2$)$_4$Re(CO)$_4$(PPh$_3$)] [14].

## 7.5 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 5

### 7.5.1 General Synthetic Route to the Compounds $[Mn(CH_2C_6H_4X)(CO)_5]$ (where X = o-Br, m-Br, p-Br, o-$NO_2$, m-$NO_2$, p-$NO_2$, p-$CH_3$, H)

The above compounds were prepared using modified literature procedures [10,11]. Typically, $[Mn_2(CO)_{10}]$ (1.50g; 3.85 mmol) in tetrahydrofuran (25ml) was stirred over a sodium amalgam (0.3g Na in 4ml Hg) for 2h at room temperature. The resulting solution of $Na[Mn(CO)_5]$ (7.70 mmol) was transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the substituted benzyl bromide, $BrCH_2C_6H_4X$ (7.70 mmol). The reaction mixture was stirred at room temperature for 2h. After this time, the solvent was removed under reduced pressure, leaving a pale yellow oily solid. This was extracted with $CH_2Cl_2$ (2 x 30ml) and centrifuged at maximum speed for *ca.* 10 mins. The solvent was then removed from the liquid portion under reduced pressure to give a pale yellow solid, which was extracted with hexane (20ml) and filtered. Chromatography on an alumina column (1.5cm x 12cm) with hexane as eluent separated two yellow bands. The first was $[Mn_2(CO)_{10}]$ and the second yellow band contained the product, which, after removal of the solvent under reduced pressure, was recrystallized from hexane at -15°C. The p-$NO_2$ derivative was recrystallized from hexane at -78°C. All of the products were pale yellow solids. The yields and characterization data are given in Tables 5.1 - 5.4 (see Chapter 5).

### 7.5.2 General Synthetic Route to the Compounds $[CpFe\{(CH_2)_nC_6H_4X\}(CO)_2]$ (n = 1, X = o-Br, m-Br, p-Br, o-Cl, m-Cl, p-Cl, o-$CH_3$, m-$CH_3$, p-$CH_3$, H; n = 2, X = H; n = 3, X = H)

The above compounds were prepared using a modified literature procedure [15]. $[CpFe(CO)_2]_2$ (2.50g; 7.06 mmol) in tetrahydrofuran (30ml) was stirred over a sodium amalgam (0.4g Na in 4ml Hg) for 2h at room temperature. The resulting solution of $Na[CpFe(CO)_2]$ (14.12 mmol) was transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the phenylalkyl bromide, $Br(CH_2)_nC_6H_5$ (14.12 mmol) or substituted benzyl bromide, $BrCH_2C_6H_4X$ (14.12 mmol). The reaction mixture was stirred at room temperature for 5h. After this time the solvent was removed under reduced pressure to give a sticky brown oil, which was extracted with $CH_2Cl_2$ (2 x 35ml) and centrifuged at maximum speed for *ca.* 15 mins. The solvent was removed from the liquid portion under reduced pressure to give a yellow/brown oil. This was extracted with hexane (35ml) and filtered. Chromatography on an alumina column (2cm x 10cm) separated two bands. The first (yellow) band containing the product was eluted with hexane, while the second (red) band containing $[CpFe(CO)_2]_2$ remained on the column. The product was recrystallized from hexane at -15°C. All of the products were yellow/orange solids. The yields and characterization data are given in Tables 5.5-5.8 (see Chapter 5).

### 7.5.3 Reaction of $[Mn(CH_2C_6H_4X)(CO)_5]$ with Triphenylphosphine : Kinetic Studies

$$[Mn(CH_2C_6H_4X)(CO)_5] + PPh_3 \xrightarrow{k} cis\text{-}[Mn(COCH_2C_6H_4X)(CO)_4(PPh_3)] \qquad (7)$$

(X = o-Br, m-Br, p-Br, o-$NO_2$, m-$NO_2$,H)

The method reported by Cotton and co-workers [10,11] was utilized for these kinetic measurements. Kinetic data for CO insertion (alkyl migration) were obtained by monitoring the decrease in intensity of the highest energy ($A_1$) carbonyl vibration (*ca.* 2108cm$^{-1}$). A solution of the manganese benzyl complex in acetonitrile (10ml of *ca.* 0.008M solution) was placed in a Schlenk tube in a constant temperature bath at 30.0°C, at which point the temperature dropped slightly. When the temperature had reached 30.0°C again, an infrared spectrum was run, corresponding to time = 0. The triphenylphosphine (typically, a 15-molar excess) was then added to the solution in the Schlenk tube. Time = 0 was taken at the point when half of the $PPh_3$ had been added. Aliquots were then removed periodically and the infrared transmission measured using the attached ordinate data processing facility. The reaction was kept under nitrogen for the duration of the experiment. The temperature remained constant to within 0.5°C. A plot of ln $(I\infty/It)$ versus time yielded $k_{OBS}$ ($I\infty$ = intensity at time = $\infty$, It = intensity at time = t). The results were analyzed over *ca.* 75% of the reaction by linear regression. Errors in the $k_{OBS}$ values are generally around 4%. Reactions were followed for approximately three half-lives. Results are given in Table 5.9 (see Chapter 5).

### 7.5.4 Reaction of $[CpFe\{(CH_2)_nC_6H_4X\}(CO)_2]$ with Triphenylphosphine : Kinetic Studies

$$[CpFe\{(CH_2)_nC_6H_4X\}(CO)_2] + PPh_3 \xrightarrow{k} [CpFe\{(CH_2)_nC_6H_4X\}(CO)(PPh_3)] \quad (8)$$

(n = 1, X = o-Br, m-Br, p-Br, o-Cl, m-Cl, p-Cl, o-$CH_3$, m-$CH_3$, p-$CH_3$,H; n = 2, X-H,; n = 3, X = H)

The method outlined by Cotton and Markwell [16] was used for these studies. Kinetic data for the CO insertion (alkyl migration) process was obtained by monitoring the decrease in intensity of the highest energy carbonyl vibration (*ca.* 2012cm$^{-1}$). A solution of the iron benzyl/alkylphenyl complex in acetonitrile (10ml of *ca.* 0.008M solution) was placed in a Schlenk tube in a constant temperature bath at 30.0°C, at which point the temperature dropped slightly. When the temperature had reached 30.0°C again, an infrared spectrum was run, corresponding to time = 0. The triphenylphosphine (typically, a 15-molar excess) was then added to the solution in the Schlenk tube. Time = 0 was taken at the point when half of the $PPh_3$ had been added. Aliquots were then removed periodically and the infrared transmission measured using the attached ordinate data processing facility. The reaction was kept under nitrogen for the duration of the experiment. The temperature remained constant to within 0.5°C. However, as was discussed in chapter 5, it was observed that none of the benzyl complexes, $[CpFe(CH_2C_6H_4X)(CO)_2]$, even the methyl-substituted species, underwent reaction with triphenylphosphine. The temperature was raised to 50°C, and then 80°C, and an oxidant, $AgBF_4$ (a 5-molar % relative to the iron benzyl complex) was added in an attempt to induce a reaction to take place, but still no reaction occurred. The only compounds that were observed to react with $PPh_3$ were the phenylethyl and phenylpropyl derivatives, $[CpFe(CH_2CH_2C_6H_5)(CO)_2]$ and $[CpFe(CH_2CH_2CH_2C_6H_5)(CO)_2]$. Thus, only the rate data for these two species could be analyzed. A plot of ln ($I\infty/It$) versus time yielded $k_{OBS}$ ($I\infty$ = intensity at time = ∞, It = intensity at time = t). The results were analyzed over *ca.* 75% of the reaction by linear regression. Errors in the $k_{OBS}$ values are generally around 5%. Reactions were followed for approximately three half-lives. Results are given in Table 5.11 (see Chapter 5).

## 7.6 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 6

### 7.6.1 The Preparation of *eq*-$[(CO)_5MnMn(CO)_4(L)]$ (L = $=\overline{CCH_2CH_2CH_2O}$, $=\overline{CCH_2CH_2CH(CH_3)O}$, $=\overline{CCH_2CH(CH_3)CH_2O}$, $=\overline{CCH_2CH_2CH_2CH_2O}$, $=\overline{CCH_2CH_2CH_2CH(CH_3)O}$)

The above compounds were prepared using a modified literature procedure [17]. $[Mn_2(CO)_{10}]$ (2.00g; 5.13 mmol) in tetrahydrofuran (25ml) was stirred over a sodium amalgam (0.4g Na in 4ml Hg) for 2h at room temperature. The resulting solution of Na$[Mn(CO)_5]$ (10.25 mmol) was transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the dihaloalkane, $Br(CH_2)_nBr$, $Br(CH_2)_nCH(CH_3)Br$ or $BrCH_2CH(CH_3)CH_2Cl$ (5.13 mmol). The reaction mixture was stirred at room temperature for 18h. For the reaction between $Na[Mn(CO)_5]$ and $BrCH_2CH(CH_3)CH_2Cl$, the reaction mixture was heated at reflux under nitrogen for 2h. The solvent was then removed under reduced pressure, leaving an orange oil which was extracted with hexane (30ml) and filtered. Chromatography on a short alumina column (2cm x 7cm) with hexane as eluent separated two yellow bands. The first band was $[Mn_2(CO)_{10}]$ and the second band contained the product. The carbene complexes were recrystallized from hexane at -15°C to give yellow/orange crystals. The yields and characterization data are given in Tables 6.2 - 6.5 (see Chapter 6).

### 7.6.2 Preparation of *eq*-$[(CO)_5MnMn(CO)_4\{=\overline{CC(CH_3)_2CH_2CH_2O}\}]$

This compound *eq*-$[(CO)_5MnMn(CO)_4(=\overline{CCH_2CH_2CH_2O})$(1.23g; 2.84 mmol) in tetrahydrofuran (15ml) was stirred over a sodium amalgam (0.2g Na in 3ml Hg) for 2h at room temperature. The resulting solution was transferred dropwise by syringe, with rapid stirring, to a Schlenk tube at 0°C covered with aluminium foil containing methyl iodide, $CH_3I$ (1.01g; 7.10 mmol). The reaction mixture was stirred at room temperature for 20h. The solvent was then removed under reduced pressure, leaving an orange oil which was extracted with hexane (15ml) and filtered. Chromatography on a short alumina column (2cm x 8cm) with hexane as eluent separated two yellow bands. The first band was *eq*-$[(CO)_5MnMn(CO)_4$-$(=\overline{CCH_2CH_2CH_2O})]$ and the second band contained the product, which was recrystallized from hexane at -15°C to give yellow/orange crystals. The yield and characterization data are given in Tables 6.2 - 6.5 (see Chapter 6).

### 7.6.3 Recrystallization of *eq*-$[(CO)_5MnMn(CO)_4(L)]$ (L = $=CCH_2CH_2CH_2O$, $=CCH_2CH_2CH(CH_3)O$, $=CCH_2CH_2CH_2CH_2O$, $=CCH_2CH_2CH_2CH(CH_3)O$) for X-ray Studies

Single crystals suitable for X-ray analysis were prepared by slow recrystallization of the carbene complexes from a dilute, filtered, $N_2$-saturated hexane solution at -15°C. After *ca.* 3 days, a few crystals had formed and a suitable crystal of each compound was selected for X-ray structural determination. See Tables 6.6 and 6.9 in Chapter 6 for experimental details of X-ray analyses.

### 7.6.4 Kinetic Studies on the Deuterium Exchange Reaction

Typically, *ca.* 130mg of carbene complex was dissolved in 0.500ml of acetone-$d_6$ in an NMR tube and a $^1H$ NMR spectrum was run on a Varian EM360 60MHz spectrometer. The solution was placed in a thermostatted water bath at 40°C and 0.100ml of deuterium oxide, $D_2O$, was added. The NMR tube was then withdrawn periodically, the solution was cooled to *ca.* 6°C and a $^1H$ NMR spectrum was run. The disappearance of the peak due to the protons attached to the $\alpha$-carbon atom of the carbene ring (*ca.* 3.5ppm) was monitored. The temperature remained constant to within a 5°C. A plot of ln (It/Io) versus time, t (It = integration at time = t, Io = integration at time = 0) gave a straight line of slope $k_{OBS}$, the observed rate constant for the deuterium exchange reaction. The results were analyzed by linear regression. The reactions were followed for approximately three half-lives. The results are given in Table 6.12 (see Chapter 6).

### 7.6.5 Reaction of *eq*-$[(CO)_5MnMn(CO)_4(L)]$ with Triphenylphosphine (L = $=\overline{CCH_2CH_2CH_2O}$, $=\overline{CCH_2CH_2CH(CH_3)O}$, $=\overline{CCH_2CH(CH_3)CH_2O}$, $=\overline{CC(CH_3)_2CH_2CH_2O}$, $=\overline{CCH_2CH_2CH_2CH_2O}$, $=\overline{CCH_2CH_2CH_2CH(CH_3)O}$)

Typically, *ca.* 0.50g of carbene complex was dissolved in 70ml $N_2$-saturated toluene. An excess (5-molar) of triphenylphosphine was then added and the reaction mixture was heated at reflux as no reaction occurred at room temperature, even after several days. After heating at reflux for *ca.* 2h the reaction mixture was cooled down to room temperature and the solvent removed under reduced pressure to give an orange oil. This was extracted with a minimum of $CH_2Cl_2$, hexane was added and the solution cooled to -15°C. After *ca.* 5 days, orange crystals had formed, which were characterized by melting point, $^1H$ NMR (in $CDCl_3$), IR ( $\nu(CO)$ in $CH_2Cl_2$) and elemental analysis. These data merely confirmed, however, that the product of the reactions was the phosphine-substituted dimer, $[Mn_2(CO)_8(PPh_3)_2]$ in each case.

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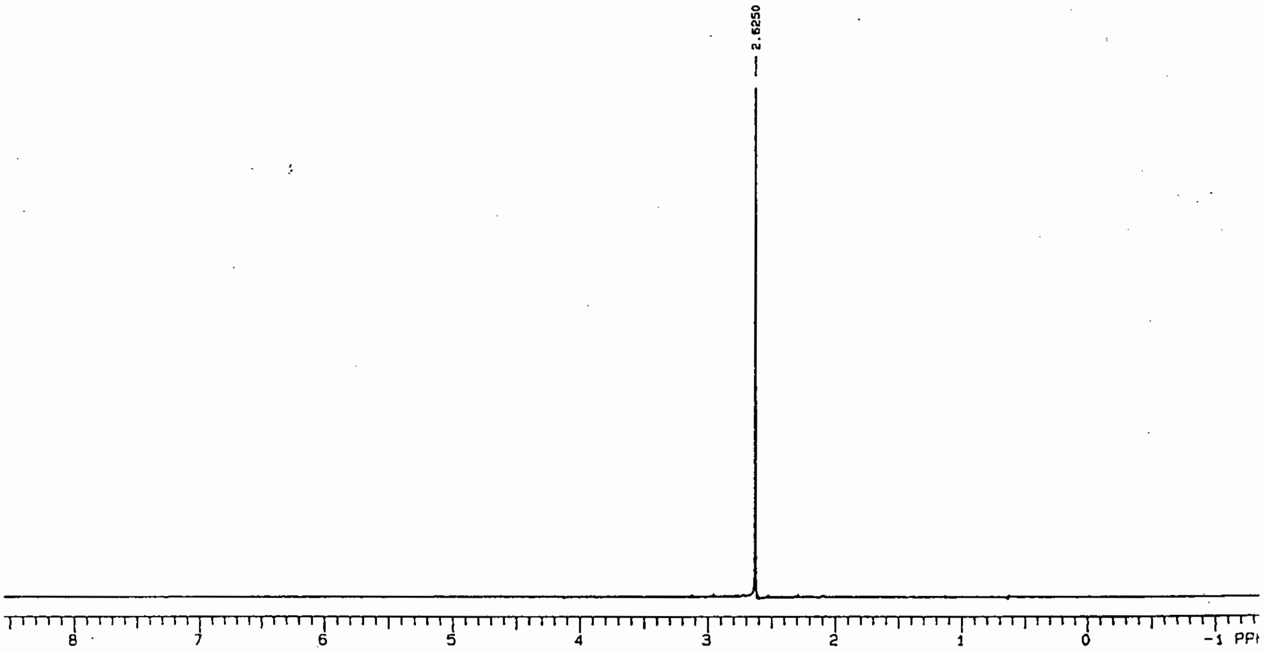
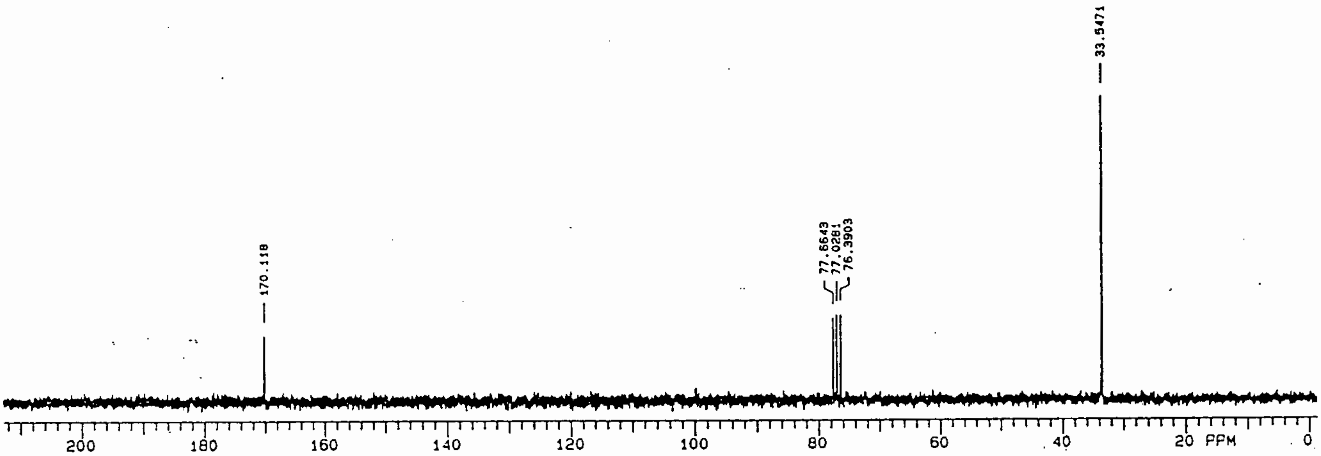
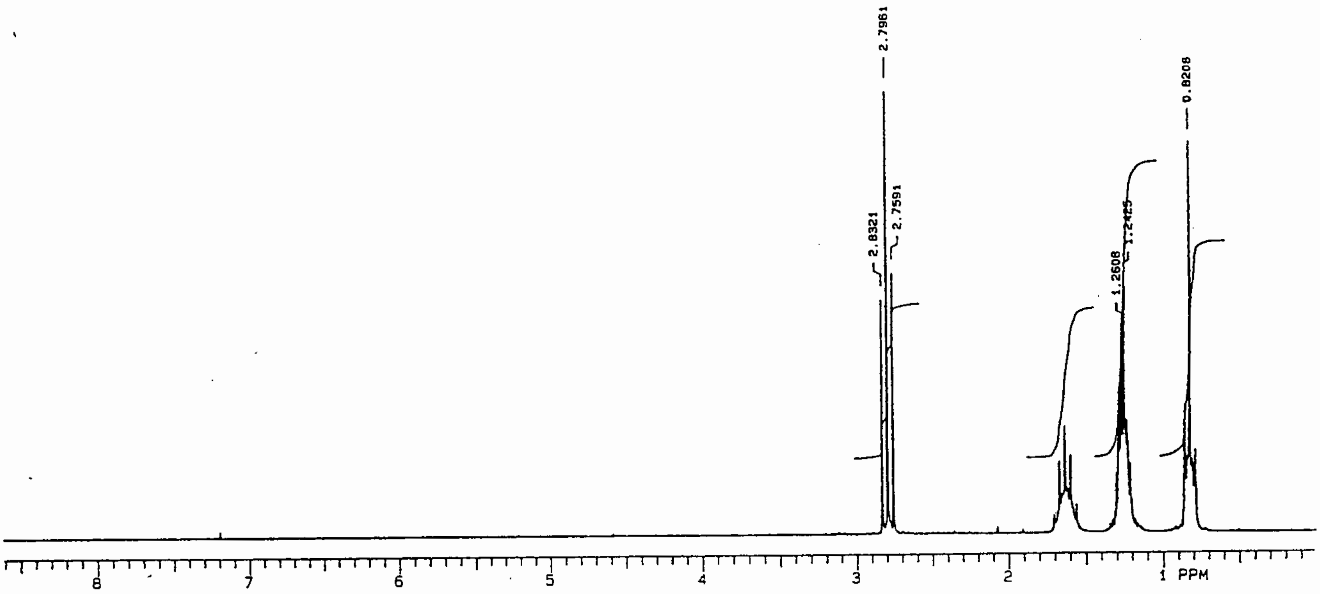
# APPENDICES



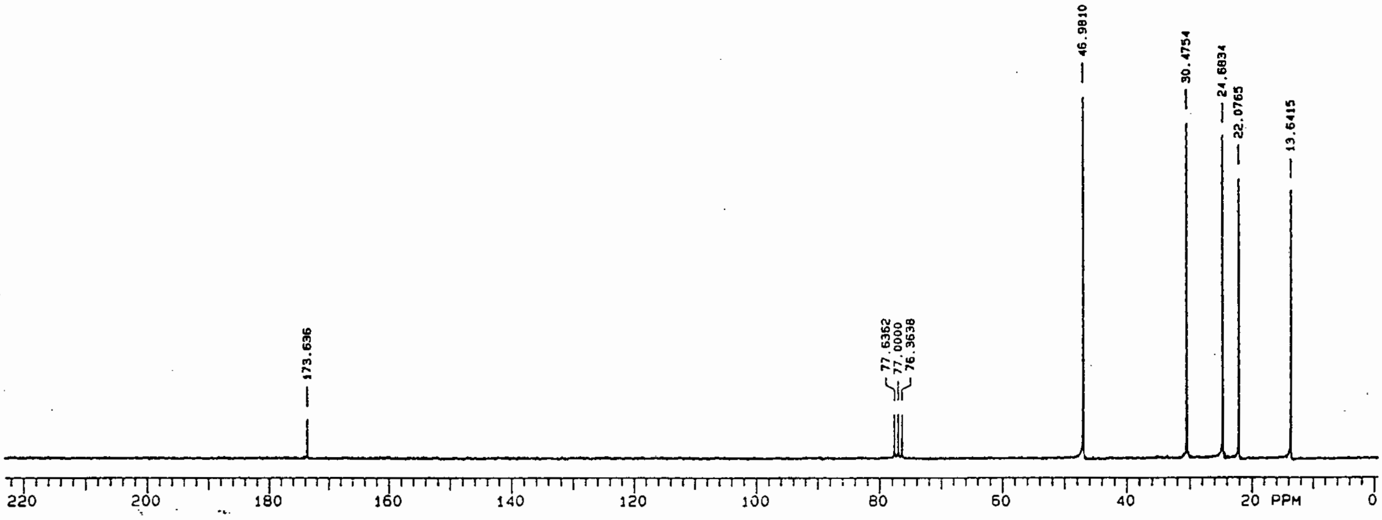
Appendix 1a $^1$H NMR Spectrum of $ClCOCH_3$



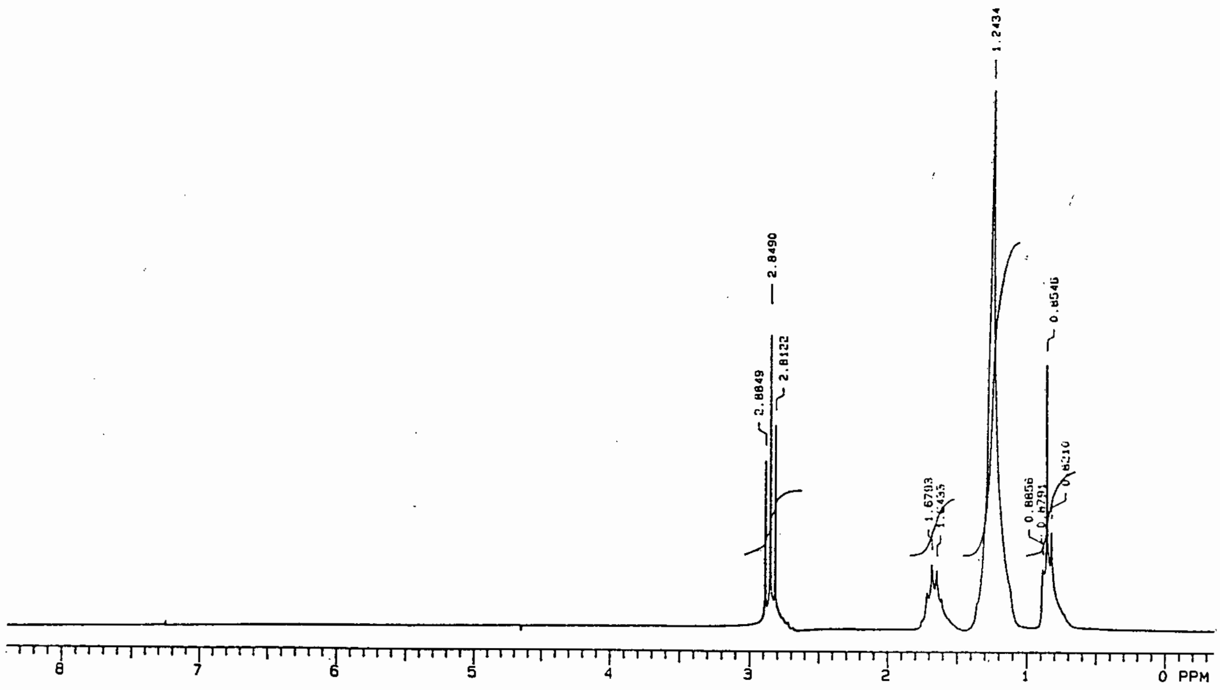
Appendix 1b $^{13}$C NMR Spectrum of $ClCOCH_3$



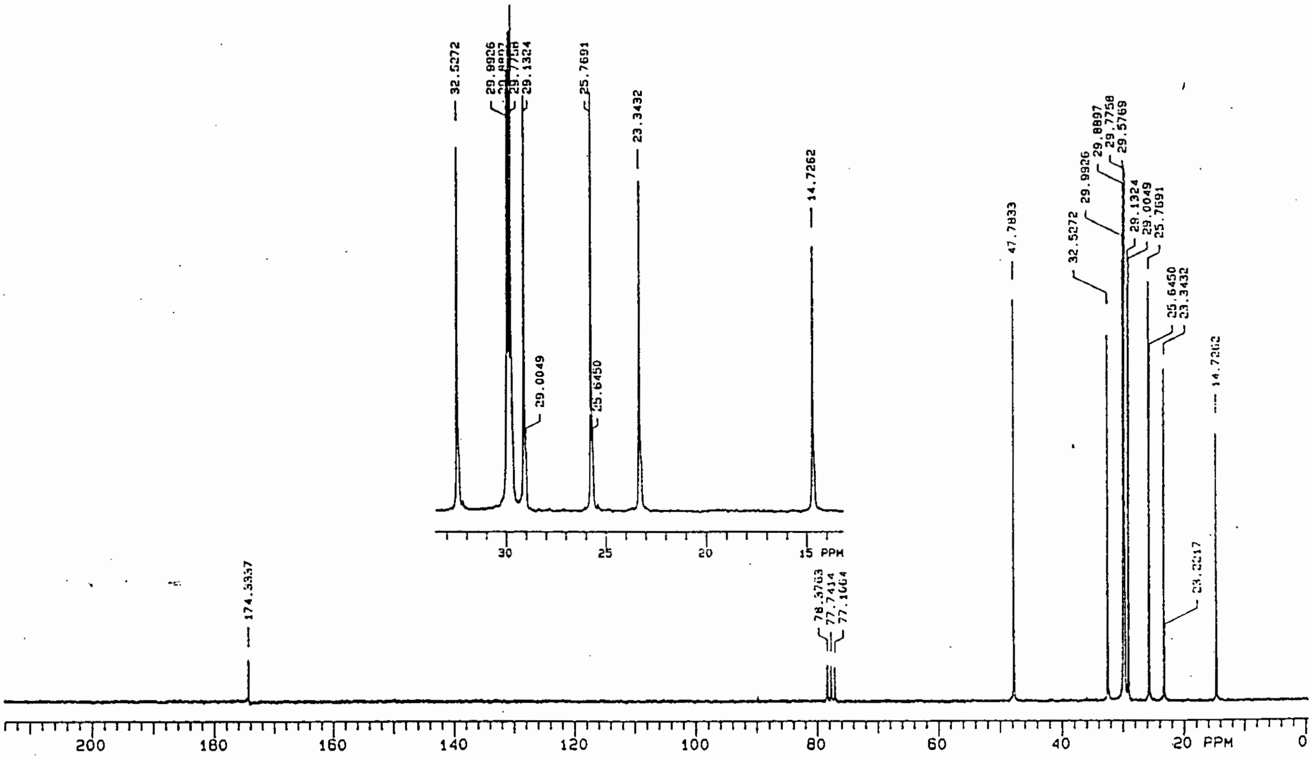
Appendix 1c $^1$H NMR Spectrum of $ClCO(CH_2)_4CH_3$



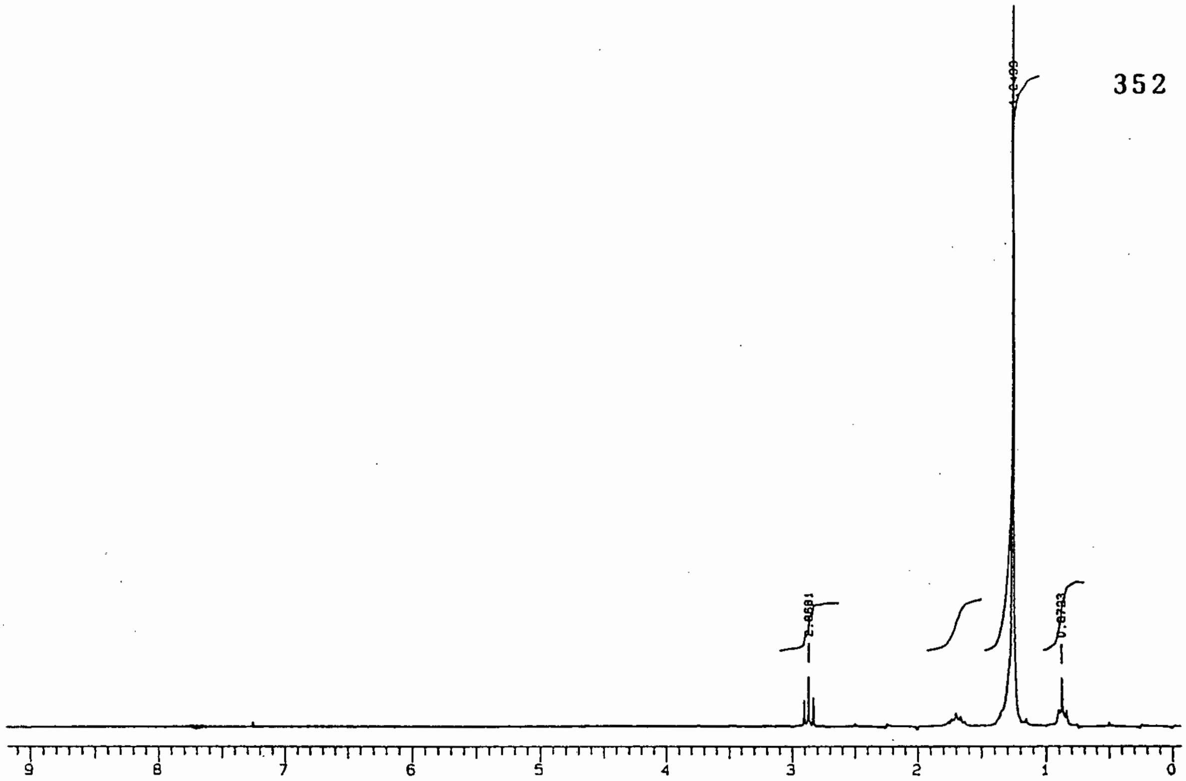
Appendix 1d $^{13}$C NMR Spectrum of $ClCO(CH_2)_4CH_3$



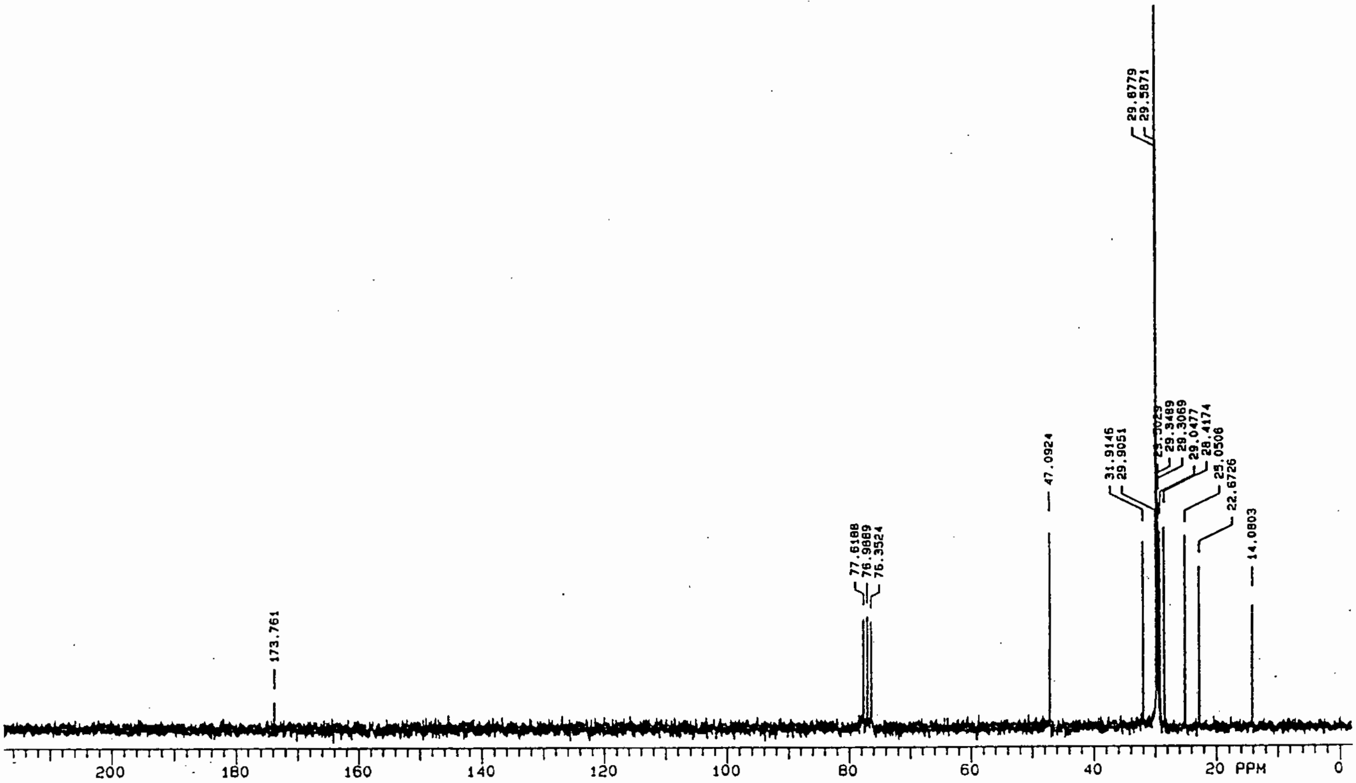
Appendix 1e $^{1}$H NMR Spectrum of ClCO(CH$_2$)$_8$CH$_3$



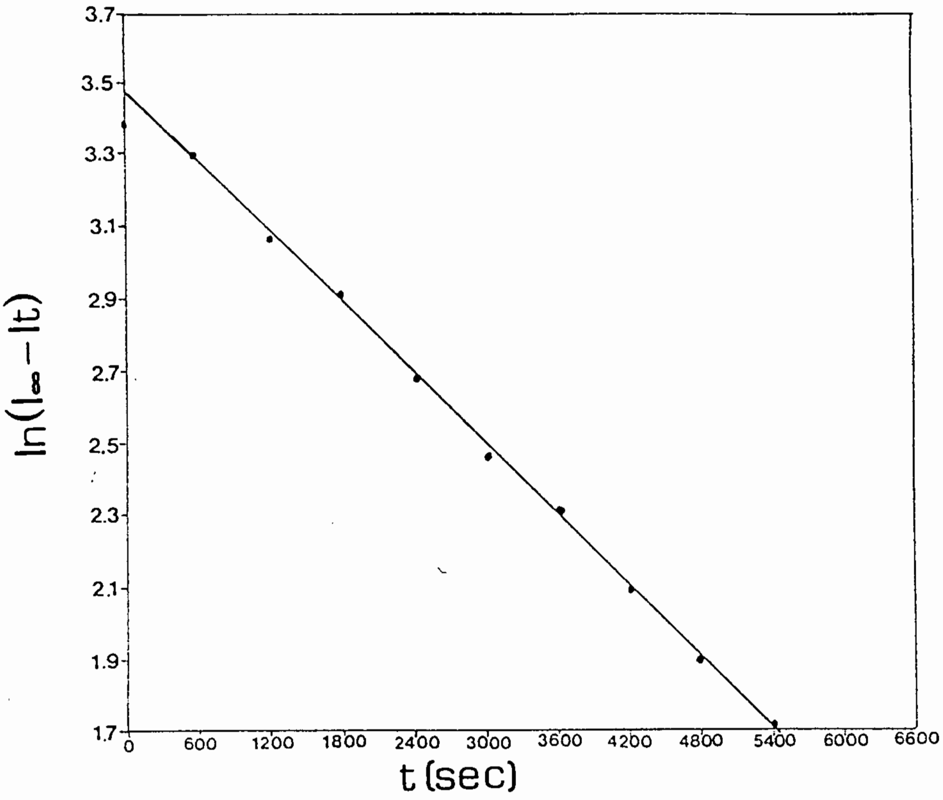
Appendix 1f $^{13}$C NMR Spectrum of ClCO(CH$_2$)$_8$CH$_3$



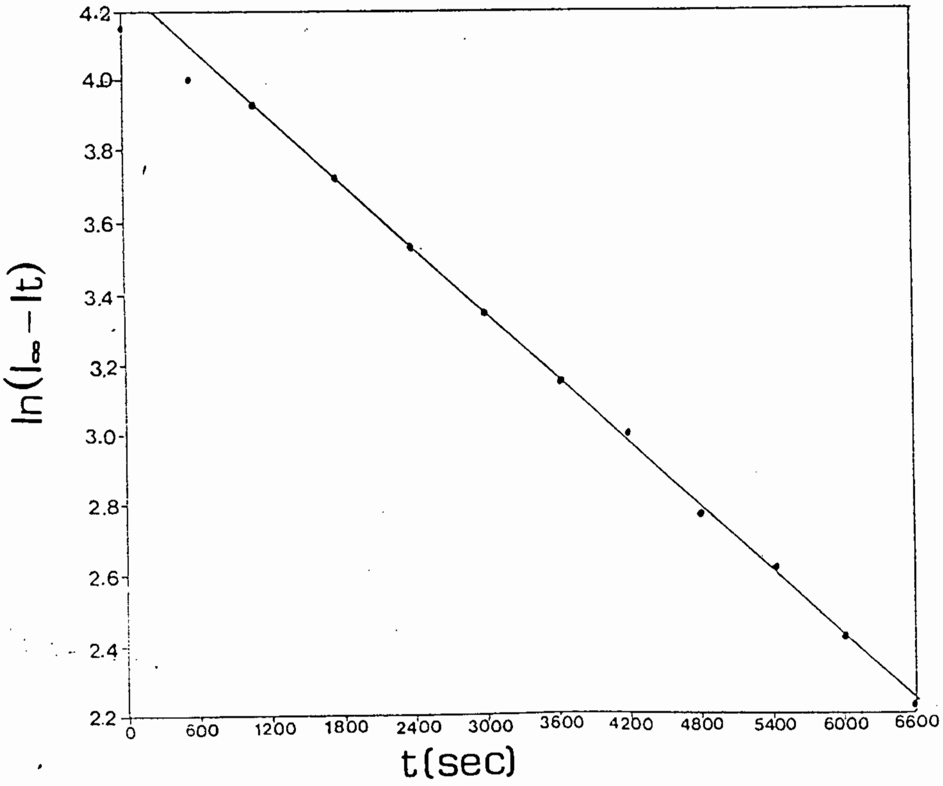
Appendix 1g $^1H$ NMR Spectrum of $ClCO(CH_2)_{16}CH_3$



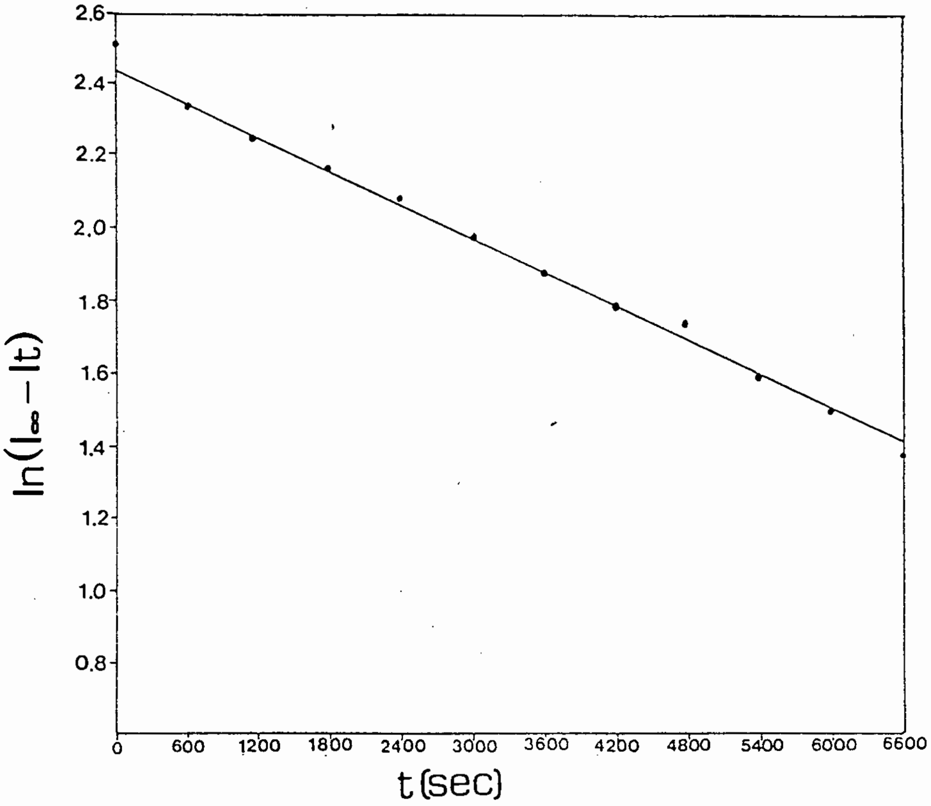
Appendix 1h $^{13}C$ NMR Spectrum of $ClCO(CH_2)_{16}CH_3$



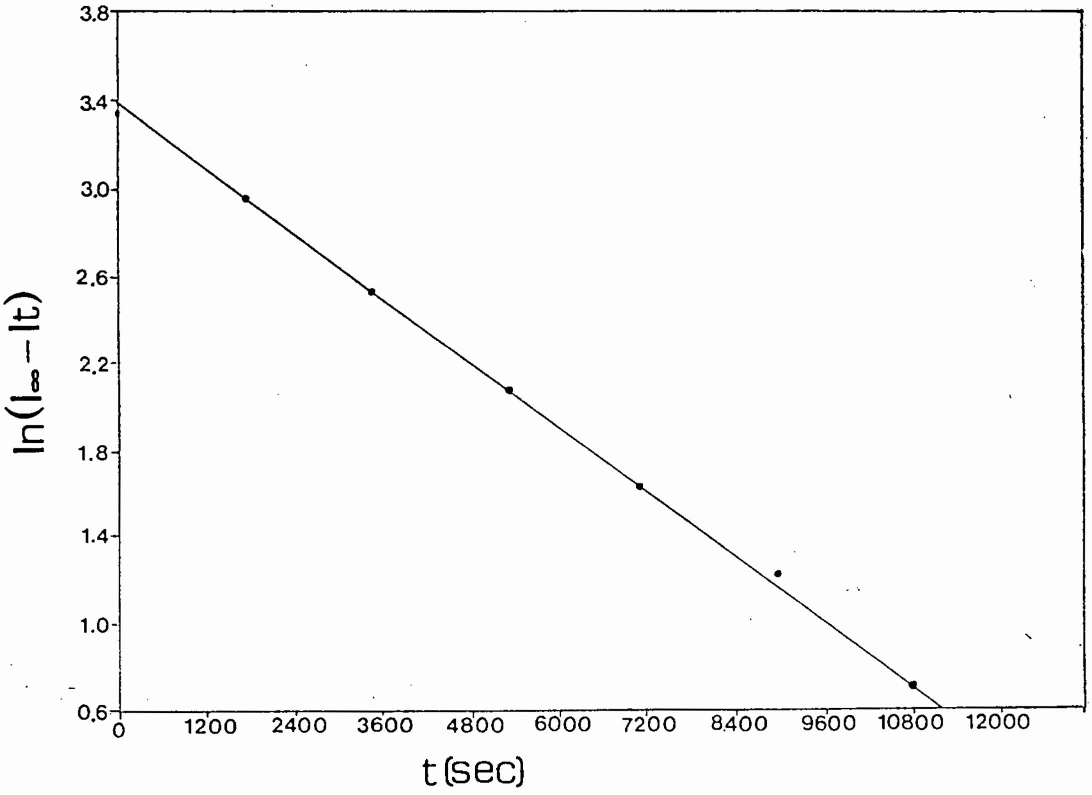
<u>Appendix 2a</u> Plot of ln(I∞-It) versus time for decarbonylation of $[Mn\{CO(CH_2)_6CH_3\}(CO)_5]$ in hexane at 55.5°C



<u>Appendix 2b</u> Plot of ln(I∞-It) versus time for the reaction of $[Mn\{(CH_2)_{12}CH_3\}(CO)_5]$ with $PPh_3$ in hexane at 32°C



<u>Appendix 3a</u> Plot of ln(I∞-It) versus time for the reaction of $[Mn(CH_2C_6H_4\text{-}m\text{-}Br)(CO)_5]$ with $PPh_3$ in acetonitrile at 30°C



<u>Appendix 3b</u> Plot of ln(I∞-It) versus time for the reaction of $[CpFe(CH_2CH_2CH_2C_6H_5)(CO)_2]$ with $PPh_3$ in acetonitrile at 30°C

| R | k<br>($\times 10^4 sec^{-1}$) |
|---|---|
| $CH_3$ | 1.5 |
| $C_2H_5$ | 2.8 |
| n-$C_3H_7$ | 3.0 |
| n-$C_4H_9$ | 3.0 |
| n-$C_5H_{11}$ | 3.1 |
| n-$C_6H_{13}$ | 3.2 |
| n-$C_7H_{15}$ | 3.6 |
| n-$C_8H_{17}$ | 3.9 |
| n-$C_9H_{19}$ | 4.0 |
| n-$C_{11}H_{23}$ | 3.7 |
| n-$C_{13}H_{27}$ | 3.6 |
| n-$C_{15}H_{31}$ | 3.4 |
| n-$C_{17}H_{35}$ | 3.2 |

## Appendix 4a Estimates of Rate Constants for the Decarbonylation Reactions of $[Re(COR)(CO)_5]$

| R | k<br>($\times 10^4$ sec$^{-1}$) |
|---|---|
| $C_2H_5$ | 0.15 |
| n-$C_3H_7$ | 0.15 |
| n-$C_4H_9$ | 0.15 |
| n-$C_5H_{11}$ | 0.20 |
| n-$C_6H_{13}$ | 0.20 |
| n-$C_7H_{15}$ | 0.20 |
| n-$C_8H_{17}$ | 0.30 |
| n-$C_9H_{19}$ | 0.30 |
| n-$C_{11}H_{23}$ | 0.30 |
| n-$C_{12}H_{25}$ | 0.30 |
| n-$C_{13}H_{27}$ | 0.30 |
| n-$C_{14}H_{29}$ | 0.30 |
| n-$C_{15}H_{31}$ | 0.30 |
| n-$C_{16}H_{33}$ | 0.20 |
| n-$C_{17}H_{35}$ | 0.20 |
| n-$C_{18}H_{37}$ | 0.20 |

Appendix 4b Estimates of Rate Constants for the Reaction of [Re(R)$(CO)_5$] with Triphenylphosphine