HETEROMETALLIC COMPLEXES CONTAINING COBALT AND CHROMIUM: SYNTHESIS, CHARACTERIZATION AND PROPERTIES

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To my wife, Charlene

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ABSTRACT

Heterometallic transition metal complexes have been extensively studied and the synthesis and chemistry of many complexes of the type has been reported. This thesis focuses on heterometallic complexes containing cobalt and chromium.

Chapter 1 is a comprehensive review of known heterometallic complexes containing cobalt and chromium, paying particular attention to the synthesis and properties of the complexes.

Chapter 2 reports the synthesis and properties of some new heterobimetallic complexes containing cobalt and chromium, as well as some new monometallic complexes of both cobalt and chromium. The monometallic complexes served either as precursors to the heterobimetallic complexes, or are potential precursors to heterobimetallic complexes containing cobalt and chromium.

The monometallic chromium complexes of the type (η^6-arene)$Cr(CO)_3$ (arene = $C_6H_5NHCH_2Ph$ **1**, $[C_6H_4(CH_2OH)_2$-1,4] **2**, $C_6H_5\{(CH_2)_4OH\}$ **3**, $[C_6H_4(CH_2Cl)_2$-1,4] **4** and $C_6H_5\{(CH_2)_4Cl\}$ **5**, were prepared for the first time. Complexes **1** - **3** were prepared by the thermal reaction between $Cr(CO)_6$ and the free arenes. The hydroxy complexes, **2** and **3**, were converted to the respective chloride complexes **4** and **5**, by the action of concentrated hydrochloric acid.

The series of mononuclear cobaloxime complexes $[\{(py)(DH)_2CoCH_2\}$-$C_6H_4\{CH_2Br\}$-1,n] (n = 4, **6**; n = 3, **7**; n = 2, **8**) have been prepared by reacting the appropriate dibromoxylene, $[C_6H_4(CH_2Br)_2$-1,n], with an equimolar amount of $[Co(DH)_2(py)Cl]$ in the presence of excess sodium borohydride. These

mononuclear cobaloxime complexes could be reacted with a further mole of $[Co(DH)_2(py)Cl]$, to yield the corresponding dinuclear cobaloxime complexes $[C_6H_4\{CH_2Co(DH)_2(py)\}_2\text{-}1,n]$ (n = 4, **9**; n = 3, **10**; n = 2, **11**). The reaction of $[C_6H_4(COCl)_2\text{-}1,4]$ with two molar equivalents of $[Co(DH)_2(py)Cl]$, yielded the phenylene bridged complex $[C_6H_4\{Co(DH)_2(py)\}_2\text{-}1,4]$ **12**, directly.

Reaction of the acylium ion, $[(CO)_9Co_3CCO]^+[AlCl_4{\cdot}AlCl_3]^-$, with benzyl alcohol, yielded the tricobalt cluster complex $(CO)_9Co_3CC(O)OCH_2Ph$ **13**. A similar reaction of the diol $[C_6H_4(CH_2OH)_2\text{-}1,4]$, with two molar equivalents of the acylium ion, resulted in the formation of the hexanuclear complex $[C_6H_4\{CH_2OC(O)CCo_3(CO)_9\}_2\text{-}1,4]$ **14**.

The heterobimetallic complexes $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **15** and $[\eta^6\text{-}C_6H_4\{CH_2Co(DH)_2(py)\}_2\text{-}1,4]Cr(CO)_3$ **16** were prepared from $[\eta^6\text{-}C_6H_5CH_2Cl]Cr(CO)_3$ and $[\eta^6\text{-}C_6H_4(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$ respectively, by similar reaction procedures to those used for the mononuclear and dinuclear cobaloxime complexes (**6** - **12**). Complexes **15** and **16** represent the first heterobimetallic complexes containing cobalt and chromium, which have been prepared from a cobaloxime. The molecular structure of **15** was determined by x-ray crystallography.

The complex $[\eta^6\text{-}C_6H_5CCo_3(CO)_9]Cr(CO)_3$ **17**, had been briefly reported previously in the literature. However, no experimental details or characterization data were provided. We now describe the successful synthesis of this complex, including the full preparative procedure and characterization data.

The complexes $[\eta^6\text{-}C_6H_5CH_2OC(O)CCo_3(CO)_9]Cr(CO)_3$ **18** and $[\eta^6\text{-}C_6H_5\{(CH_2)_4OC(O)CCo_3(CO)_9\}]Cr(CO)_3$ **19**, were prepared from the respective

reactions of $[\eta^6\text{-}C_6H_5CH_2OH]Cr(CO)_3$ and **3**, with equimolar amounts of the acylium ion. A similar reaction of **2** with two molar amounts of the acylium ion, yielded $[\eta^6\text{-}C_6H_4\{CH_2OC(O)CCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$ **20**.

Chapter 3 describes some studies into the use of the new heterobimetallic complexes as precursors to supported metal catalysts for the CO hydrogenation reaction. Complexes **15**, **16** and **19** were loaded onto inorganic oxide supports and studied by FT-IR, DSC and SEM techniques. Decomposed samples of supported **15** and **16**, were found to be active CO hydrogenation catalysts with the activities increasing as Co:Cr atomic ratios increased.

GLOSSARY OF ABBREVIATIONS

Å	Angstrom
Bu^n	n-Butyl group
Bu^t	t-Butyl group
cdpp	1,1′-bis(diphenylphosphino)cobaltocenium
CI	Chemical ionisation
[Co]	$Co(DH)_2(py)$ group
Cp	Cyclopentadienyl group
Cp′	Methylcyclopentadienyl group
Cp^*	Pentamethylcyclopentadienyl group
C^{tert}	Tertiary carbon atom
dec.	Decomposed
DH	Monoanion of dimethylglyoxime
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
DSC	Differential scanning calorimetry
E. I.	Electron impact (mass spectrometry)
Et	Ethyl group
FT-IR	Fourier transform infrared spectroscopy
GHSV	Gas hourly space velocity
HETCOR	Heteronuclear correlation
hr(s)	Hour(s)
IR	Infrared
K	Kelvin
L, Ln	Ligand/s

M	Transition metal atom
M^+	Molecular ion
M.P.	Melting point
Me	Methyl group
mes	Mesityl group
ms	mass spectroscopy
mw	molecular weight
m/z	mass to charge ratio
nbd	norbornadiene
NMR	Nuclear magnetic resonance
Ph	Phenyl group
ppm	Parts per million
Pr^i	isopropyl group
py	Pyridine
R	Alkyl group
RT	Room temperature
sal	Salicylaldiminato group
salen	N,N′-ethylenebis(salicylideneiminato) group
SEM	Scanning electron microscopy
SV	Space velocity
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Tetramethylsilane

PUBLICATIONS AND CONFERENCE PROCEEDINGS

PUBLICATIONS

1. Transition metal complexes containing cobalt and chromium: Synthesis, characterization and properties.
   M. R. Domingo and J. R. Moss, Manuscript in preparation

2. Synthesis, characterization and properties of some new heterobimetallic complexes of cobalt and chromium, and their precursors.
   M. R. Domingo, A. Irving and J. R. Moss, Manuscript in preparation

CONFERENCE PROCEEDINGS

1. Heterobimetallic complexes containing cobalt and chromium as catalysts.
   M. R. Domingo, A. Nash, St. J. Babb and J. R. Moss
   Abstracts, Annual Meeting Catalysis and Catalytic Processing, Catalysis Society of South Africa, Gordons Bay, Republic of South Africa, September 1990

2. Early-late heterobimetallic complexes.
   M. R. Domingo, M. Naidoo and J. R. Moss
   31st Convention of the South African Chemical Institute, Grahamstown, Republic of South Africa, June 1991

LECTURES

Heterobimetallic complexes of cobalt and chromium as catalyst precursors.
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CHAPTER 1

HETEROMETALLIC TRANSITION METAL COMPLEXES CONTAINING BOTH COBALT AND CHROMIUM - SYNTHESIS, CHARACTERIZATION AND PROPERTIES:- A REVIEW

1.1 INTRODUCTION

Heterometallic transition metal complexes have been the object of much research. Among the reasons for interest in such complexes is their potential catalytic applications, both as models for understanding catalytic systems and as catalysts, or catalyst precursors [1]. Currently, the synthesis and reactivity of heterometallic complexes containing widely divergent transition metals, are enjoying much attention [1 - 5].

Complexes containing both an early and a late transition metal are of particular interest, since they possess both the electron-pushing and electron-withdrawing characters of the late and early transition metals, respectively. The cooperative activation of small substrate molecules, such as CO, could thus be envisaged for such complexes. Late transition metals are known to activate CO by bonding to the electron deficient carbon atom [6]. If the bound CO interacts further with a proximate acidic, early transition metal through the electron rich oxygen atom, the interaction could result in an enhancement of activation. As late transition metals also have the ability to activate H_2 [7], it can be seen how such early-late heterobimetallic compounds could be exploited in catalytic applications.

Our interest in heterometallic complexes arises primarily from their potential use as catalyst precursors for the Fischer-Tropsch reaction. Cobalt has long been known to be an active Fischer-Tropsch metal. A patent for the production of liquid hydrocarbons using a cobalt catalyst [8] was issued as far back as 1913 and by 1936 four Fischer-Tropsch production plants were operating in Germany using cobalt as a catalyst. Other metals have also proved to be active CO hydrogenation catalysts, these include iron [9], ruthenium [10] and rhodium [11]. However, due to certain

factors (mostly economic) the only commercial Fischer-Tropsch plants in the world, Sasol (South Africa), presently operate an iron-based catalytic system. There has, however, been a resurgence in the interest of cobalt based catalytic systems.

Developments in the field of promoted metal catalysis have seen the incorporation of the promoter metal into the complex containing the active metal. This ensures, at least initially, that there is an intimate relationship between the active metal and the promoter metal. Since there has been an interest in the use of chromium as a promoter metal, we have reviewed heterometallic complexes containing both **cobalt** and **chromium**. Quite a few of these complexes are cluster compounds having various Co:Cr atomic ratios. The availability of such transition metal clusters is of particular interest in connection with their potential use as catalytic agents, namely, as homogeneous catalysts in solution and/or as highly dispersed metal crystallites obtained from the removal of ligands after attachment on solid supports [12].

Numerous reviews have been published on heterometallic complexes [1 - 5, 13]. However, none have covered those containing both cobalt and chromium in any systematic or comprehensive manner. This chapter thus reviews the synthesis and properties of transition metal complexes containing both cobalt and chromium. We have included complexes of this type which also contain other transition metals and have attempted to compile a comprehensive listing of all the known mixed-metal complexes of this type. The discussion has however been restricted to complexes which are organometallic. This restriction has ruled out mixed metal oxides such as $AlCrCoO_4$ and $CrCo_2O_4$. Also excluded are complexes which contain only simple ligands, such as metal carbide complexes (for example $Cr_5Co_2C_3$) and those

complexes containing mainly aqua and ammine ligands (for example {pentaaqua-[μ-(cyanomethyl-C:N)]pentaamminecobalt}chromium(V)).

The complexes that we have surveyed are collected in Table 1.1. These complexes are listed in the order that they appear in the text and are numbered accordingly. The material is organized according to the Co:Cr atomic ratios of the complexes. Those complexes having ratios of 1 and greater are discussed first in increasing order, and then those having ratios less than 1 in decreasing order.

Table 1.1 reveals some interesting statistics. Of the 82 entries, complexes having a Co:Cr atomic ratio of 1:1 dominate, having 34 (41%) entries. Complexes having a Co:Cr atomic ratio of 2:1 are next with 19 (23%) entries. There are 12 (15%) complexes having a Co:Cr atomic ratio of 3:1 and only 1 complex having an atomic ratio of 4:1. Only 12 (15%) complexes have a Co:Cr atomic ratio less than 1. Of the complexes having atomic ratios of 1:1, 25 (74%) are dinuclear, 7 (21%) are tetranuclear and there is 1 trinuclear and 1 octanuclear complex. Fifteen percent (12 entries) of the complexes listed contain Co, Cr and another transition metal (Fe = 7 entries; Mo = 2 entries; Re, W and and Mn = 1 entry each). There are no complexes which contain Co, Cr and *two* or more different transition metals, that is, only heterotrimetallic complexes of this type exist. The largest complex listed is the octanuclear complex $Cp'Cr_2(\mu_3\text{-}S)_4Co_2[(\mu_3\text{-}S)_2Fe_2(CO)_6][(\mu_3\text{-}S)_2Fe_2(CO)_6]$. The structure of this complex has been confirmed by an x-ray crystallographic study.

Table 1.1: Transition metal complexes containing both Co and Cr

Complex	Colour	M.P(°C)	% Yield	Spectral[a] Data	Crystal Structure	Refe-rence
1a $[\eta^6\text{-}C_6H_5CH_2Co(CO)_4]Cr(CO)_3$	orange-red	75-78	56	IR, ^1H	No	14,15
b $[\eta^6\text{-}(4\text{-}MeC_6H_4CH_2Co(CO)_4)]Cr(CO)_3$	orange-red	–	61	IR, ^1H	Yes	15
2a $[\eta^6\text{-}(4\text{-}MeC_6H_4CH_2C(O)Co(CO)_3PPh_3)]Cr(CO)_3$	yellow	–	–	IR, ^1H	No	15
b $[\eta^6\text{-}(4\text{-}MeC_6H_4CH_2Co(CO)_3PPh_3)]Cr(CO)_3$	yellow	–	40-70	IR, ^1H	No	15
3 $[\eta^6\text{-}C_6H_5CH_2OC(O)Co(CO)_4]Cr(CO)_3$	red-brown	60(dec.)	55	IR	No	16
4 $[\eta^6\text{-}C_6H_5SiMe_2Co(CO)_4]Cr(CO)_3$	yellow	112	71	IR, ^1H	No	17
5 $[\eta^6\text{-}(C_6H_5CH_2Co(py)(DH)_2)]Cr(CO)_3$	orange	200(dec.)	72	IR, ^1H, ^{13}C	Yes	18,19
6a $Co(II)(Me\text{-}N\text{-}sal)_2Cr(CO)_3$	green	100(dec.)	27	IR, Mag, UV	No	21
b $Co(II)(Ph\text{-}N\text{-}sal)_2Cr(CO)_3$	green	100(dec.)	5-10	IR, Mag, UV	No	21
c $Co(III)[(Me\text{-}N\text{-}sal)_3]Cr(CO)_3$	green	100(dec.)	22	IR, Mag, UV	No	21
d $[Co(II)(salen)]Cr(CO)_3$	brown	100(dec.)	53	IR, Mag, UV	No	21
7 $(CO)_9CoCrN(PPh_3)_2$	orange	73-75	–	IR	No	23
8 $(CO)_4CoCrCp(CO)_3$	green	–	70	IR, ^1H, UV	No	24
9 $CpCo(\mu\text{-}NO)_2CrCp(NO)$	dark	290(dec.)	50	IR, ^1H	No	25
10 $(CO)_4Co(\mu\text{-}AsMe_2)Cr(CO)_5$	red	29(dec.)	34	IR	No	26

(continued...)

Table 1.1: (...Continued)

Complex	Colour	M.P(°C)	% Yield	Spectral[a] Data	Crystal Structure	Reference
11a $(CO)CpCo(\mu\text{-}Me_2PMe_2P)Cr(CO)_5$	–	–	–	–	No	27
b $(CO)_2(NO)Co(\mu\text{-}Me_2PMe_2P)Cr(CO)_5$	–	–	–	–	No	27
c $(CO)_2(NO)Co(\mu\text{-}PMe_2PMe_2)Cr(CO)_4PMe_2PMe_2$	red-brown	150(dec.)	98	IR	No	28
d $(CO)(NO)Co(\mu\text{-}Me_2PMe_2P)_2Cr(CO)_4$	orange	223(dec.)	32	IR, ^{31}P	No	27,28
12 $(CO)_4CrCo(\mu\text{-}CO)(\mu\text{-}PBu^t_2)(PMe_3)_2$	yellow	123-128	56	IR, ^1H, ^{31}P	Yes	29
13 $Cp(PMe_3)Co(SCS)Cr(CO)_5$	blue-black	124(dec.)	73	IR, ^1H	No	30
14 $Cp(PMe_3)Co(SC\{C_6H_6(Me)_4\text{-}2,2,6,6\})Cr(CO)_5$	black	145(dec.)	5	IR, ^1H	No	31
15 $[Cr(CO)_4(cdpp)]PF_6$	tan	239(dec.)	68	IR, ^1H	No	32
16 $Cp^*Co(\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7)(\mu\text{-}H)Cr(CO)_3$	red-brown	180(dec.)	25	IR, ^1H, ^{13}C	Yes	33
17 $CpCo(C_8H_8)Cr(CO)_3$	red	–	42	IR, ^1H, ^{13}C	Yes	34
18 $(CO)_2CpCrFeCo(\mu_3\text{-}S)(CO)_6$	red	102	–	IR, ^1H, MS	No	35
19a $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4(CO)_2$	red-brown	–	–	IR, ^1H, MS	No	38
b $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4(CO)\{P(OMe)_3\}$	red-brown	–	27	IR, ^1H, MS	No	39
c $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4\{P(OMe)_3\}_2$	dark green	–	30	IR, ^1H, MS	Yes	39
d $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4(CO)\{PPh_3\}$	dark-green	–	42	IR, ^1H, MS	No	39
e $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4\{PPh_3\}_2$	dark-green	–	–	IR, ^1H, MS	No	39

(continued...)

Table 1.1: (...Continued)

Complex	Colour	M.P(°C)	% Yield	Spectral[a] Data	Crystal Structure	Refe-rence
20a $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$	brown	–	26	IR	Yes	12
b $Cp'_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$	brown	–	49	IR	Yes	12
21 $Cp'_2Cr_2(\mu_3\text{-}S)_4Co_2[(\mu_3\text{-}S)_2Fe_2(CO)_6][(\mu_3\text{-}S)Fe_2(CO)_6]$	brown	–	7	IR	Yes	40
22 $\{Cp(CO)_3CrAsMe_2\}_2Co_3(\mu_3\text{-}GeBu^t)(CO)_7$	red-brown	116-118	86	IR, ^1H	No	41
23 $Cp_2Cr_2(\mu\text{-}OCMe_3)_2[OCCo_3(CO)_9]$	brown	–	61	IR, Mag	Yes	42
24 $(\eta^6\text{-}C_6H_5Me)CrCo_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)Cp^*_2$	dark-brown	–	37	IR, ^1H, MS	No	43
25 $(CO)_{11}Co_2Cr(\mu_3\text{-}PH)$	dark-red	90(dec.)	100	IR, ^1H, MS	No	44
26a $Cp(CO)_2CrCo_2(\mu_3\text{-}CH)(CO)_6$	green	129	45	IR, ^1H	No	45,46
b $Cp(CO)_2CrCo_2(\mu_3\text{-}CMe)(CO)_6$	green	155(dec.)	21	IR, ^1H	No	45,46
c $Cp(CO)_2CrCo_2(\mu_3\text{-}CPh)(CO)_6$	green	137(dec.)	17	IR, ^1H	No	45,46
d $Cp(CO)_2CrCo_2(\mu_3\text{-}C\text{-}p\text{-}tolyl)(CO)_6$	green	135(dec.)	17	IR, ^1H	No	45
e $Cp(CO)_2CrCo_2(\mu_3\text{-}CF)(CO)_6$	green	142(dec.)	26	IR, ^1H, ^{19}F	No	45
27 $[\eta^6\text{-}(C_6H_4\{CH_2Co(DH)_2(py)\}_2\text{-}1,4)]Cr(CO)_3$	orange	165(dec.)	77	IR, ^1H, ^{13}C	No	47
28 $[\eta^6\text{-}(C_6H_4\{SiMe_2Co(CO)_4\}_2\text{-}1,4)]Cr(CO)_3$	yellow	102	32	IR, ^1H	No	48

(continued...)

Table 1.1: (...Continued)

Complex	Colour	M.P(°C)	% Yield	Spectral[a] Data	Crystal Structure	Refe-rence
29a $(CO)_4Cr\{(\mu\text{-}Me_2PMe_2P)Co(NO)(CO)_2\}_2$	orange	118	59	IR, ^1H, ^{31}P	No	27
b $(CO)_4Cr\{(\mu\text{-}Me_2PMe_2P)Co(CO)Cp\}_2$	brown	50(dec.)	27	IR, ^1H, ^{31}P	No	27
30 $\{(CO)_5Cr\}PCo_2(\mu_3\text{-}CCH_3)(CO)_6$	purple	65-66	–	IR, MS	No	49
31 $(CO)_9Co_2Fe(\mu_3\text{-}S\{Cr(CO)_5\})$	black	107-109	46	IR, MS	Yes	50
32 $\{Cp(CO)_3CrAsMe_2\}Co_2Fe(\mu_3\text{-}S)(CO)_8$	–	–	–	–	No	35
33 $(CO)_{15}Co_2CrRe(\mu_3\text{-}C\{C_6H_4Me\text{-}4\})$	green	119	69	IR, ^1H, ^{13}C	No	54
34 $\{Cp(CO)_2FeAsMe_2\}Co_2Cr(\mu_3\text{-}CMe)(CO)_7Cp$	dark-brown	138(dec.)	45	–	No	45
35a $Cp(CO)_8MoCo_2[\mu_3\text{-}C\{(C_6H_5OMe\text{-}2)Cr(CO)_3\}]$	brown	–	75	IR, ^{13}C	No	55
b $Cp(CO)_8WCo_2[\mu_3\text{-}C\{(C_6H_5OMe\text{-}2)Cr(CO)_3\}]$	brown	–	78	IR, ^1H, ^{13}C	No	55
36 $Cp(CO)_6MoCo_2[\mu_3\text{-}C\{(C_6H_5OMe\text{-}2)Cr(CO)_3\}](dppm)$	brown	–	–	IR, ^1H, ^{13}C	No	55
37 $(CO)_9Co_3(\mu_3\text{-}P\{Cr(CO)_5\})$	–	–	–	IR, ^1H	No	59
38 $(CO)_9Co_3(\mu_3\text{-}Ge\{CrCp(CO)_3\})$	violet	138(dec.)	–	IR, ^1H	No	41

(continued...)

Table 1.1: (...Continued)

Complex	Colour	M.P(°C)	% Yield	Spectral[a] Data	Crystal Structure	Refe-rence
39a $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}CH)(CO)_8$	red-brown	105	63	IR, ^1H	No	45
b $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}CMe)(CO)_8$	red	114	67	IR, ^1H	No	45
c $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}CPh)(CO)_8$	brown	117(dec.)	51	IR, ^1H	No	45
d $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}p\text{-tolyl})(CO)_8$	brown	115(dec.)	84	IR, ^1H	No	45
e $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}F)(CO)_8$	brown	82	69	IR, ^1H	No	45
40 $[\eta^6\text{-}C_6H_5CCo_3(CO)_9]Cr(CO)_3$	black-red	–	37	–	No	52,60
41 $(CO)_9Co_3\{\mu_3\text{-}CNC\text{-}Cr(CO)_5\}$	–	–	24	IR, MS	Yes	61
42 $[\eta^6\text{-}C_6H_5CH_2OC(O)CCo_3(CO)_9]Cr(CO)_3$	purple	163(dec.)	54	IR, ^1H, ^{13}C, MS	No	47a
43 $[\eta^6\text{-}C_6H_5(CH_2)_4OC(O)CCo_3(CO)_9]Cr(CO)_3$	red	71-74	60	IR, ^1H, ^{13}C, MS	No	47a
44 $[\eta^6\text{-}C_6H_5CH_2OCCo_3(CO)_9]Cr(CO)_3$	purple	137-141	89	IR, ^1H	No	62
45 $(CO)_3CrMes(CH_2)_3MesCo_4(CO)_9$	dark-green	105-110	30	IR, ^{13}C	No	63
46 $[\eta^6\text{-}C_6H_4\{CH_2OC(O)CCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$	black	–	15	IR, ^1H, ^{13}C	No	47a
47 $[\eta^6\text{-}C_6H_4\{CH_2OCCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$	purple	120-124	87	IR, ^1H	No	62
48a $Co(III)(Me\text{-}N\text{-}sal)_3[Cr(CO)_3]_2$	brown	–	13	Mag, near-IR	No	21
b $Co(III)(Ph\text{-}N\text{-}sal)_3[Cr(CO)_3]_2$	brown	–	8	UV-vis	No	21

(continued...)

Table 1.1: (...Continued)

Complex	Colour	M.P(°C)	% Yield	Spectral[a] Data	Crystal Structure	Refe-rence
49a $Cr_2Co(\mu_3\text{-}S)_2(CO)_2Cp_2(\mu\text{-}SBu^t)$	dark-brown	160(dec.)	–	IR, Mag	Yes	65
b $Cr_2Co(\mu_3\text{-}S)_2(CO)_2Cp'_2(\mu\text{-}SBu^t)$	dark-green	–	46	IR, Mag	Yes	64
50a $(CO)_4FeAsMe_2Co(CO)_3AsMe_2Cr(CO)_2CpAsMe_2Cr(CO)_3Cp$	violet	115(dec.)	–	IR, ^1H	No	66
b $(CO)_4MnAsMe_2Co(CO)_3AsMe_2Cr(CO)_2CpAsMe_2Cr(CO)_3Cp$	violet	106-109	–	IR, ^1H	No	66
51 $(NO)(CO)Co\{Me_2PMe_2PCr(CO)_5\}_2$	orange	126(dec.)	20	IR, ^1H, ^{31}P	No	27
52 $Cp'Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2Co(\mu_3\text{-}S)_2Fe_2(CO)_6$	brown	–	–	IR	Yes	67
53a $Cp_3Cr_3Co(CO)(\mu_3\text{-}S)_4$	brown	–	20	IR	Yes	68
b $Cp'_3Cr_3Co(CO)(\mu_3\text{-}S)_4$	brown	–	–	IR, Mag, MS	Yes	69
54 $[Cr_3Co(\mu_3\text{-}O)(\mu_3\text{-}S)_3Cp_3(CO)_3]Me_3CCOOH$	brown	–	–	IR	Yes	70
55 $[Cp_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2]_2Co$	brown	–	–	IR	Yes	70

[a]: IR = infrared spectral data, Mag = magnetic data, MS = mass spectral data, UV = electronic absorption spectral data, ^1H = ^1H NMR data, ^{13}C = ^{13}C NMR data, ^{31}P = ^{31}P NMR data, ^{19}F = ^{19}F NMR data

1.2 COMPOUNDS HAVING A CO:CR ATOMIC RATIO OF 1 OR GREATER

1.2.1 Compounds with a Co:Cr atomic ratio of 1

1.2.1.1 Dinuclear complexes

The heterobimetallic complexes $[\eta^6\text{-}(4\text{-}RC_6H_4CH_2Co(CO)_4)]Cr(CO)_3$ (R = H **1a** and Me **1b**) were recently synthesized and characterized by Galamb and co-workers [14, 15]. These complexes were prepared by the reaction of $[\eta^6\text{-}(4\text{-}RC_6H_4CH_2Cl)]Cr(CO)_3$ (R = H, Me) with $Na[Co(CO)_4]$ (equation 1).

$$[\eta^6\text{-}(4\text{-}RC_6H_4CH_2Cl)]Cr(CO)_3 + Na[Co(CO)_4] \xrightarrow{Et_2O} [\eta^6\text{-}(4\text{-}RC_6H_4CH_2Co(CO)_4)]Cr(CO)_3 \qquad (1)$$

	R
1a	H
1b	Me

When **1b** was reacted further with PPh_3, the corresponding mono-substituted acylcobalt complex $[\eta^6\text{-}(4\text{-}MeC_6H_4CH_2C(O)Co(CO)_3PPh_3)]Cr(CO)_3$ **2a**, resulted. The latter complex could be decarbonylated to the corresponding alkylcobalt derivative $[\eta^6\text{-}(4\text{-}MeC_6H_4CH_2Co(CO)_3PPh_3)]Cr(CO)_3$ **2b** [15]. It is notable that in the formation of **2a**, substitution occurs exclusively at the Co atom. This, however, could be expected on the basis of the relative positions of the $\nu(CO)$ bands corresponding to the $Co(CO)_4$ and $Cr(CO)_3$ fragments in the IR spectra of **1**. The band positions indicate that the carbonyl ligands of the Co atom are more reactive, relative to those of the Cr atom. No stable metal carbonyl complex could be

isolated when **1a** was reacted with PPh_3. A notable feature of compounds **1** and **2**, is the lack of vibrational coupling between the cobalt and chromium carbonyl parts of the complexes.

The (alkoxycarbonyl)cobalt carbonyl complex $[\eta^6\text{-}C_6H_5CH_2OC(O)Co(CO)_4]\text{-}Cr(CO)_3$ **3**, analogous to the acylcobalt carbonyl complex **2a**, was reported by Palyi and Tasi [16]. The complex was prepared by reacting a THF solution of $ICo(CO)_4$ with the appropriate alkali-metal alkoxide (Li, Na, K) in the presence of a suitable crown ether (equation 2). The crown ether was used as a liquid/solid phase-transfer catalyst. A significant amount of tetracarbonyl cobaltate is also formed in this reaction. Complex **3** is a crystalline solid and can be obtained in analytically pure form.

$$ROM(cr) + ICo(CO)_4 \xrightarrow[THF]{CO} \underset{\mathbf{3}}{ROC(O)Co(CO)_4} + M(cr)I \quad (2)$$

{R = $(\eta^6\text{-}C_6H_5CH_2)Cr(CO)_3$; M = Li, cr = 12-crown-4 ether
M = Na, cr = 15-crown-5 ether
M = K, cr = 18-crown-6 ether}

The organosilicon complex $[\eta^6\text{-}C_6H_5SiMe_2Co(CO)_4]Cr(CO)_3$ **4**, was prepared by reacting $[\eta^6\text{-}C_6H_5SiMe_2H]Cr(CO)_3$ with $Co_2(CO)_8$ in methylene chloride [17]. In the solid state **4** decomposes slowly in air, but is stable indefinitely when stored under an atmosphere of dry nitrogen. Methylene chloride solutions of **4** decompose rapidly when exposed to air.

The only known dinuclear complex containing cobalt and chromium, that has been prepared from a cobaloxime, $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **5**, has been

recently synthesised [18] (see also Chapter 2 of this thesis). Its synthesis involves reacting chloro(pyridine)cobaloxime(III), $Co(DH)_2(py)Cl$, with the appropriate (arene)tricarbonyl chromium complex in the presence of $NaBH_4$ (equation 3).

$$Co(DH)_2(py)Cl + [\eta^6\text{-}C_6H_5CH_2Cl]Cr(CO)_3 \xrightarrow{MeOH,\ NaBH_4} [\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3 \quad (3)$$

5

The molecular structure of **5**, suggested on the basis of its spectroscopic properties, was confirmed by x-ray crystallography (figure 1) [19] (see also Chapter 2 of this thesis). Complex **5** is an air stable solid and decomposes slowly in solution. When supported on an inorganic oxide and decomposed, the resulting material was found to be a CO hydrogenation catalyst [20] (see also Chapter 3 of this thesis).

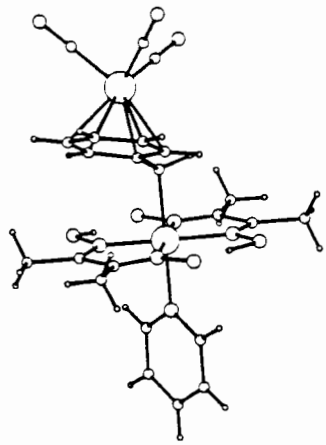


Figure 1: Molecular structure of $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **5**

Gogan and Siddiqui recently reported the synthesis of some chromium tricarbonyl complexes of transition metal Schiff bases [21]. When they reacted Co(II) and Co(III) chelates of Schiff bases derived from salicylaldehyde with $Cr(CO)_6$, mixed metal complexes containing a $Cr(CO)_3$ group (compounds **6**) or two $Cr(CO)_3$

groups (see compounds **48** discussed later) π-bonded to a benzene ring, resulted. Thus, reaction of [Co(II)(Me-N-sal)$_2$] with Cr(CO)$_6$ resulted in the formation of [Co(II)(Me-N-sal)$_2$]Cr(CO)$_3$·H$_2$O **6a** (figure 2).

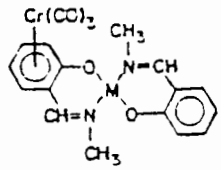


Figure 2: Structure of [Co(II)(Me-N-sal)$_2$]Cr(CO)$_3$ **6a**

This tetrahedral complex shows two carbonyl bands in its IR spectrum, characteristic of (arene)Cr(CO)$_3$ type complexes [22]. The octahedral complexes [Co(II)(Ph-N-sal)$_2$]Cr(CO)$_3$·nH$_2$O (n = 2, 3) **6b**, were prepared in a similar fashion from [Co(II)(Ph-N-sal)$_2$]. In these complexes the Cr(CO)$_3$ unit could be bonded to either the disubstituted or the monosubstituted phenyl ring (figure 3). Due to the low solubility of the compounds, NMR spectroscopy could not be employed to determine, unambiguously, which ring the Cr(CO)$_3$ unit is attached to. It is however believed that the Cr(CO)$_3$ unit is attached to the monosubstituted benzene ring (N-Ph). The complexes [Co(III)(Me-N-sal)$_3$]Cr(CO)$_3$·2H$_2$O **6c** and [Co(II)(salen)]Cr(CO)$_3$·2H$_2$O **6d**, were obtained in analogous reactions from [Co(III)(Me-N-sal)$_3$] and [Co(II)salen] respectively.

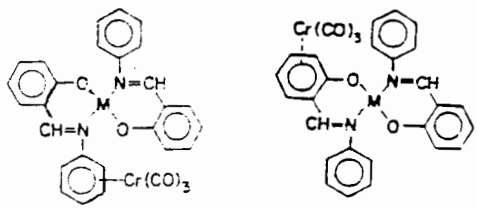


Figure 3: Possible structures for [Co(II)(Ph-N-sal)$_2$]Cr(CO)$_3$ **6b**

Ruff prepared the complex $[(Ph_3P)_2N]CrCo(CO)_9$ **7** (equation 4) during a study of dinuclear metal carbonyls [23]. Compound **7** is a crystalline solid of low thermal stability which is relatively air stable. The complex is unstable in solution, which results in low yields and further thwarts efforts for a complete and unambiguous characterization. It was not possible to obtain a pure product by recrystallization. The IR spectrum (Nujol mull) of compound **7**, gave no bands which could be assigned to μ-CO ligands, expected to be found below 1830cm^{-1}. This suggests that it contains a simple metal-metal bond and, from symmetry considerations, it was proposed to have the formula $(CO)_5Cr\text{-}Co(CO)_4$.

$$[(Ph_3P)_2N]_2Cr_2(CO)_{10} + Co_2(CO)_8 \longrightarrow 2[(Ph_3P)_2N]CrCo(CO)_9 \quad (4)$$

The compound $Cp(CO)_3CrCo(CO)_4$ **8**, was prepared by reacting the two dimeric complexes $[CpCr(CO)_3]_2$ and $Co_2(CO)_8$ in benzene [24]. This complex could not be isolated in pure form and significant amounts of both starting complexes were present.

Treatment of $[CpCo(NO)]_2$ with a Na/Hg amalgam in Et_2O resulted in the formation of Na[CpCo(NO)]. When a THF solution of this anion was treated with $CpCr(NO)_2Cl$, dark air-stable crystals of $CpCo(\mu\text{-}NO)_2CrCp(NO)$ **9** were isolated [25]. This complex represents a rare example of a heteronuclear bridging nitrosyl dimer. The structure of **9** (figure 4) was inferred from its M-NO stretching frequencies as compared with those of the structurally characterized complex $[CpCr(NO)_2]_2$. The complex was formed in approximately 50% yield as determined by NMR spectroscopic analysis of the reaction mixture; however, it was isolated in only 11% yield after recrystallization.

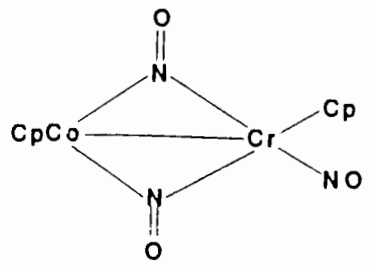
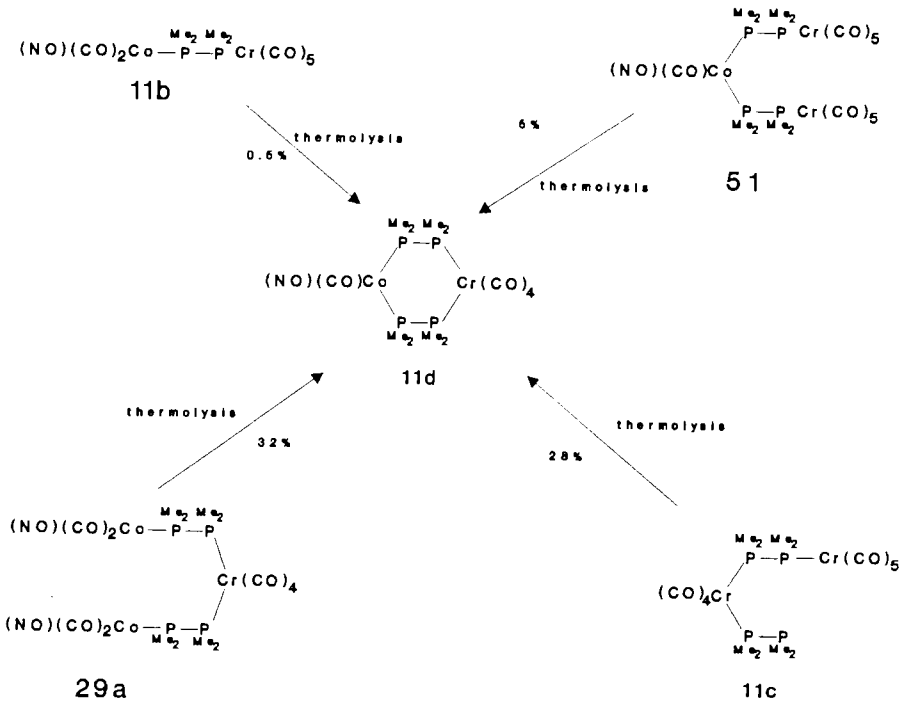


Figure 4: Proposed structure of $CpCo(\mu\text{-}NO)_2CrCp(NO)$ **9**

Ehrl and Vahrenkamp reported the synthesis of $(CO)_5CrAsMe_2Co(CO)_4$ **10** [26]. Complex **10** was formed in a metathetical reaction between $(CO)_5CrAsMe_2Cl$ and $Na[Co(CO)_4]$. This dinuclear complex containing a single arsenic bridge was isolated as bright-red crystals in 34% yield. The complex was found to be stable towards air and moisture. Attempts to thermally or photochemically convert **10** into a mixed metal cluster complex, resulted only in disproportionation and formation of *homonuclear* complexes.

The dinuclear complexes $(CO)_5Cr(\mu\text{-}Me_2PMe_2P)MLn$ {MLn = Co(CO)Cp **11a** and $Co(CO)_2(NO)$ **11b**} were prepared by reacting the corresponding monofunctional organometallic Lewis bases, $LnMPMe_2PMe_2$, with $Cr(CO)_6$ [27]. Reaction of the bifunctional Lewis base $(CO)_4Cr(PMe_2PMe_2)_2$ with an equimolar amount of $Co(NO)(CO)_3$ resulted in the formation of $(Me_2PMe_2P)(CO)_4CrPMe_2PMe_2$-$Co(NO)(CO)_2$ **11c** [28]. Thermolysis of **11c** led to the formation of the six-membered ring compound $(CO)_4Cr(Me_2PMe_2P)_2Co(CO)(NO)$ **11d** [28]. The latter compound was also formed from the thermolysis of **11b**, **29a**, and **51**, in 0.5, 32 and 5% yields respectively (see Scheme 1). Compound **11d** possesses a high thermal stability, decomposing above 223°C.



Scheme 1: Thermolysis reactions leading to the formation of **11d**

Reaction of $Cr(CO)_5(PBu^t_2)Li$, generated in situ from $Cr(CO)_5$(t-Bu_2PH) and n-BuLi, with $CoCl(PMe_3)_3$ yields the heterobimetallic complex $(CO)_3(PMe_3)Cr(\mu\text{-}PBu^t_2)(\mu\text{-}CO)Co(PMe_3)(CO)$ **12** [29]. This complex contains a metal-metal bond bridged by single di-tert-butyl-phosphido and CO units. During the formation of **12**, exchange of PMe_3 and CO occurs between the Co and Cr atoms. The structure of this moderately air-sensitive, hexane soluble compound was determined by x-ray crystallography, aided by the usual analytical techniques (figure 5).

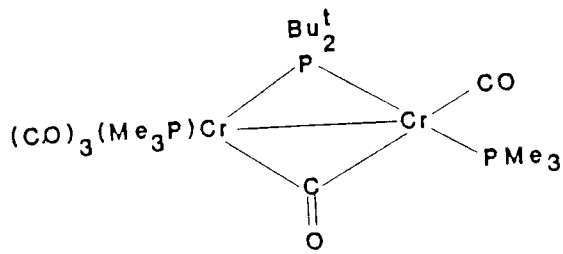
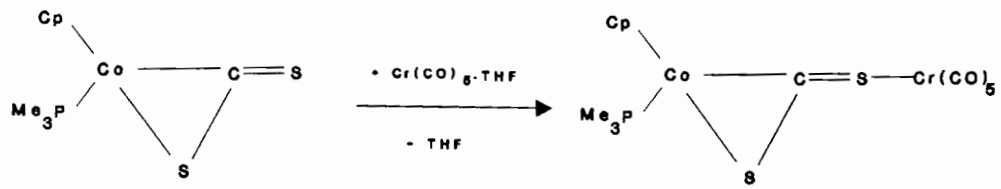


Figure 5: Structure of $(CO)_3(PMe_3)Cr(\mu\text{-}PBu^t_2)(\mu\text{-}CO)Co(PMe_3)(CO)$ **12**

When $CpCo(PMe_3)CS_2$, obtainable in virtually quantitative yield by reacting $CpCo(PMe_3)_2$ or $Cp(PMe_3)Co(CO)_2Mn(CO)C_5H_4Me$ with CS_2, was reacted with $Cr(CO)_5THF$, it gave rise to the formation of $Cp(PMe_3)Co(SCS)Cr(CO)_5$ **13** (equation 5) [30]. The sulphur atom that is not bound to cobalt coordinates to the 16-electron fragment $Cr(CO)_5$. The blue-black compound **13** was isolated in 73% yield.



(5)

The synthesis of a seemingly similar complex to **13**, $Cp(Me_3P)Co(SCX)Cr(CO)_5$ (X = 2,2,6,6-tetramethylhexane **14**) was recently reported by Behrens and co-workers (figure 6) [31]. The complex is produced in 5% yield by the reaction of $Cp(Me_3P)Co(SCX)$ (X = 2,2,6,6-tetramethylhexane) with $Cr(CO)_6$ in THF. Although this dinuclear thioketene complex is produced in low yield, it possesses a relatively high thermal stability, decomposing above 145°C.

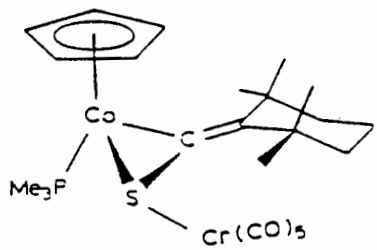


Fig. 6: Structure of $Cp(Me_3P)Co(SCX)Cr(CO)_5$, X = $C_6H_6(Me)_4$-2,2,6,6 **14**

Complexes **13** and **14** have similar structures with regard to the cobalt end of the molecules. Both compounds have a Co atom bound to a Cp, PMe_3 and a η^2-CS ligand. In **13** however, the $Cr(CO)_5$ unit is bound to the sulphur atom which *is not* bound to the cobalt atom. Also, the second sulphur atom of **13** is substituted by a much bulkier 2,2,6,6-tetramethylhexane group in **14**.

Davison and co-workers studied the reactivity of 1,1′-bis(diphenylphosphino)-cobaltocenium hexafluorophosphate, $[cdpp]PF_6$, more than a decade ago [32]. They reported the reaction of $[cdpp]PF_6$ with $Cr(CO)_6$ in a diglyme solution. The reaction product $[Cr(CO)_4(cdpp)]PF_6$ **15**, is a tan microcrystalline powder isolated in 68% yield. Its structure (figure 7) was elucidated by conventional spectroscopic methods.

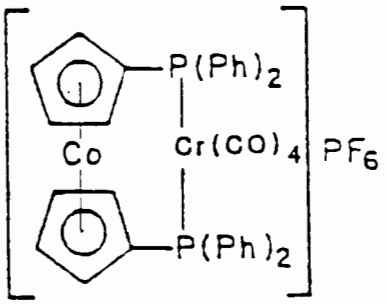


Fig. 7: Structure of $[Cr(CO)_4(cdpp)]PF_6$ **15**

The synthesis of the novel heterobimetallic complex, $Cp^*Co(\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7)(\mu\text{-}H)Cr(CO)_3$ **16**, was recently reported [33]. When an etherial solution of $[\eta^6\text{-}C_7H_8]Cr(CO)_3$ and $[Cp^*Co(C_2H_4)_2]$ was heated, red-brown crystals of **16** could be isolated in 25% yield, with $[Cp^*Co(CO)]_2$ being formed in a side reaction. To clarify the position of the cycloheptatrienyl ring an x-ray crystal structure of **16** was obtained (figure 8).

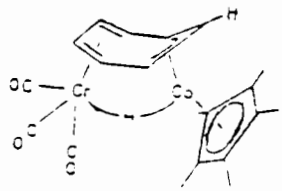


Figure 8: Structure of $Cp^*Co(\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7)(\mu\text{-}H)Cr(CO)_3$ **16**

Th cycloheptatrienyl ring of **16** was found to have a boat conformation, with the dihedral angle between the η^4-diene and the η^3-enyl planes being 59°. The cobalt, chromium and bridging hydrogen atom make up a 32 electron MHM′ system. This contrasts with other syn-$M(\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7)M'$ systems, in that it has a large metal-metal bond distance (2.899 Å). It had not previously been possible to freeze out the rotation of the cycloheptatrienyl ring in syn-$M(\mu\text{-}C_7H_7)M'$ complexes on the NMR time scale. The ^1H and ^{13}C NMR spectra (200 K) of **16**, however, showed the expected signal patterns for a *rigid* $\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7$ structure.

Reaction of the cyclooctatriene complex $CpCo(C_8H_8)$ with $(CH_3CN)_3Cr(CO)_3$ yields the bimetallic complex $CpCo(C_8H_8)Cr(CO)_3$ **17** [34]. NMR experiments conducted at -50°C revealed fluxional Cp and C_8H_8 ligands, as well as rapid exchange of the carbonyl ligands. It was not possible to freeze out the structure by further cooling due to the low solubility of the complex. The x-ray structural analysis of **17**, shows a Co-Cr bond length of 2.92 Å, and a significantly shorter Cr-CO bond length trans to the Co atom (figure 9).

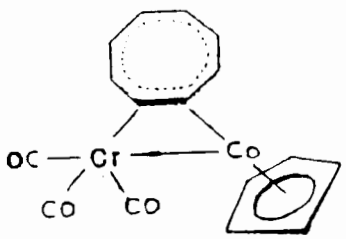


Figure 9: Structure of $CpCo(C_8H_8)Cr(CO)_3$ **17**

1.2.1.2. Trinuclear complexes

Vahrenkamp and Richter outlined, in a paper published over a decade ago, the syntheses of the first μ_3-bridged trinuclear complexes whose tetrahedral skeletons were made up of four different entities, and were thus necessarily chiral [35]. They proposed that being chiral, such polynuclear complexes could serve as models for asymmetric catalysis on the basis of the analogy proposed between clusters and metal surfaces [36]. One of the complexes reported was formulated as $Cp(CO)_2CrFeCo(\mu_3\text{-}S)(CO)_6$ **18** (figure 10). The chirality of this complex was demonstrated by ^1H NMR spectroscopy of suitable phosphane derivatives with diastereotopic P-substituents.

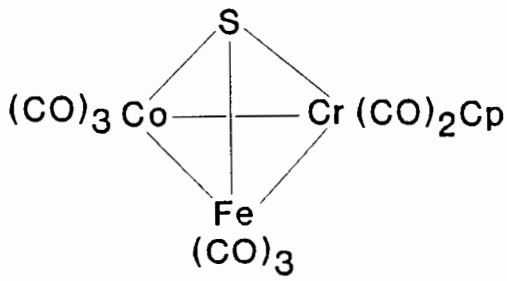


Fig. 10: Structure of $Cp(CO)_2CrFeCo(\mu_3\text{-}S)(CO)_6$ **18**

The compound was prepared from $\{Cp(CO)_3CrAsMe_2\}Co_2Fe(\mu_3\text{-}S)(CO)_8$ **32** by a newly discovered method of eliminating a $[(CO)_3CoAsMe_2]_x$ fragment from cobalt-containing, arsenic-bridged polynuclear complexes [26, 35, 37]. The reaction involves heating (70°C) the starting material in cyclohexane for several days [35]. Compound **18** is dark-red to black in the solid state, and red in solution. It exhibits

a large number of ν(CO) bands in its IR spectrum. The molecular mass was confirmed by mass spectrometry.

1.2.1.3. Tetranuclear complexes

Brunner and Wachter reported that the reaction of $Co_2(CO)_8$ with a toluene solution of $Cp^*_2Cr_2S_5$ led to the formation of a new heterobimetallic cluster of composition $Cr_2Co_2(\mu_3\text{-}S)_4(CO)_2Cp^*_2$ **19a** [38]. This was confirmed by elemental analysis and mass spectrometry. Crystals of **19a**, suitable for an x-ray diffraction study, could not be isolated. They used the usual spectroscopic data, however, and the assumption that the structure involves equal distribution of the four sulphur atoms over all the metal atoms, *i.e.* that they serve as μ_3 ligands, to propose the structure given in figure 11.

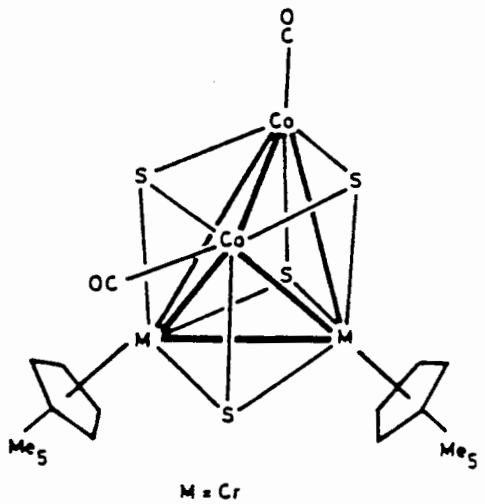


Fig. 11: Proposed structure of $Cr_2Co_2(\mu_3\text{-}S)_4(CO)_2Cp^*_2$ **19a**

Brunner, Meier and Wachter then reported the reaction of **19a** with PR_3 (R = Ph and OMe) [39]. This resulted in a stepwise substitution of the two CO ligands by PR_3. Thus, when **19a** was reacted with a molar equivalence of $P(OMe)_3$, $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4(CO)\{P(OMe)_3\}$ **19b** and $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4\{P(OMe)_3\}_2$ **19c** were isolated. The compounds $Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4(CO)\{PPh_3\}$ **19d** and

$Cp^*_2Cr_2Co_2(\mu_3\text{-}S)_4\{PPh_3\}_2$ **19e** were formed in analogous reactions. An x-ray diffraction study of **19c** (figure 12) confirmed that the 60-electron core, of composition $Cr_2Co_2S_4$ was retained. This also served to prove the structure proposed for **19a**.

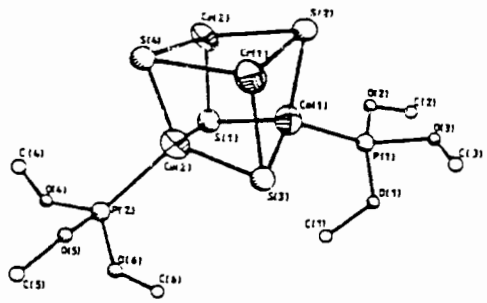


Fig. 12: Perspective view of $Cp^*_2Cr_2Co_2\{P(OMe)_3\}_2(\mu_3\text{-}S)_4$ **19c**

The synthesis of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ **20a**, and $Cp'_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ **20b**, was recently reported by Pasynskii and co-workers [12]. Complex **20a** was obtained by applying moderate heat to equimolar quantities of $(CpCrSCMe_3)S$ and $Co_2(CO)_8$ in benzene. The IR spectrum of **20a** showed two bands arising from terminal CO groups and vibrations typical of Cp rings. X-ray structural determination (figure 13) revealed a "butterfly" framework of metal atoms with the Cr-Cr axis acting as the body, and the two $CoCr_2$ triangles forming the wings. The Co···Co separation {4.047(1) Å} is non-bonded.

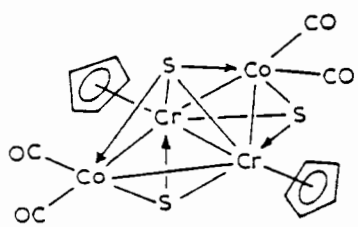


Figure 13: Structure of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ **20a**

Complex **20b** was obtained by an analogous reaction involving equimolar quantities of $(Cp'CrSCMe_3)S$ and $Co_2(CO)_8$ in a heptane/benzene mixture at room temperature. An x-ray structural determination of **20b** reveals an almost identical metal butterfly framework as found in **20a**, although the methylcyclopentadienyl ligands are in a staggered conformation in contrast to the eclipsed conformation of **20a.**

1.2.1.4. Octanuclear complexes

Pasynskii and co-workers reported the synthesis of the octanuclear cluster $Cp'Cr_2(\mu_3\text{-}S)_4Co_2[(\mu_3\text{-}S)_2Fe_2(CO)_6][(\mu_3\text{-}S)_2Fe_2(CO)_6]$ **21** [40]. The cluster is formed, albeit in low yield, by the interaction of **20b** with two molar equivalents of $Fe_2S_2(CO)_6$ under UV irradiation in benzene. The IR spectrum of **21** shows the presence of terminal CO groups. Its structure was confirmed by x-ray crystallography (figure 14).

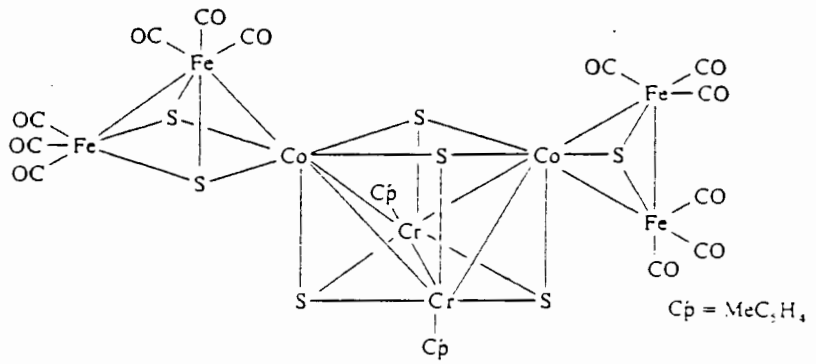


Figure 14: Structure of $Cp'Cr_2(\mu_3\text{-}S)_4Co_2[(\mu_3\text{-}S)_2Fe_2(CO)_6][(\mu_3\text{-}S)_2Fe_2(CO)_6]$ **21**

This showed the central fragment of **21** to be a distorted cube consisting of $Cr_2Co_2(\mu_3\text{-}S)_4$, with its Cr_2Co_2 metal core having a butterfly structure (two $CoCr_2$ triangles sharing a common Cr-Cr edge). The non-bonded Co···Co separation {3.160(1) Å} was found to be shorter than the corresponding distance (4.052 Å) of

the initial butterfly cluster **20b**. The dihedral angle between the $CrCo_2$ wings thus changes considerably from 124.8° in **20b**, to 85.1° in **21**. One of the Co atoms is asymmetrically bonded to the binuclear $S_2Fe_2(CO)_6$ fragment {Co-Fe bond lengths of 2.645(2) Å and 3.366(2) Å}. The other Co atom is symmetrically bonded to a $SFe_2(CO)_6$ fragment {Co-Fe bond lengths of 2.584(2) Å and 2.571(2) Å}.

1.2.2 Compounds having a Co:Cr ratio of 1.5

Vahrenkamp and Gusbeth found that the cluster $(CO)_9Co_3(\mu_3\text{-}GeBu^t)$ reacts with the organometallic dimethylarsenide, $Cp(CO)_3CrAsMe_2$, to give the disubstituted product $\{Cp(CO)_3CrAsMe_2\}_2Co_3(\mu_3\text{-}GeBu^t)(CO)_7$ **22** [41]. Compound **22** could not be isolated in analytically pure form and decomposes at room temperature and in the presence of light. It further appears that the organometallic dimethylarsenide fragment comes off during the decomposition process.

The cluster complex $Cp_2Cr_2(\mu\text{-}OCMe_3)_2[OCCo_3(CO)_9]$ **23** [42], is formed instantaneously on reacting the binuclear complex $Cp_2Cr_2(\mu\text{-}OCMe_3)_2$ with $Co_2(CO)_8$ in benzene at room temperature. An equimolar ratio of reagents produces **23** in 27% yield. Reaction of the chromium and cobalt containing starting complexes in a 1/3 molar ratio results in a yield of 61%. Complex **23** is extremely air and moisture sensitive. X-ray diffraction studies of **23** reveal the preservation of the initial binuclear $Cp_2Cr_2(\mu\text{-}OCMe_3)_2$ fragment, having a mean Cr-O bond length of 1.950(3) Å (figure 15). The trinuclear cluster $OCCo_3(CO)_9$ fragment {Co-Co bond lengths of 2.483(1) - 2.489(1) Å}, is bonded to one of the chromium atoms *via* an oxygen atom of the bridging carbonyl group {Cr-O bond length of 1.988(3) Å and a μ-C-O bond length of 1.247(6) Å}.

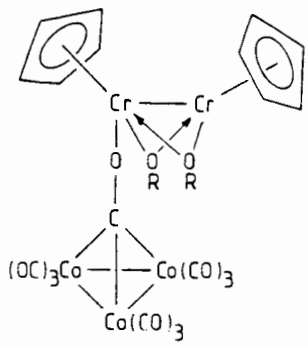


Figure 15: Structure of $Cp_2Cr_2(\mu\text{-}OCMe_3)_2[OCCo_3(CO)_9]$ **23**

This antiferromagnetic complex may be regarded as part of the well known class of compounds of the type $(CO)_9Co_3CR$ (of which other examples are mentioned elsewhere in this chapter). Complex **23** may also be regarded as a tris-alkoxide complex of the type $Cp_2Cr_2(OR')(\mu\text{-}OCMe_3)_2$, where the tricobalt fragment acts as the R′ group.

1.2.3 Compounds having a Co:Cr ratio of 2

1.2.3.1 Compounds containing only Co and Cr

In order to illustrate the apparent diversity and scope of photochemically generating a desired variety of mixed metal clusters, a paper by Dahl and co-workers described the photogenerated metal-fragment addition across a metal-metal multiple-bonded dimer [43]. The dimer, $[Cp^*Co(\mu\text{-}CO)]_2$, was produced photochemically from $CoCp^*(CO)_2$. Of interest to the authours was the net addition of electronically equivalent $(\eta^6\text{-}C_6H_5Me)Cr(CO)_2$, obtained by irradiation of the corresponding chromium tricarbonyl compound, to $CoCp^*(CO)_2$. A triangular, diamagnetic dicobalt-chromium cluster $(\eta^6\text{-}C_6H_5Me)CrCo_2Cp^*_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ **24**, was obtained (figure 16).

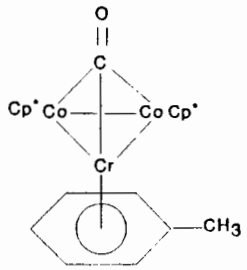


Fig 16: Structure of $(\eta^6\text{-}C_6H_5Me)CrCo_2Cp^*_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ **24** shown without the μ_3-CO groups

It contained one triply bridging and three doubly bridging carbonyl ligands. Complex **24** is air sensitive and highly soluble in a range of organic solvents. It was produced in non-optimized 37% yield. It is noteworthy that although the complex is conveniently photogenerated under relatively mild conditions (25°C), it was not obtainable from the corresponding thermal reaction. Although the mass spectra of **24** did not exhibit a parent ion peak, its fragmentation pattern did show relatively large peaks at m/z 444 and 228, assigned to the ions $Co_2Cp^*_2(CO)_2^+$ and $Cr(C_6H_5Me)(CO)_3^+$ respectively.

A novel phosphorus-centered heterometallic cluster containing Co and Cr, was reported by Urray and Austin [44]. They found that when a THF solution of pentacarbonylphosphinochromium, $H_3PCr(CO)_5$, was treated with a deficiency of cobalt octacarbonyl, the trinuclear complex $HPCrCo_2(CO)_{11}$ **25** was formed (equation 6). The reaction was complete after 60h at room temperature, producing **25** in quantitative yield.

$$H_3PCr(CO)_5 + Co_2(CO)_8 \longrightarrow HPCrCo_2(CO)_{11} + H_2 + 2\,CO \qquad (6)$$

25

Compound **25** is soluble in CH_2Cl_2 and THF, but sparingly soluble in n-hexane. It is indefinitely stable *in vacuo* at room temperature and air stable for short periods. The compound is slightly volatile *in vacuo* at elevated temperatures, but decomposes at temperatures in excess of 90°C. The IR spectrum of **25** shows no bands assignable to bridging carbonyl ligands. Its mass spectrum shows the parent ion and fragments resulting from the successive loss of eleven CO ligands, without significant loss of the underlying cluster structure. The ion $PCrCo_2^+$ is observed in high abundance, suggesting that the loss of hydrogen is facile, and that co-ordinatively unsaturated clusters possess moderate stability. Both of these properties should be useful in catalytic applications. The most probable structure for **25** in agreement with its IR, NMR and mass spectral data, is given in figure 17. Of note is the absence of a Co-Co bond, usually present in complexes containing a trinuclear metal core.

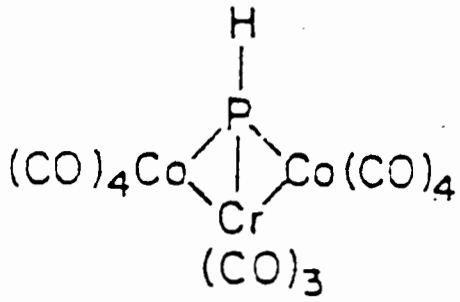


Fig 17: Probable structure for $HPCrCo_2(CO)_{11}$ **25**

The mixed metal clusters $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}CR)(CO)_8$ **39** (R = H, Me, Ph, *p*-Tolyl, F), were reported by Vahrenkamp and Beurich. These complexes contain a Co:Cr atomic ratio of 3, and are discussed in more detail in Section 1.2.4. They found that on heating **39**, a $[(CO)_3CoAsMe_2]$ fragment is eliminated, leading to the formation of the new mixed metal clusters $Cp(CO)_2CrCo_2(\mu_3\text{-}CR)(CO)_6$ **26**

[45, 46] for all R substituents. The yields range from 17 - 45%, with the best yield obtained for R = H. The green, air-stable compounds were identified on the basis of their simple NMR spectra. The Mo analogue of the phenyl compound, $(CO)_2CpMoCo_2(\mu_3\text{-}CPh)(CO)_6$, which was prepared in an analogous reaction, was characterized crystallographically and thus compounds **26** were assigned similar structures (figure 18).

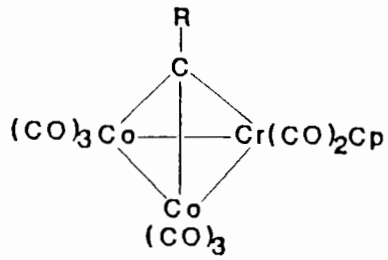


Fig. 18: Structure of $Cp(CO)_2CrCo_2(\mu_3\text{-}CR)(CO)_6$ R = H, Me, Ph, *p*-tolyl, F **26**

Domingo and Moss recently prepared the trinuclear cobaloxime complex $[\eta^6\text{-}C_6H_4\{CH_2Co(DH)_2(py)\}_2\text{-}1,4]Cr(CO)_3$ **27** [47] (see also Chapter 2 of this thesis). This complex represents the only known trinuclear complex containing Co and Cr that has been prepared from a cobaloxime. It was synthesized by a reaction analogous to equation (3), by reacting $[\eta^6\text{-}C_6H_4(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$ with a twofold excess of $[Co(DH)_2(py)Cl]$ in the presence of $NaBH_4$. The compound is an air-stable, orange solid isolated in 77% yield. Methylene chloride solutions of the compound exposed to air, show signs of decomposition only after several days.

Mance and co-workers reported the synthesis of $[\eta^6\text{-}C_6H_4\{SiMe_2Co(CO)_4\}_2\text{-}1,4]Cr(CO)_3$ **28** [48], by a method similar to that used in the preparation of **4**. The thermal reaction between $Cr(CO)_6$ and $[C_6H_4\{SiMe_2H\}_2\text{-}1,4]$ produced $[\eta^6\text{-}C_6H_4\{SiMe_2H\}_2\text{-}1,4]Cr(CO)_3$, which reacted smoothly with $Co_2(CO)_8$ to form **28**.

The compound was characterized by elemental analysis, IR and ^{1}H NMR. Like its dinuclear analogue, **4**, the solid compound is stable indefinitely when stored under nitrogen.

An aromatic solution of $(CO)_4Cr\{PMe_2PMe_2\}_2$ treated with a two molar excess of $(NO)Co(CO)_2$ or $CpCo(CO)_2$, resulted in the formation of the respective trinuclear compounds $(CO)_4Cr\{(\mu\text{-}Me_2PMe_2P)Co(NO)(CO)_2\}_2$ **29a**, and $(CO)_4Cr\text{-}\{Me_2PMe_2PCoCp(CO)\}_2$ **29b** [27]. These compounds possess a chain-like arrangement of metal atoms. The nitrosyl compound was found to be much more stable than the Cp analogue. This was reflected in both the yields and the melting points of the compounds. The yield of **29a** was 59% while **29b** was formed in 27% yield. The former compound decomposed at 118°C, while the latter compound decomposed at 50°C.

A study by Seyferth and Henderson resulted in the formation of the organophosphorus-cobalt carbonyl clusters, $(RCP)Co_2(CO)_6$ (R = Me, Ph, Me_3Si), in which the P atom is a site of Lewis basiscity. They further found [49] that $(CH_3CP)Co_2(CO)_6$ reacts readily with $Cr(CO)_5\cdot THF$, to give $\{(CO)_5Cr\}PCo_2(\mu_3\text{-}CCH_3)(CO)_6$ **30** (figure 19), as a purple-red, air stable crystalline solid.

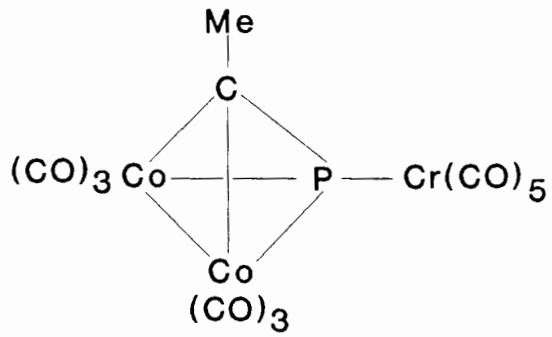


Fig. 19: Structure of $\{(CO)_5Cr\}PCo_2(\mu_3\text{-}CCH_3)(CO)_6$ **30**

1.2.3.2 Compounds containing another metal, in addition to cobalt and chromium

The first compound containing a sulphur atom linked to three different metal atoms was isolated and characterized by Vahrenkamp and Richter [50]. This compound, formulated as $(CO)_9Co_2Fe(\mu_3\text{-}S\{Cr(CO)_5\})$ **31**, had its structure determined by x-ray crystallography (figure 20).

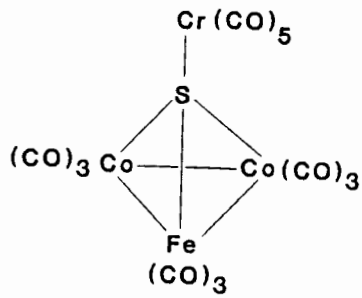


Fig. 20: Molecular structure of $(CO)_9Co_2Fe(\mu_3\text{-}S\{Cr(CO)_5\})$ **31**

Compound **31** was prepared by the addition of $(CO)_5Cr\cdot THF$, generated by irradiation, to a hexane solution of $(CO)_9Co_2Fe(\mu_3\text{-}S)$. The complex is air-stable in the solid state, but unstable in solution at room temperature. Experiments by Vahrenkamp and Richter [50] support the prediction for the complex to have good Lewis base properties. The bond delocalization of **31**, apparent from its structure, together with its IR spectral properties has led them to conclude that **31** is an electron reservoir with similar properties to complexes of the type $(Co)_9Co_3CR$ [51, 52].

The synthesis of $\{Cp(CO)_3CrAsMe_2\}Co_2Fe(\mu_3\text{-}S)(CO)_8$ **32**, was also reported by Vahrenkamp and Richter [35]. It was prepared from the readily accessible trinuclear cluster complex $(CO)_9Co_2Fe(\mu_3\text{-}S)$ [53], which also served as a precursor

to **31**. Reacting $(CO)_9Co_2Fe(\mu_3\text{-}S)$ with $Cp(CO)_3CrAsMe_2$ in a typical substitution reaction [35, 41, 45] led to the formation of **32**.

Treatment of $[ReCr(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ with $Co_2(CO)_8$ in light petroleum at room temperature affords the tetranuclear complex $[Co_2CrRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ **33** [54]. The compound was characterized by microanalysis and its spectroscopic properties. Its structure (figure 21), was based on the molecular structure determined for the tungsten analogue, $[Co_2WRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$, which was prepared in an analogous reaction.

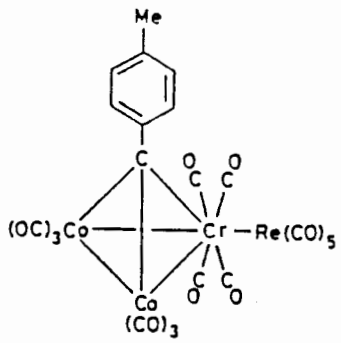


Fig 21: Molecular structure of $[Co_2CrRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ **33**

An attempt by Vahrenkamp and Beurich to perform a metal exchange reaction on compounds **26**, using the organometallic dimethylarsenide $AsMe_2Fe(CO)_2Cp$, resulted in a substitution reaction. The substitution product, $Cp(CO)_2CrCo_2(\mu_3\text{-}CMe)(CO)_5\{AsMe_2FeCp(CO)_2\}$ **34** [45], was isolated in 45% yield and contained a triangular Co_2Cr core, with the Fe atom being extraneous to the internal metal framework.

Fernandez and Stone recently synthesized the complexes $[CrM\{\mu\text{-}\sigma\text{:}\eta^6\text{-}CC_6H_4(OMe\text{-}2)\}(CO)_5Cp]$ (M = Mo, W) [55]. It has been found that complexes of

the type $[M(\equiv CR)(CO)_2Cp]$ (M = Mo, W; R = alkyl or aryl) react with $Co_2(CO)_8$ to yield the family of compounds $[MCo_2(\mu_3\text{-}CR)(CO)_8Cp]$, containing a trimetallahedrane μ_3-$CMCo_2$ core [56, 57, 58]. This observation prompted Fernandez and Stone to react their newly prepared complexes $[CrM\{\mu\text{-}\sigma\text{:}\eta^6\text{-}CC_6H_4(OMe\text{-}2)\}(CO)_5Cp]$ (M = Mo, W) with $Co_2(CO)_8$ in a similar manner [55]. The reaction was carried out in Et_2O at room temperature, yielding the tetranuclear complexes $[CrMCo_2\{\mu_3\text{-}\sigma,\sigma',\sigma'':\eta^6\text{-}CC_6H_4(OMe\text{-}2)\}(CO)_{11}Cp]$ (M = Mo **35a**, W **35b**) (figure 22).

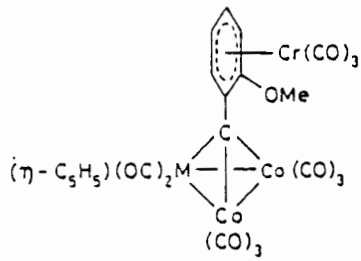


Figure 22: Structures of $[CrMCo_2\{\mu_3\text{-}\sigma,\sigma',\sigma'':\eta^6\text{-}CC_6H_4(OMe\text{-}2)\}(CO)_{11}Cp]$
M = Mo **35a** and W **35b**

A notable feature of the synthesis of **35a** and **35b** is the spectator role played by the $Cr(CO)_3$ group in all the reactions. This and other evidence [55], has led the authors to believe that the CO groups of the $Cr(CO)_3$ fragment are strongly bonded to the Cr center, hence the reason why loss of CO and condensation reactions to form clusters of higher nuclearity were not observed. They also tried to link the M and Co atoms of these compounds by reacting them with dppm ($Ph_2PCH_2PPh_2$). The product of this reaction, however, was $[CrMCo_2\{\mu_3\text{-}\sigma,\sigma',\sigma'':\eta^6\text{-}CC_6H_4(OMe\text{-}2)\}(\mu\text{-dppm})(CO)_9Cp$ (M = Mo, **36**) in which dppm bridges the Co-Co bond.

1.2.4 Compounds having a Co:Cr atomic ratio of 3

The compounds in this category are structurally similar. They all contain a triangular Co_3 metal framework with a triply bridging atom, with chromium being extraneous to the internal metal framework. In the first case, $(CO)_5Cr(PH_3)$ was reacted with $Co_2(CO)_8$ to yield the tetranuclear metal cluster $(CO)_9Co_3(\mu_3\text{-}P\{Cr(CO)_5\})$ **37** [59]. The second complex, $(CO)_9Co_3(\mu_3\text{-}Ge\{CrCp(CO)_3\})$ **38** (figure 23), was produced by thermolysis of **22** [41].

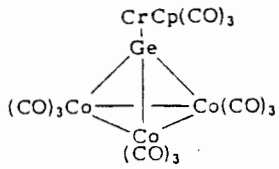


Figure 23: Structure of $(CO)_9Co_3(\mu_3\text{-}Ge\{CrCp(CO)_3\})$ **38**

The third class of compounds $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}CR)(CO)_8$ **39** (R = H, Me, Ph, *p*-Tolyl and F) [45], have the distinction of being the precursors to compounds **26** and **34**. Compounds **39** are different from the other complexes in this section in that the Cr atom *is not* linked to the internal triangular Co_3 framework *via* the μ_3-ligand (figure 24).

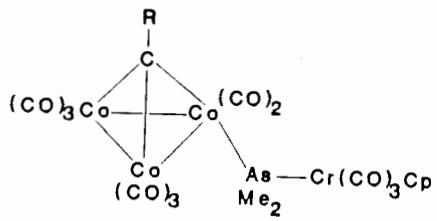


Figure 24: Structures of $\{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}CR)(CO)_8$ **39**

R = H, Me, Ph, *p*-Tolyl and F

Compounds **39** were synthesized by the reaction of $(CO)_9Co_3(\mu_3\text{-}CR)$ with the organometallic dimethylarsenide $Cp(CO)_3CrAsMe_2$ [45] (equation 7). The yields are good, ranging from 51 - 84%, with the highest yield obtained for R = *p*-tolyl.

$$(CO)_9Co_3(\mu\text{-}CR) + Cp(CO)_3CrAsMe_2 \longrightarrow \{Cp(CO)_3CrAsMe_2\}Co_3(\mu_3\text{-}CR)(CO)_8 \quad (7)$$

	R
39a	H
b	Me
c	Ph
d	*p*-tolyl
e	F

A review article by Seyferth briefly mentioned the tetranuclear complex $[\eta^6\text{-}C_6H_5CCo_3(CO)_9]Cr(CO)_3$ **40** [52]. It was reported as having been synthesized by reacting $(CO)_9Co_3CH$ with $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ in THF, under an atmosphere of CO. No experimental details or characterization data were however provided. Domingo and Moss have synthesised and characterized this compound [60] (see also Chapter 2 of this thesis). They found the complex to be a black, air-stable solid. The compound is soluble in most organic solvents, producing dark-red solutions.

The synthesis of $(CO)_9Co_3(\mu_3\text{-}C\{NCCr(CO)_5\})$ **41**, was reported nearly a decade ago [61]. When $Cr(CO)_5CNCl_3$ was reacted with $Co_2(CO)_8$ in a 4:9 molar ratio, air-stable crystals of **41** was isolated in 24% yield. It's mass spectrum showed the molecular ion, as well as peaks corresponding to the sequential loss of *all* fifteen carbonyl ligands to give $[CrCNCCo_3]^+$ as the base peak. The structure of **41** was confirmed by x-ray crystallography (figure 25).

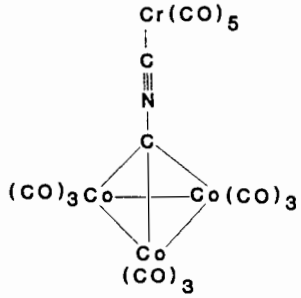
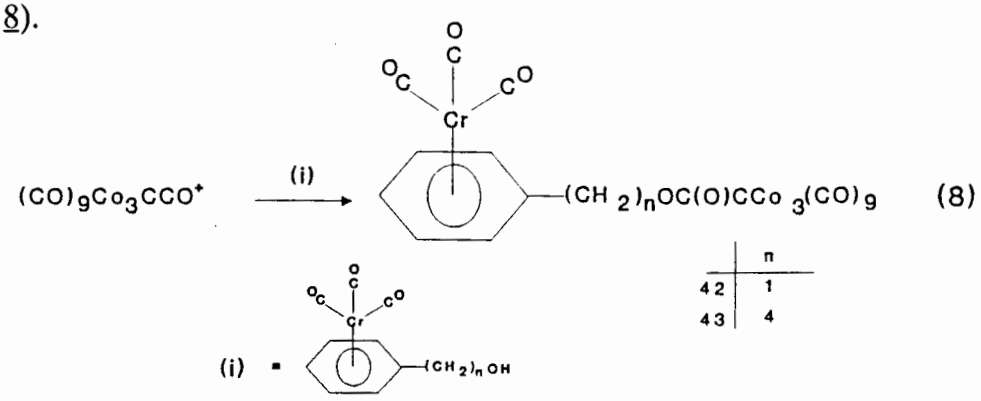


Figure 25: Structure of $(CO)_9Co_3(\mu_3\text{-}C\{NCCr(CO)_5\})$ **41**

The two complexes $[\eta^6\text{-}C_6H_5CH_2OC(O)CCo_3(CO)_9]Cr(CO)_3$ **42** and $[\eta^6\text{-}C_6H_5\text{-}(CH_2)_4OC(O)CCo_3(CO)_9]Cr(CO)_3$ **43** have recently been prepared [47a] (see also Chapter 2 of this thesis). The compounds were both prepared by a method first developed by Seyferth and co-workers [47b]. The authors reported the reaction of the acylium ions, $[(CO)_9Co_3CCO]^+X^-$ (X = $AlCl_4\cdot AlCl_3$ [47b], PF_6 [47c]), with a variety of alcohols and ammines, giving addition products of the type $(CO)_9Co_3CC(O)OR$ and $(CO)_9Co_3CCONHR$ respectively. Domingo and Moss [47a] have prepared **42** and **43** using an analogous method. Thus, when they reacted the alcohols $[\eta^6\text{-}C_6H_5CH_2OH]Cr(CO)_3$ and $[\eta^6\text{-}C_6H_5(CH_2)_4OH]Cr(CO)_3$ with the acylium ion $[(CO)_9Co_3CCO]^+[AlCl_4\cdot AlCl_3]^-$, under similar reaction conditons employed by Seyferth [47b], the complexes **42** and **43** were isolated respectively (equation 8).

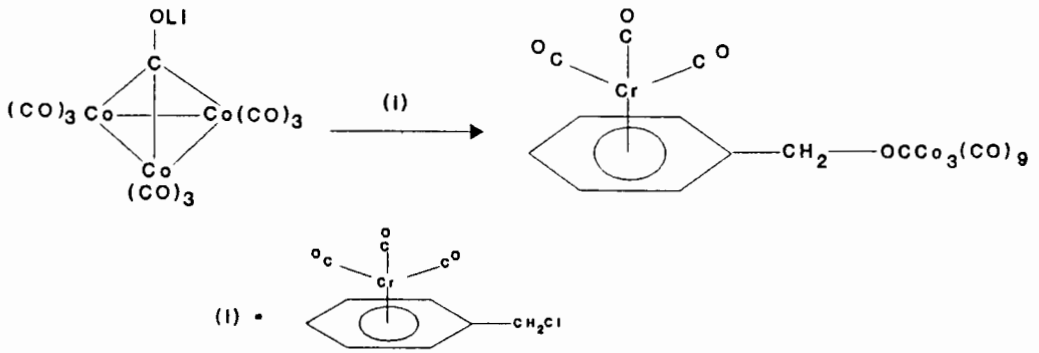


(8)

Both complexes were isolated as dark-purple, air-stable solids. The complexes were characterized by the usual spectroscopic methods. In particular, the IR{ν(CO)}

spectra of **42** and **43** showed bands characteristic of $(CO)_9Co_3CR$ type complexes as well as bands characteristic of (η^6-arene)$Cr(CO)_3$ type complexes. A singlet band due to the acyl group was also observed.

The complex $[\eta^6\text{-}C_6H_5CH_2OCCo_3(CO)_9]Cr(CO)_3$ **44** has been recently prepared by reacting the anionic cluster $(CO)_9Co_3CO^-Li^+$ with $[\eta^6\text{-}C_6H_5CH_2Cl]Cr(CO)_3$ (equation 9) [62].



(9)

Even though the complex is structurally very similar to the previous two complexes, its physical properties are remarkably different. In contrast to complexes **42** and **43**, compound **44** is highly unstable towards air moisture, both in solution and in the solid state. The complex is stable indefinitely (at RT) under an inert atmosphere in the solid state. Solutions of this complex, however, decompose slowly under an inert atmosphere.

1.2.5 Compounds having a Co:Cr atomic ratio of 4

The only compound in this class, $(CO)_3CrMes(CH_2)_3MesCo_4(CO)_9$ **45**, was formed in 30% yield by the reaction of the arene $Mes(CH_2)_3MesCr(CO)_3$, with $Co_2(CO)_8$ (figure 26) [63].

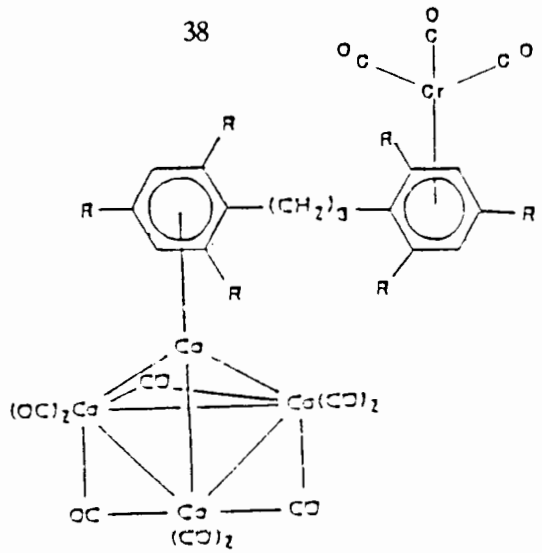


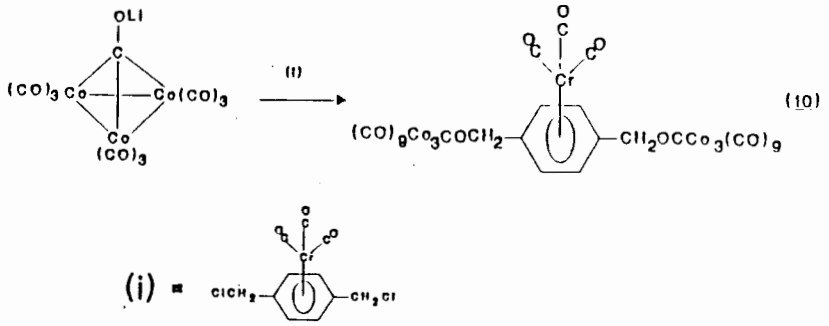
Figure 26: Structure of $(CO)_3CrMes(CH_2)_3MesCo_4(CO)_9$ **45**

The vibrational spectrum of this air-stable compound shows the presence of terminal and bridging carbonyl ligands. It is decomposed by alcoholic alkali solutions, and the arene-Co bond was found to be less resistant towards nucleophiles than the arene-Cr bond. In contrast, irradiation (UV light) of **45** results in the loss of the $Cr(CO)_3$ fragment. This demonstrates the greater photochemical stability of the arene-Co bond over that of the arene-Cr bond, the reverse of the trend with respect to nucleophiles.

1.2.6 Compounds having a Co:Cr atomic ratio of 6

The synthesis of $[\eta^6\text{-}C_6H_4\{CH_2OC(O)CCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$ **46** [47a] (see also Chapter 2 of this thesis), was accomplished by a method analogous to that described earlier for the synthsesis of **42** and **43**. Thus, reaction of the diol $[\eta^6\text{-}C_6H_4(CH_2OH)_2\text{-}1,4]Cr(CO)_3$, with two molar equivalents of the acylium cation $(CO)_9Co_3CCO^+$, resulted in the formation of **46**. This heptanuclear complex has properties similar to those described earlier for complexes **42** and **43**. This complex also possesses remarkable stability and is soluble in a range of organic solvents.

A related complex $[\eta^6\text{-}C_6H_4\{CH_2OCCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$ **47** was prepared by reacting $[\eta^6\text{-}C_6H_4(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$ with a two molar equivalence of the anionic tricobalt cluster, $(CO)_9Co_3CO^-Li^+$ (equation 10) [62]. The complex has been partially characterized by IR and ^1H NMR spectroscopy. Unlike **46**, complex **47** is highly unstable with respect to air and moisture.



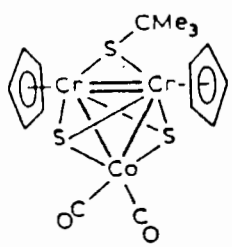
1.3 COMPOUNDS HAVING A Co:Cr ATOMIC RATIO LESS THAN 1

1.3.1 Compounds having a Co:Cr atomic ratio of 0.5

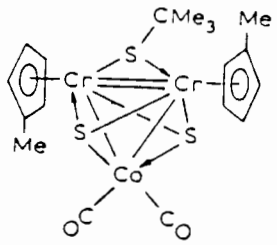
When [Co(III)(Me-N-sal)$_3$] was reacted with $Cr(CO)_6$ to form [Co(III)(Me-N-sal)$_3$]-$Cr(CO)_3 \cdot 2H_2O$ **6c**, the disubstituted product Co(III)(Me-N-sal)$_3$[$Cr(CO)_3$]$_2 \cdot 3H_2O$ **48a**, was also isolated [21]. In a similar reaction Co(III)(Ph-N-sal)$_3$[$Cr(CO)_3$]$_2 \cdot 3H_2O$ **48b** was obtained from [Co(III)(Ph-N-sal)$_3$] [21].

The complexes $[Cr_2Co(\mu_3\text{-}S)_2(\mu\text{-}SBu^t)(CO)_2X_2]$ (X = Cp **49a** and Cp′ **49b**) were reported by Pasynskii and co-workers. The two complexes are structurally identical, except for the identity of two of the associated ligands. Compound **49b** was prepared by reacting $Cp'_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)$ with $Co_2(CO)_8$ in heptane [64]. The compound is moderately sensitive to oxygen and moisture, and is readily soluble even in aliphatic hydrocarbons. The cyclopentadienyl analogue **49a** was formed in an

analogous reaction from $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)$ [65]. The latter compound decomposes slowly in air and has good solubility in aromatic solvents and THF. It is, however, only sparingly soluble in saturated hydrocarbons. The structures of both trinuclear metallocycles, **49a** and **49b**, were proven by x-ray crystallography (figure 27). Their main geometric parameters are similar, with the Cr-Cr bond lengths in **49b** being shorter (by 0.02 - 0.04 Å) than those of **49a**. The Cp′ rings of **49b** are in a staggered conformation, in contrast to the eclipsed conformation of the Cp rings of **49a**. The formation of **49a** and **49b** represents a major reorganization of both starting complexes.



49a



49b

Fig. 27: Molecular Structures of $[Cr_2Co(\mu_3\text{-}S)_2(\mu\text{-}SBu^t)(CO)_2X_2]$

X = Cp **49a** and Cp′ **49b**

The complexes, $LnMAsMe_2Co(CO)_3AsMe_2Cr(CO)_2CpAsMe_2Cr(CO)_3Cp$ (MLn = $Fe(CO)_4$ **50a** and $Mn(CO)_2Cp$ **50b**), were reported by Vahrenkamp and co-workers [66]. The synthesis of these complexes, having chain like arrangements of metal atoms with bridging arsenic atoms, was accomplished in a two step reaction. The first step in the synthesis of **50a** involves the opening of the metal-metal bond of $(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ by norbornadiene (nbd), giving the species $(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_2(nbd)$. Norbornadiene is then replaced in the second step by two molecules of the Lewis base $Cp(CO)_3CrAsMe_2$, resulting in the formation of **50a**.

Complex **50b** was formed in an analogous two-step reaction from $Cp(CO)_2Mn(\mu\text{-}AsMe_2)Co(CO)_3$. The structures of the complexes were deduced from their spectroscopic properties and confirmed by an x-ray crystal structure analysis of **50a** (figure 28).

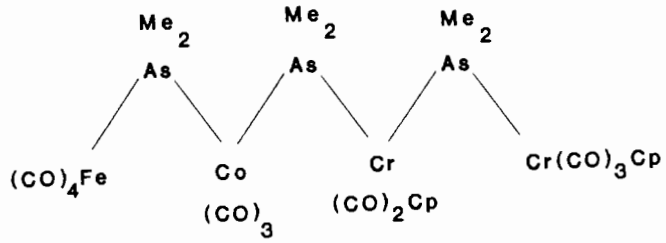


Figure 28: Structure of

$(CO)_4FeAsMe_2Co(CO)_3AsMe_2Cr(CO)_2CpAsMe_2Cr(CO)_3Cp$ **50a**

Vahrenkamp and Trenkle reported the synthesis of $(NO)(CO)Co\{Me_2PMe_2PCr(CO)_5\}_2$ **51** [27]. The compound was prepared from the reaction of $(NO)(CO)Co(\mu\text{-}Me_2PMe_2P)Cr(CO)_5$ with $Me_2PMe_2PCr(CO)_5$. When the reactants were kept at 100°C for 1.5 hr, compound **51** was isolated in 20% yield.

Air-stable brown crystals of $Cp'Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2Co(\mu_3\text{-}S)_2Fe_2(CO)_6$ **52** were obtained when a benzene solution of **49b** and $Fe_2(CO)_6S_2$ was kept at 45°C for 2 hrs under UV irradiation [67]. Four bands (1960, 1970, 2015, 2050 cm^{-1}), assigned to CO stretching vibrations, are present in the IR spectrum of **52**. An x-ray diffraction study showed strong Cr-Co {2.629(1) Å) and S-Co (2.182(2) - 2.198(2) Å} bonds, as well as two short Co-Fe {2.538(2) and 2.554(2) Å} bonds (figure 29). The Fe···Fe distance of 3.399(2) Å is non-bonding. The dihedral angle between the planes of the Cr_2Co and $CoFe_2$ triangles is 90°.

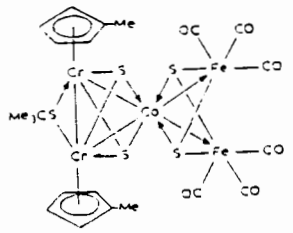


Figure 29: Structure of $Cp'Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2Co(\mu_3\text{-}S)_2Fe_2(CO)_6$ **52**

1.3.2 Compounds having a Co:Cr atomic ratio of 0.3

Reaction of **49a** with diphenylacetylene in refluxing toluene leads to the formation of the metallahedron, $Cp_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ **53a** [68]. This diamagnetic compound is formed in 20% yield and can be isolated in analytically pure form. X-ray structural analysis shows that **53a** has a Cp_3Cr_3 triangle {mean Cr-Cr bond length of 2.818(4) Å} at the base and a Co(CO) group at the vertex {mean Co-Cr bond length of 2.658(4) Å}. The four sulphur atoms are located on a tetrahedron face {mean Co-S and Cr-S bond lengths of 2.163(6) Å and 2.244(6) Å respectively}, resulting in a psuedo-cubanic structure of Co and Cr atoms.

The methylcyclopentadienyl analogue of **53a**, $Cp'_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ **53b,** was synthesized by a similar method [69]. Heating (100°C) a heptane solution of **49b** in the presence of diphenylacetylene produced **53b**. The compound could be obtained in analytically pure yield after one recrystallization. An x-ray diffraction study revealed a psuedo-cubanic structure similar to that of **53a.**

The complex $Cp_3Cr_3(\mu_3\text{-}S)_3(\mu_3\text{-}O)Co(CO)_3 \cdot HOOCCMe_3$ **54** [70] was formed by adding pivalic acid to the reaction mixture used for the formation of **49a.**

Compound **54** crystallizes with a 0.5 mole of solvent. The structure of **54** was proved by x-ray crystallography (figure 30).

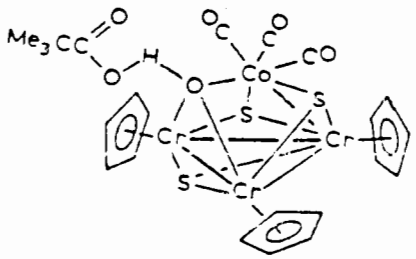


Fig. 30: Molecular structure of $Cp_3Cr_3(\mu_3\text{-}S)_3(\mu_3\text{-}O)Co(CO)_3 \cdot HOOCCMe_3$ **54**

The cluster contains an isoscles metal triangle, Cp_3Cr_3 {Cr-Cr bond lengths of 2.692(7) Å, 2.868(8) Å and 2.884(8) Å}, which is capped by a tridentate bridging sulphur atom {mean Cr-S bond length of 2.26(1) Å}. The short Cr-Cr bond is bridged by an oxygen atom, and the long Cr-Cr bonds have sulphide bridges which in turn are weakly bonded to the $Co(CO)_3$ group. In addition the μ_3-O atom forms a hydrogen bond with one $HOOCCMe_3$ molecule.

1.3.3 Compounds having a Co:Cr atomic ratio of 0.25

Heating (100°C, 4 hr) a mixture of **49a** in xylol in the presence of Me_3CCOOH, led to the formation of the antiferrromagnetic cluster $[Co\{Cp_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2\}_2]$ **55** (figure 31), which could be obtained in analytically pure form [70].

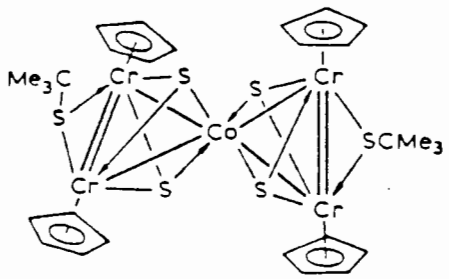


Fig 31: Molecular structure of $[Co\{Cp_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2\}_2]$ **55**

The metal atoms of this pentanuclear complex form a distorted "bow-tie" Cr_4Co framework, with the central Co atom surrounded by four μ_3-bridging sulphide atoms. The structure of the complex was determined by x-ray diffraction methods. The dihedral angle between the planes of the two Cr_2Co triangles was found to be 85.4°C.

1.4 CONCLUDING REMARKS

This chapter reviewed the synthesis and properties of heterometallic complexes containing both cobalt and chromium. A variety of synthetic routes have been established, leading to complexes having varying Co:Cr atomic ratios. Complexes having Co:Cr atomic ratios of 1 dominate. Prior to the work covered by this thesis, the highest Co:Cr atomic ratio present in an organometallic complex, was 4. Of the complexes reported in the literature, less than 29% contained only the elements Co, Cr, C, H, O and N. Of these, the highest yield was reported for the complex **8**, estimated from IR spectroscopic analysis of the reaction mixture. This complex could not, however, be isolated in analytically pure form. Thus it appears that no stable, heterobimetallic complex of cobalt and chromium, containing only the elements C, H, O and N, has been synthesised in high yield.

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CHAPTER 2

THE SYNTHESIS AND PROPERTIES OF SOME NEW HETEROBIMETALLIC TRANSITION METALS COMPLEXES CONTAINING COBALT AND CHROMIUM, AND THEIR PRECURSORS

2.1 INTRODUCTION

Many heterobimetallic complexes containing cobalt and chromium have been synthesized (see Chapter 1). Our interest in complexes of this type arises primarily from the potential of these complexes to serve as catalysts or catalyst precursors. We were particularly interested in using such complexes as catalyst precursors for the CO hydrogenation reaction (see Chapter 3). Of the complexes reported in the literature (see Table 1.1), many were however not suitable for our purposes. In order to meet our requirements[1], these compounds had to:

1) be synthesized in high yield
2) possess moderate to good stability, and
3) be free of known catalyst poisons, such as As, P, S, and halogens

Most of the known complexes were excluded on the basis of failing to meet the third requirement. Virtually all of the remaining complexes failed to meet the first and/or the second requirement.

We thus embarked on a project specifically directed towards the *high yield* synthesis of *new*, *stable* heterobimetallic complexes containing both the metals cobalt and chromium and only the elements C, H, N or O. Our research was further targeted towards the synthesis of complexes having Co:Cr atomic ratios greater than or equal to 1. We were thus interested in the synthesis of complexes of the type:

---

1. These requirements had to be met, since if these complexes were to have any commercial value at all they would have to be easily obtainable at the lowest possible cost.

$[Co_mCr_nL]$, where m = 1, 2, 3..., n = 1

L = associated ligands.

Quite a few synthetic approaches are detailed in the literature for the preparation of complexes of the type $[Co_mCr_nL]$ (m, n = 1, 2, 3 ...). The following synthetic rationale was adopted in our work (see Scheme 2.1).

$$[Co_mL'] + [Cr_nL''] \longrightarrow [Co_mCr_nL]$$

where [ ] represents an organometallic synthon or molecule;

L′, L′′, L = associated ligands;

m = 1, 2, 3... and n = 1

Scheme 2.1: Synthetic rationale for the syntheses of new heterobimetallic complexes containing cobalt and chromium

It was thought that the interaction of appropriate *stable* monometallic cobalt synthons ($[Co_mL']$, m = 1, 2, 3...), with *stable* monometallic chromium synthons ($[Cr_nL'']$, n = 1), would produce *stable* heterobimetallic complexes of the type $[Co_mCr_nL]$ (m = 1, 2, 3... and n = 1). The main cobalt containing synthon used was "$Co(DH)_2(py)$", whose reagent equivalent is $Co(DH)_2(py)Cl$. Reduction of $Co(DH)_2(py)Cl$ with sodium borohydride, effectively gives rise to the anion $[Co(DH)_2(py)]^-$ in solution.

Arene tricarbonylchromium complexes are generally found to be stable compounds [1]. Thus, suitably substituted (η^6-arene)$Cr(CO)_3$ complexes were chosen as the chromium containing synthon ($[CrL'']$). The arene substituent thus had to be such

that it contained an electron deficient atom which could be attacked by the anion $[Co(DH)_2(py)]^-$. This method was used in the syntheses of the complexes $[Co_mCr_nL]$ (where m = 1, 2 and n = 1). In the case where m = 2, two units of "$Co(DH)_2(py)$" were reacted with the appropriate disubstituted arene complex (η^6-arene)$Cr(CO)_3$.

When attempting to synthesise complexes of the type $[Co_3CrL]$ we used "$(CO)_9Co_3C$", whose reagent equivalent is the complex $(CO)_9Co_3CCl$, as the cobalt containing synthon. The cationic species $[(CO)_9Co_3C(CO)]^+$, can be conveniently generated from $[(CO)_9Co_3CCl]$ by the action of $AlCl_3$. This cationic species can then be reacted with an appropriate nucleophilic (η^6-arene)$Cr(CO)_3$ complex to yield complexes of the type $[Co_3CrL]$.

The synthesis and properties of the new complexes are dealt with in this chapter. Many of the complexes reported here, are *homometallic* complexes containing either cobalt or chromium, which were prepared during the course of our studies. All of these complexes are however precursors to, or potential precursors to, heterobimetallic complexes containing both cobalt and chromium. The complexes were all fully characterized by the usual spectroscopic methods and the x-ray crystal structure of one of them was determined.

2.2 RESULTS AND DISCUSSION[2]

2.2.1 Synthesis of the new complexes

2.2.1.1 Synthesis of the monometallic chromium complexes

All the monometallic chromium complexes prepared are substituted (η^6-arene)tricarbonyl chromium complexes. Many complexes of this type have been reported in the literature. The parent (benzene)tricarbonylchromium complex $[\eta^6\text{-}C_6H_6]Cr(CO)_3$, was first synthesized in 1957 [2] by the reaction of $[Cr(\eta^6\text{-}C_6H_6)_2]$ with $Cr(CO)_6$ (equation 1).

$$[Cr(\eta^6\text{-}C_6H_6)_2] + Cr(CO)_6 \longrightarrow 2[\eta^6\text{-}C_6H_6]Cr(CO)_3 \qquad (1)$$

The reaction however requires vigorous conditions (sealed tube, 220°C) and gives only moderate (25%) yields. A variety of more straightforward, and often high yield synthetic routes, are now available for the preparation of complexes of this type. Of all the methods available however, the thermal replacement of CO from $Cr(CO)_6$ by arenes (equation 2) has been the most widely used [3 - 6].

$$\text{arene} + Cr(CO)_6 \xrightarrow{\Delta} [\eta^6\text{-arene}]Cr(CO)_3 + 3CO \qquad (2)$$

A multitude of substituted (η^6-arene)tricarbonyl chromium complexes have been synthesized by this method. It has been found that electron-donating substituents (e.g. Me, NH_2) facilitate the reaction, whereas electron-withdrawing substituents

2. All numbered complexes are from present work

(e.g. Cl, CO_2Me) retard the reaction. It has been found further that with strongly electron-withdrawing groups (CHO, CO_2H) the reaction conditions are too drastic to allow isolation of any (η^6-arene)tricarbonylchromium complex.

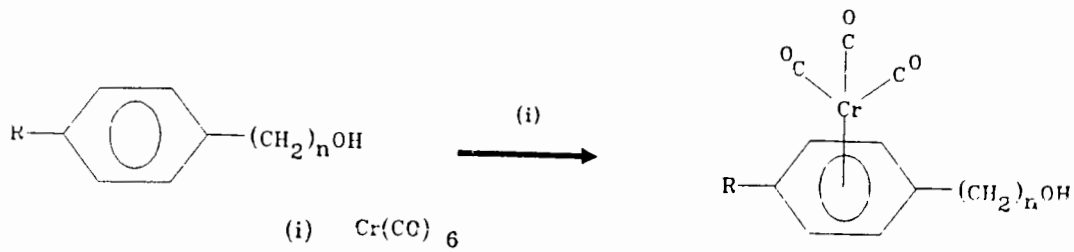
The reaction (equation 2), is conveniently performed by refluxing under dinitrogen in an open system where the loss of CO helps drive the reaction to completion. Numerous solvent systems have been used (decalin [6], diglyme [6, 7], di-n-butyl ether and THF [8], among others). An approximately 10/1 mixture of di-n-butyl ether and THF, has been found to be the most convenient solvent system for this reaction. It has been used in a wide range of high yield syntheses of (arene)$Cr(CO)_3$ complexes [4, 9, 10].

The latter method was employed in our work for the preparation of the new (arene)tricarbonyl chromium complexes $[\eta^6\text{-}C_6H_5NHCH_2Ph]Cr(CO)_3$ **1**, $[\eta^6\text{-}C_6H_4(CH_2OH)_2\text{-}1,4]Cr(CO)_3$ **2**, and $[\eta^6\text{-}C_6H_5(CH_2)_4OH]Cr(CO)_3$ **3**. Thus, reaction of N-benzylaniline with an equimolar amount of $Cr(CO)_6$ under reflux in a 10/1 mixture of di-n-butyl ether and THF, leads to the formation of **1** (equation 3).

$$C_6H_5NHCH_2Ph + Cr(CO)_6 \xrightarrow[\text{reflux}]{\text{di-n-butyl ether/THF}} \underset{\mathbf{1}}{[\eta^6\text{-}C_6H_5NHCH_2Ph]Cr(CO)_3} \quad (3)$$

There is no apparent formation of the disubstituted complex, that is, the complex which has a $Cr(CO)_3$ group attatched to both of the two phenyl rings of N-benzylaniline. Only the complex which has the $Cr(CO)_3$ unit attached to the benzene ring derived from aniline (that is, the more electron-rich ring) was isolated.

Similar reactions (equation 4) led to the formation of **2** and **3** from $[C_6H_4(CH_2OH)_2\text{-}1,4]$ and $[C_6H_5(CH_2)_4OH]$ respectively.

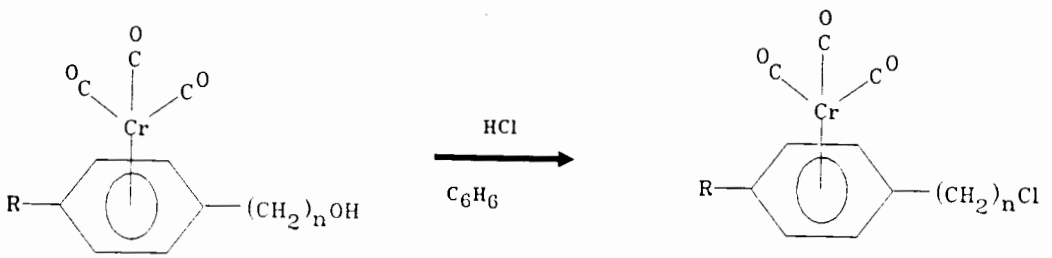


(i) $Cr(CO)_6$
di-n-butyl ether/THF
reflux, 20 -24 hrs

(4)

	n	R
2	1	CH_2OH
3	4	H

Holmes and co-workers reported the reaction of the monosubstituted analogue of **2**, $[\eta^6\text{-}C_6H_5CH_2OH]Cr(CO)_3$, with concentrated hydrochloric acid which yielded the benzyl chloride complex $[\eta^6\text{-}C_6H_5CH_2Cl]Cr(CO)_3$ [11].. This prompted us to react our new complexes **2** and **3** with hydrochloric acid in a similar manner. Thus, when we reacted **2** with HCl, following the method of Holmes (we however used double the amount of HCl that they used), the corresponding disubstituted complex $[\eta^6\text{-}C_6H_4(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$ **4** was isolated (equation 5).



(5)

	n	R
4	1	CH_2Cl
5	4	H

Similarly, reaction of $[\eta^6\text{-}C_6H_5\{(CH_2)_4OH\}]Cr(CO)_3$ **3** with HCl yielded $[\eta^6\text{-}C_6H_5\{(CH_2)_4Cl\}]Cr(CO)_3$ **5** (equation 5). In the latter reaction however, the method of Holmes was strictly followed.

2.2.1.2 Synthesis of the monometallic cobalt complexes of the type $Co(DH)_2(py)R$

The mononuclear cobaloxime complexes $[\{(py)(DH)_2CoCH_2\}C_6H_4(CH_2Br)\text{-}1,n]$ (n = 4, **6**; n = 3, **7**; n = 2, **8**), were prepared by a similar method to that described by Finch and Moss for the preparation of the mononuclear haloalkyl complexes of the type $[Co(DH)_2(py)\{(CH_2)_nX\}]$, X = Br, I, and n = 3 - 7 [12]. They reported the formation of these complexes from the reaction of $[Co(DH)_2(py)Cl]$ with a 1.5 molar excess of the appropriate dihaloalkanes, $X(CH_2)_nX$, in the presence of sodium borohydride (equation 6).

$$[Co]Cl + X\text{-}(CH_2)_n\text{-}X \xrightarrow[MeOH]{NaBH_4} [Co]\text{-}(CH_2)_n\text{-}X \qquad (6)$$

X = Br, I; n = 3 - 7 [12]

When we thus reacted $[Co(DH)_2(py)Cl]$ with $[C_6H_4(CH_2Br)_2\text{-}1,n]$ (n = 4, 3, 2), under similar reaction conditions, we isolated the complexes **6**, **7** and **8** (equation 7).

$$[Co]Cl + C_6H_4(CH_2Br)_2\text{-}1,n \xrightarrow[MeOH]{NaBH_4} ([Co]\text{-}CH_2)C_6H_4(CH_2Br)\text{-}1,n \qquad (7)$$

n = 4, **6**; n = 3, **7**; n = 2, **8**

When **6**, **7** and **8** were each reacted further with an equimolar amount of $[Co(DH)_2(py)Cl]$ (again under similar reaction conditions), they were found to yield

the dinuclear *xylylene-bridged* complexes $[C_6H_4\{CH_2Co(DH)_2(py)\}_2\text{-}1,n]$ (n = 4, **9**; n = 3, **10**; n = 2, **11**) (equation 8). The reaction was similar to that reported for the preparation of the dinuclear *polymethylene-bridged* complexes $[(py)(DH)_2Co]_2$-$[\mu\text{-}(CH_2)_n]$ [12] and $[L(CO)_2Fe]_2[\mu\text{-}(CH_2)_n]$ (L = Cp [13], Cp′ and Cp* [14]).

$$[Co]Cl + (BrCH_2)C_6H_4(CH_2[Co])\text{-}1,n \xrightarrow[MeOH]{NaBH_4} C_6H_4(CH_2[Co])_2\text{-}1,n \qquad (8)$$

n = 4, **9**; n = 3, **10**; n = 2, **11**

Finch and Moss also reported the *direct* synthesis of the dinuclear, *polymethylene-bridged* cobaloximes $[(py)(DH)_2Co]_2[\mu\text{-}(CH_2)_n]$ (n = 4 - 8) [12]. This involved reacting the appropriate dihaloalkane $X(CH_2)_nX$ (X = Cl, Br) with a *two molar equivalence* of $[Co(DH)_2(py)Cl]$ in the presence of $NaBH_4$. We adopted their preparative procedure for the *direct* synthesis of the three isomeric dinuclear *xylylene-bridged* cobaloxime complexes **9**, **10** and **11**. Thus when we reacted $[C_6H_4(CH_2Br)_2\text{-}1,n]$ (n = 4, 3, 2) with two molar equivalents of $[Co(DH)_2(py)Cl]$ in the presence of $NaBH_4$, it resulted in the formation of complexes **9**, **10** and **11** respectively (equation 9).

$$[Co]Cl + C_6H_4(CH_2Br)_2\text{-}1,n \xrightarrow[MeOH]{NaBH_4} C_6H_4\{CH_2[Co]\}_2\text{-}1,n \qquad (9)$$

n = 4, **9**; n = 3, **10**; n = 2, **11**

When $[C_6H_4(COCl)_2\text{-}1,4]$ and $[Co(DH)_2(py)Cl]$ were reacted in an analogous manner to that described above (in equation 9), the *phenylene-bridged* dinuclear cobaloxime complex $[C_6H_4\{Co(DH)_2(py)\}_2\text{-}1,4]$ **12**, was isolated. Complex **12** represents the decarbonylated product. The reaction most likely proceeds *via* the

formation of the intermediate *di-acyl* complex, $[C_6H_4\{C(O)Co(DH)_2(py)\}_2\text{-}1,4]$, followed by decarbonylation leading to the formation of **12**. However, no evidence could be found to prove the presence of the latter complex in the crude reaction product. When the reaction was monitored with IR spectroscopy, from the time the reaction was started, no bands assignable to an acyl metal-carbonyl group could be detected. In fact, the initial acyl band (due to the starting acid chloride complex) dissapeared within minutes of starting the reaction. It thus seems that the carbonylated complex is either too unstable, or that the rate of decarbonylation (under the conditions of the reaction) is too rapid to allow for the isolation of the proposed intermediate complex. Further experiments are thus necessary to prove the existence of the carbonylated complex, for example carrying out the reaction using a very short reaction time and/or lower temperatures to slow down the rate of decarbonylation.

2.2.1.3 Synthesis of the monometallic cobalt complexes of the type $(CO)_9Co_3CR$

A paper by Seyferth, Williams and Nivert [15], reported the formation of the acylium haloaluminate salts $[(CO)_9Co_3CCO]^+[AlX_4 \cdot AlX_3]^-$ (X = Cl, Br, I), from the action of aluminium halides on halomethylidynetricobalt nonacarbonyl complexes. Thus for example, they reported the reaction (equation 10) of

$$(CO)_9Co_3CCl + AlCl_3 \xrightarrow[30\ min]{CH_2Cl_2} [(CO)_9Co_3CCO]^+[AlCl_4 \cdot AlCl_3]^- \quad (10)$$

$(CO)_9Co_3CCl$ with $AlCl_3$ (3 molar equivalents), which yielded the acylium cation $[(CO)_9Co_3CCO]^+[AlCl_4 \cdot AlCl_3]^-$ having the structure shown in figure 2.1.

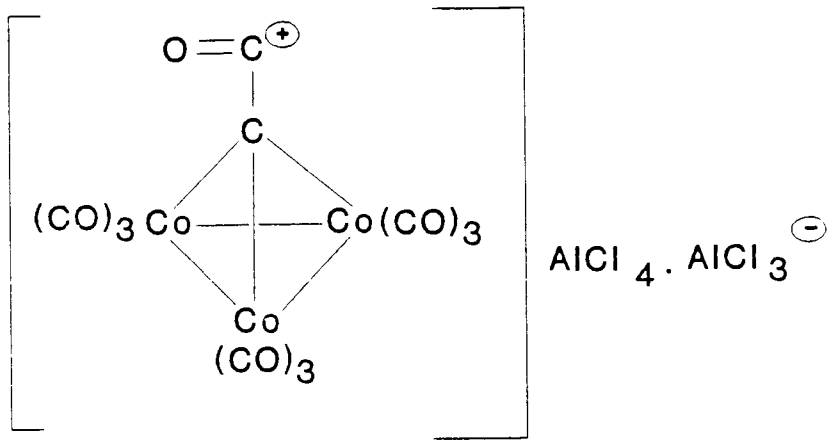


Figure 2.1: Structure of $[(CO)_9Co_3CCO]^+[AlCl_4 \cdot AlCl_3]^-$

They reported further that the addition of a diversity of nucleophiles (alcohols, phenols, amines, thiols and reactive aromatics) to the acylium cation yielded cluster complexes of the type $(CO)_9Co_3CC(O)Y$ (with Y = OR, OAr, RR'N, RS, R, Ar) in moderate yields. A typical example is the reaction of $[(CO)_9Co_3CCO]^+[AlCl_4 \cdot AlCl_3]^-$ with phenol which yields the complex $(CO)_9Co_3CC(O)OPh$ (equation 11) [15].

$$[(CO)_9Co_3CCO]^+[AlCl_4 \cdot AlCl_3]^- + HOPh \xrightarrow{CH_2Cl_2} (CO)_9Co_3CC(O)OPh \quad (11)$$

We adopted this synthetic method for the synthesis of the complex $(CO)_9Co_3CC(O)OCH_2Ph$ **13**. Thus, upon reacting benzyl alcohol with an equimolar amount of $[(CO)_9Co_3CCO]^+[AlCl_4 \cdot AlCl_3]^-$, complex **13** was isolated (equation 12).

$$[(CO)_9Co_3CCO]^+ + HOCH_2Ph \xrightarrow[RT]{CH_2Cl_2} (CO)_9Co_3CC(O)OCH_2Ph \quad (12)$$

13

$$[(CO)_9Co_3CCO]^+ + C_6H_4(CH_2OH)_2\text{-}1,4 \xrightarrow{CH_2Cl_2} [C_6H_4\{CH_2OC(O)CCo_3(CO)_9\}_2\text{-}1,4] \quad (13)$$

14

When the diol $[C_6H_4(CH_2OH)_2\text{-}1,4]$, was reacted with two-molar equivalents of the acylium cation in a similar manner, the reaction yielded the disubstituted complex $[C_6H_4\{CH_2OC(O)CCo_3(CO)_9\}_2\text{-}1,4]$ **14** (equation 13).

2.2.1.4 Synthesis of the heterobimetallic complexes containing cobalt and chromium

The heterobimetallic complex $[\{\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)\}Cr(CO)_3]$ **15** had been previously prepared and partially characterized [16a]. We have modified the preparative procedure which has led to increased yields, and have confirmed the structure of the complex by x-ray crystallography. The complex was prepared by a similar method to that described for the preparation of the mononuclear haloalkylcobalt complexes **6** - **8**. Thus, reaction of $[\{\eta^6\text{-}C_6H_5CH_2Cl\}Cr(CO)_3]$ with an equimolar amount of $[Co(DH)_2(py)Cl]$ in the presence of $NaBH_4$, yielded **15** (equation 14).

$$[Co]Cl + (\eta^6\text{-}C_6H_5CH_2Cl)Cr(CO)_3 \xrightarrow[MeOH]{NaBH_4} (\eta^6\text{-}C_6H_5CH_2[Co])Cr(CO)_3 \quad (14)$$

15

In an analogous reaction, we prepared the trinuclear complex $[\{\eta^6\text{-}C_6H_4(CH_2Co(DH)_2(py))_2\text{-}1,4\}Cr(CO)_3]$ **16**, from **4** (equation 15). Similar reaction conditions were employed except that **4** was reacted with a two molar excess of $[Co(DH)_2(py)Cl]$. Complex **16** can thus be regarded as the *disubstituted* analogue of

15. Complexes **15** and **16** represent the first heterobimetallic complexes containing cobalt and chromium that are derived from a cobaloxime.

$$2\,[Co]Cl + (\eta^6\text{-}C_6H_4\{CH_2Cl\}_2\text{-}1,4)Cr(CO)_3 \xrightarrow[MeOH]{NaBH_4} (\eta^6\text{-}C_6H_4\{CH_2[Co]\}_2\text{-}1,4)Cr(CO)_3 \quad (15)$$

4 **16**

The syntheses of **15** and **16** were also attempted *via* the thermal reaction of $Cr(CO)_6$ with the free arenes (equation 16). However when $[C_6H_5CH_2Co(DH)_2(py)]$ was reacted with $Cr(CO)_6$ in a similar manner to that described earlier for the preparation of complexes **1** - **3** (see equation 2), no π-arene complex could be isolated.

$$RC_6H_4(CH_2[Co])\text{-}1,4 + Cr(CO)_6 \xrightarrow[reflux]{n\text{-}Bu_2O/THF} [\eta^6\text{-}RC_6H_4(CH_2[Co])\text{-}1,4]Cr(CO)_3 \quad (16)$$

$$R = H, CH_2[Co]$$

The same observation was made when **7** was reacted with $Cr(CO)_6$ in a similar fashion. It has been noted earlier (Section 2.2.1.1) that free arenes having strongly electron-withdrawing substituents fail to undergo the thermal reaction (equation 2) with chromium hexacarbonyl. The failure of our reactions (equation 16) cannot, however, be ascribed to the same reason. Evidence, in fact, suggests that the "$CH_2Co(DH)_2(py)$" group is mildly electron-donating[3]. It would thus seem that the reaction conditions (di-n-butyl ether/THF, reflux, 2 - 3 hrs) employed, result in the decomposition of the starting arene and/or the product π-arene complexes. When

3. IR evidence suggests that the $CH_2Co(DH)_2(py)$ unit is more electron donating than two methyl groups (see Section 2.2.2.5.)

15 was heated (di-n-butyl ether/THF, 1 hr) at reflux, it was indeed found to decompose completely (as indicated by IR spectroscopy).

As mentioned earlier (Section 1.2.4), the synthesis of $[\eta^6\text{-PhCCo}_3(\text{CO})_9]\text{Cr}(\text{CO})_3$ **17** was briefly described by Seyferth in a review article [16b]. No experimental details or characterization data were provided, nor were any found in the references listed. We thus repeated the synthesis of this complex by the method implied by Seyferth [16b]. The complex was indeed found to be formed upon reacting $(\text{CO})_9\text{Co}_3\text{CH}$ with $[(\eta^6\text{-Ph})\text{Cr}(\text{CO})_3]_2\text{Hg}$ (equation 17).

$$(\text{CO})_9\text{Co}_3\text{CH} + [(\eta^6\text{-Ph})\text{Cr}(\text{CO})_3]_2\text{Hg} \xrightarrow[\text{THF}]{\text{CO}} \underset{\textbf{17}}{[\eta^6\text{-PhCCo}_3(\text{CO})_9]\text{Cr}(\text{CO})_3} \quad (17)$$

The reaction was performed in THF under an atmosphere of CO (CO was also bubbled through the reaction mixture during the reaction). The reaction is conveniently monitored by IR spectroscopy. The appearance (at higher wavenumber) of new $\nu(\text{CO})_{\text{Cr-CO}}$ bands is observed with the concomittant disappearance of the $\nu(\text{CO})$ bands of the starting $(\text{arene})\text{Cr}(\text{CO})_3$. At the same time the starting $\nu(\text{CO})_{\text{Co-CO}}$ bands remain virtually unchanged. This is, however, not too surprising, since $\nu(\text{CO})_{\text{Co-CO}}$ bands of $(\text{CO})_9\text{Co}_3\text{CR}$ complexes, in general, are relatively insensitive to the nature of the R group [17].

We also attempted the preparation of **17** from the thermal reaction (as in the preparation of **1** - **3**) of the free arene and $\text{Cr}(\text{CO})_6$. Thus $(\text{CO})_9\text{Co}_3\text{CPh}$ was reacted with $\text{Cr}(\text{CO})_6$ in a mixture of refluxing di-n-butyl ether/THF (equation 18).

$$(CO)_9Co_3CPh + Cr(CO)_6 \xrightarrow[\text{reflux}]{\text{di-n-butyl ether/THF}} [\eta^6\text{-}PhCCo_3(CO)_9]Cr(CO)_3 \quad (\underline{18})$$

17

This route did not, however, yieid **17**. The reaction was monitored by IR spectroscopy which showed no evidence to indicate the formation of any π-arene complex. It was further noted that the decomposition of the starting cobalt complex was quite rapid under the conditions of the reaction. A milder method of putting a "$Cr(CO)_3$" unit onto an arene ring was thus needed. Several such methods are reported in the literature. These include the reaction of the free arene with $Cr(CO)_3(py)_3$ (Et_2O, RT, $BF_3 \cdot Et_2O$) [18 - 20], $Cr(CO)_3(NH_3)_3$ (dioxane, 100°C, 7 hr) [20, 21], $Cr(CO)_3(CH_3CN)_3$ (THF, RT, 24 hr [22]; THF, reflux, 3 hr [23]) (equation 19).

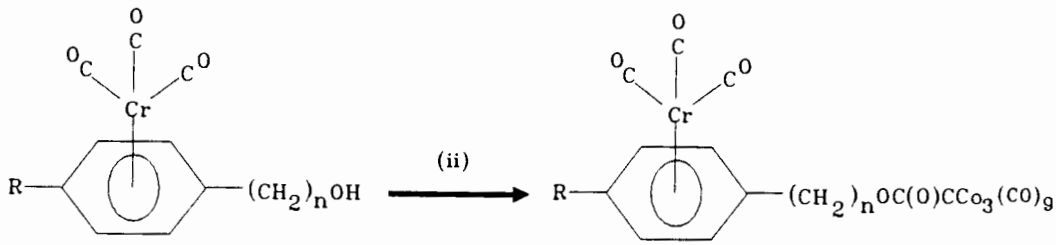
$$\text{arene} + Cr(CO)_3L_3 \xrightarrow[L = py,\ NH_3,\ CH_3CN]{\text{"mild conditions"}} (\eta^6\text{-arene})Cr(CO)_3 \qquad (\underline{19})$$

The photochemical synthesis of (arene)tricarbonylchromium complexes can also be achieved under mild conditions [24], although the yields are generally lower than those attained by the thermal methods. We only investigated the reaction of $(CO)_9Co_3CPh$ with $Cr(CO)_3(py)_3$ (Et_2O, RT, $BF_3 \cdot Et_2O$) (equation 20). This resulted in the formation of **17**, albeit in low yield. No yield optimisation experiments were however performed. IR spectroscopy (ν(CO)), showed clearly the appearance of two carbonyl bands characteristic of an (arene)tricarbonyl chromium complex. The relative intensity of the latter bands increased as the reaction proceeded, while the ν(CO) bands characteristic of substituted $(CO)_9Co_3CR$ complexes persisted.

$$(CO)_9Co_3CPh + Cr(CO)_3(py)_3 \xrightarrow[Et_2O,\ RT]{BF_3\cdot Et_2O} [\eta^6\text{-}PhCCo_3(CO)_9]Cr(CO)_3 \quad (\underline{20})$$

17

The complexes $[\eta^6\text{-}C_6H_5\{(CH_2)_nOC(O)CCo_3(CO)_9\}]Cr(CO)_3$ (n = 1, **18**; n = 4, **19**) were prepared using the same synthetic methodology employed for the synthesis of **13** and **14** (see equations 13 and 14). Thus the reaction of the acylium cation $[(CO)_9Co_3CCO]^+[AlCl_4\cdot AlCl_3]^-$ with an equimolar amount of $[\eta^6\text{-}C_6H_5\{(CH_2)_nOH\}]Cr(CO)_3$ (n = 1 [11] and n = 4, **3**) led to the formation of **18** and **19** respectively (equation 21).



(ii) CH_2Cl_2, $AlCl_3$, $(CO)_9Co_3CCl$

	n	R
18	1	H
19	4	H
20	1	$CH_2OC(O)CCo_3(CO)_9$

(21)

A similar reaction of **2** with two molar equivalents of the acylium cation led to the formation of **20** (equation 21).

2.2.2 Physical and spectroscopic properties of the new complexes

All the compounds reported here were characterized by the usual spectroscopic methods. These include ^1H NMR, ^{13}C NMR and infrared spectroscopy. Except for

the organocobaloxime complexes, the molecular weights of the complexes were confirmed by molecular ion peaks in their mass spectra. The mass spectra of virtually all of the complexes studied by this technique exhibited fragmentation patterns characteristic of the class of compounds to which they belong. In all cases, the compounds gave satisfactory elemental analysis. The molecular structure of **15** (suggested on the basis of the available spectroscopic data) was confirmed by x-ray crystallography.

2.2.2.1 Properties of the monometallic Chromium complexes

All the new mononuclear (η^6-arene)$Cr(CO)_3$ complexes (Table 2.1), are yellow crystalline solids which are highly soluble in a range of organic solvents. The latter property allows purification of the complexes to be conveniently carried out by column chromatography and/or recrystallization. As seen from Table 2.1, all the complexes may be prepared in moderate to high yield.

Table 2.1: Yield and melting point data for the monometallic chromium complexes

Complex No.	Formula	Colour	M.P. (°C)	Yield (%)
1	$[\eta^6\text{-}C_6H_5NHCH_2Ph]Cr(CO)_3$	yellow	120 - 121	67
2	$[\eta^6\text{-}C_6H_4(CH_2OH)_2\text{-}1,4]Cr(CO)_3$	yellow	108 - 109	90
3	$[\eta^6\text{-}C_6H_5\{(CH_2)_4OH\}]Cr(CO)_3$	yellow	48 - 52	81
4	$[\eta^6\text{-}C_6H_4(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$	yellow	77 - 79	80
5	$[\eta^6\text{-}C_6H_5\{(CH_2)_4Cl\}]Cr(CO)_3$	yellow	oil	60

Compounds **1**, **2** and **3** are highly stable in air in the solid state[4], although refrigeration is recommended for prolonged storage. The chlorinated complexes **4** and **5**, on the other hand, are much more sensitive to air and moisture[5]. Solutions of **4** and **5**, when exposed to air, decompose rapidly and in the solid state form a green decomposition product after a few hours. Solutions of **1** - **5** are stable for extended periods under an inert atmosphere.

^{1}H NMR

The ^{1}H NMR data for compounds **1** - **5** are contained in Table 2.2. All show signals due to the phenyl ring in the region δ 4.7 - 5.9 ppm. The symmetrical disubstituted complexes (**2** and **4**) have singlets (δ 5.70 and δ 5.85 ppm respectively) for the four equivalent phenyl protons. As expected, the signal for phenyl protons of **4** is slightly more upfield, due to the greater electron-withdrawing nature of its substituents. The phenyl protons of the other complexes (**1, 3, 5**) all show the pattern expected for monosubstituted derivatives of this type, namely, a doublet and two triplets coresponding to the ortho, meta and para protons respectively. The signals due the ortho and para protons of **1**, were however unresolved, and occur together as a multiplet (δ 4.78 ppm) integrating for three protons.

The methylene and hydroxy protons occur more or less in the expected positions. The different nature of the various substituents does not allow for comparison and identification of any trends for these signals.

---

4. Samples exposed to air showed no sign of decomposition even after several months

5. The monosubstituted analogue of **4**, $[\eta^6$-$C_6H_5CH_2Cl]Cr(CO)_3$, displays a similar sensitivity [11]

Table 2.2: ^{1}H NMR ($CDCl_3$) data[a] for compounds **1** - **5** (multiplicity and integration are shown in brackets)

Compound	arene			other				
No.	*o*-H	*m*-H	*p*-H	$PhC\underline{H}_2$	$PhCH_2C\underline{H}_2$	$C\underline{H}_2CH_2X$[b]	$C\underline{H}_2X$[b]	O<u>H</u>
1[c]	4.78[d]	5.55 (t, 2H)	4.78[d]	4.18 (d, 2H)	—	—	—	—
2[c]	5.70 (s, 4H)	—	—	4.40 (s, 4H)	—	—	—	4.61 (s, 2H)
3	5.52 (d, 2H)	5.68 (t, 2H)	5.47 (t, 1H)	2.44 (t, 2H)	1.64[f]	1.64[f]	3.54 (m, 2H)	3.36 (t, 1H)
4	5.85 (s, 4H)	—	—	4.54 (s, 4H)	—	—	—	—
5	5.58[g]	5.58[g]	5.58[g]	2.43 (t, 2H)	1.68[h]	1.68[h]	4.01 (d, 2H)	—

[a]: Chemical shifts (δ ppm) are relative to TMS [b]: X = OH **3**, X = Cl **5** [c]: Also signals at 7.35 ppm (s, 5H) assigned to the free phenyl ring, and 3.80 ppm (bs, 1H) assigned to N<u>H</u> [d]: Signals unresolved, occur as a multiplet integrating for three protons [e]: Recorded in acetone-d_6 [f]: Signals unresolved, occur as a multiplet integrating for four protons [g]: Signals unresolved, occur as a multiplet integrating for five protons [h]: Signals unresolved, occur as a multiplet integrating for four protons

The spectrum of **2** exhibits some interesting features. In the first instance, on forming **2** from $[C_6H_4(CH_2OH)_2$-1,4], a loss of multiplicity is observed for the methylene and hydroxy protons. The free arene $[C_6H_4(CH_2OH)_2$-1,4] has signals at δ 4.61 (d, 4H) and δ 4.14 ppm (t, 2H) assigned to the methylene and hydroxy protons respectively. In contrast, the spectrum of **2** shows both these signals as sharp *singlets*. In the second instance, the relative positions of the methylene and hydroxy signals (of **2**) are reversed with respect to the free arene. The methylene protons (δ 4.40 ppm, 4H) have moved slightly upfield, while the hydroxy protons (δ 4.61 ppm, 2H) have become more deshielded. It was initially thought that the two signals had been erroneously assigned (inferred by the integration values alone), but the original assignments were confirmed by a HETCOR experiment.

NMR spectroscopy proved to be a useful method for identifying the product of reaction between $PhCH_2NHPh$ and $Cr(CO)_6$. Analysis of the ^1H NMR spectrum of the reaction product showed that only one set of phenyl protons moved upfield. The upfield signal consisted of a multiplet (δ 4.78 ppm, 3H) and a triplet (δ 5.55 ppm, 2H). The downfield signal consisted of a singlet (7.35 ppm, 5H). Since the splitting patterns of the up- and downfield singals were consistent with those expected for aniline and toluene respectively, the upfield signal was assigned to the PHNH ring while the downfield signal was assigned to the benzyl ring. It was thus easily proved that only the monosubstituted product, **1**, was formed, and that the "$Cr(CO)_3$" unit had complexed solely to the more electron rich phenyl ring (PhNH).

^{13}C NMR

In general, a large upfield shift occurred in the ^{13}C resonances (Table 2.3) of the arene carbon atoms, on complexing with a $Cr(CO)_3$ unit. Analysis of the ^{13}C

Table 2.3: ^{13}C NMR spectral data[a] for compounds **1** - **5** recorded in $CDCl_3$

Compound	complexed arene				$PhCH_2$	$PhCH_2CH_2$	CH_2CH_2X	CH_2X	Cr-CO
No.	C^{tert}	*o*-C	*m*-C	*p*-C					
1[b]	132.5[c]	75.7	96.6	83.4	48.0	—	—	—	234.5
2[d]	113.2	93.4	—	—	62.9	—	—	—	234.4
3	115.8	96.1[e]	95.5[e]	92.9	35.9	33.4	28.9	62.3	234.1
4	107.9	94.8	—	—	45.2	—	—	—	233.0
5	116.2	96.1	95.8	93.0	36.2	35.0	28.6	66.2	234.1

[a]: Chemical shifts (δ ppm) are relative to TMS

[b]: Signals for the uncomplexed phenyl ring at 136.7[c] (C^{tert}), 128.9 (*o*-C), 127.8 (*m*-C) and 127.9 (*p*-C) were also observed

[c]: Signals not unambiguously assigned

[d]: Recorded in acetone-d_6

[e]: Assignments confirmed by a HETCOR experiment

resonances of the reaction product of equation (3), showed that one set of phenyl carbon atoms moved upfield while the position of the other remained largely unaffected (as was found with the ^{1}H resonances). This again confirmed that only one phenyl ring had been complexed while the other remained free. A HETCOR experiment showed coupling between the upfield arene ^{13}C resonances with the upfield ^{1}H resonances. A similar coupling was observed between the downfield arene ^{13}C and ^{1}H resonances. Since the ^{1}H resonances were unambiguously assigned, the ^{13}C resonances were easily assigned.

It is also of note that the ^{13}C resonances of the chromium carbonyl ligands, in complexes **1** - **5**, are all independent of the nature of the arene substituent/s. They are all found, without exception, in the region δ 233.0 and 235.5 ppm. This is in direct contrast to IR spectroscopic data (see Section 2.2.2.5), which shows that the ν(CO) bands of the chromium carbonyl ligands are extremely sensitive to the nature of the arene substituents.

IR spectral data

The solution (CH_2Cl_2) IR spectra of complexes **1** - **5** all exhibit two bands in the ν(CO) region. The results obtained are discussed in more detail later (Section 2.2.2.5) in relation to the other (η^6-arene)$Cr(CO)_3$ complexes (**15** - **20**).

Mass Spectral data

The low resolution mass spectra of the (η^6-arene)$Cr(CO)_3$ complexes (**1** - **5**), are fairly simple and relatively easy to interpret. In all cases, molecular ion peaks of low intensity (10 - 20%) were observed.

The spectra initially show the sequential loss of all three carbonyl groups. This appears to be the major fragmentation pathway, leading to the formation of the ion $[(\eta^6\text{-arene})Cr]^+$ (m/z 235 **1**; 190 **2**; 202 **3**; 221 **5**). This represents an arene ring coordinated to a naked chromium atom. The intensity of these peaks ranges from moderate to strong.

In most cases the $[(\eta^6\text{-arene})Cr]^+$ ion further fragments by losing the chromium atom to give the $[arene]^+$ ion, followed by patterns characteristic of the free arenes.

The spectrum of $[\eta^6\text{-}C_6H_4(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$ **4**, proved to be the only one which showed any significant deviation from the pattern discussed above. This complex first loses one chlorine atom to form the ion $[\{\eta^6\text{-}C_6H_4(CH_2Cl)(CH_2)\text{-}1,4\}Cr(CO)_3]^+$ (m/z 275). It is this ion which then undergoes stepwise loss of CO to form $[\{\eta^6\text{-}C_6H_4(CH_2Cl)(CH_2)\text{-}1,4\}Cr]^+$ (m/z 191). This latter ion then fragments further forming $[C_6H_4(CH_2Cl)(CH_2)\text{-}1,4]^+$ (m/z 139), with loss of chromium. The base peak corresponds to the ion $[C_6H_4(CH_2)_2\text{-}1,4]^+$ (m/z 104).

2.2.2.2 Properties of the monometallic cobalt complexes of the type $Co(DH)_2(py)R$

All the substituted cobaloxime complexes **6** - **12**, are air-stable orange solids (Table 2.4). The complexes can be conveniently stored in air for months without any apparent decompostion. Methylene chloride solutions of these compounds decompose within a few hours when exposed to air. They exhibit moderate to good solubility in organic solvents. Unlike methyl(pyridine)cobaloxime [25], they are not light sensitive.

Table 2.4: Yield and melting point data for the cobaloxime complexes

Complex No.	Formula[a]	Colour	M.P. (°C)	Yield (%)
6	$C_6H_4(CH_2[Co])(CH_2Br)$-1,4	orange	205(dec.)	48
7	$C_6H_4(CH_2[Co])(CH_2Br)$-1,3	orange-yellow	195(dec.)	50
8	$C_6H_4(CH_2[Co])(CH_2Br)$-1,2	orange-yellow	>207(dec.)	50
9	$C_6H_4(CH_2[Co])_2$-1,4	orange	>180(dec.)	79
10	$C_6H_4(CH_2[Co])_2$-1,3	orange	>200(dec.)	44
11	$C_6H_4(CH_2[Co])_2$-1,2	orange	>170(dec.)	40
12	$C_6H_4([Co])_2$-1,4	beige	142	33

All the new complexes have been fully characterized by melting point (Table 2.4), ^{1}H NMR (Tables 2.5 and 2.6), ^{13}C NMR (Tables 2.7) and IR spectroscopy (Table 2.16).

^{1}H NMR

For ease of discussion, the ^{1}H NMR data of the two heterobimetallic complexes **15** and **16**, are reported and discussed here. The discussion is divided into those for the monocobaloxime complexes (complexes containing only one cobaloxime unit, **6** - **8**, and **15**), and those of the dicobaloxime complexes (complexes containing two cobaloxime units **9** - **12**, **16**). Due to the variety of the compounds reported, and the relative ease of interpretation, no attempt will be made to discuss each of the individual complexes in great detail.

^{1}H NMR spectral data for the monocobaloxime complexes (**6 - 8, 15**)

The data for these complexes are given in Table 2.5. The complexes of the type $[\{(py)(DH)_2CoCH_2\}C_6H_4(CH_2Br)$-1,n] (**6 - 8**), all show a characteristic singlet in the region δ 4 - 6 ppm assigned to the methylene bromide protons (this signal is thus absent in the dicobaloxime complexes $[C_6H_4\{CH_2Co(DH)_2(py)\}_2$-1,n] **9 - 11**).

Table 2.5: ^{1}H NMR data[a] of the monocobaloxime complexes (**6 - 8, 15**) recorded in $CDCl_3$

Compound	pyridine			dimethylglyoxime		other	
No.	*o*-H	*m*-H	*p*-H	O-H···O	CH_3	Co-CH_2	CH_2Br
	d(2H)	t(2H)	t(1H)	bs(2H)	s(12H)	s(2H)	s(2H)
6[b]	8.50	7.24	7.68	18.22	1.94	2.74	5.29
7[c]	8.50	7.22	7.60	18.34	1.93	2.91	4.39
8[d]	8.49	7.20	7.70	18.34	1.99	2.90	4.40
15[e]	8.45	7.25	7.70	18.82	2.00	2.25	–

[a]: Chemical shifts (δ ppm) are relative to TMS [b]: also a signal for the phenyl protons at δ 6.60 ppm (s, 4H, $C_6\underline{H}_4$) [c]: also signals for the phenyl protons at δ 7.01 ppm (s, 1H, $1_{equivalent}$ *o*-H) and δ 6.76 ppm (m, 3H, $2_{equivalent}$ *o*-H's + 1 x *m*-H) [d]: also a signal for the phenyl protons at δ 6.80 ppm (bm, 4H, $C_6\underline{H}_4$) [e]: also a signal for the phenyl protons at δ 5.05 (m, 5H, $C_6\underline{H}_5$)

The signals of the basal (pyridine) and axial (dimethylgloxime) ligands are readily identified and do not show any significant shifts on variation of the nature of the arene. This is found to be the case even when the arene is coordinated to a powerful electron-withdrawing "$Cr(CO)_3$" group (as in **15**). This result is consistent with those found by other workers [12, 26, 27].

With respect to the other signals, those of complex **15** deserve a special mention. The arene protons of **6** - **8** are all found above δ 6.5 ppm. Those of **15** are, however, found in the region around δ 5.0 ppm. The methylene protons (Co-C$\underline{H}_2$) of **15** are similarly (although the shifts are not nearly as large as those found for the phenyl protons) found further upfield, as compared to those for the complexes **6** - **8**. This effect is attributed to the coordination of the "$Cr(CO)_3$" group to the arene ring.

^{1}H NMR spectral data for the dicobaloxime complexes (**9** - **12**, **16**)

The spectra for the *xylylene-bridged* dinuclear cobaloxime complexes $[C_6H_4\{CH_2Co(DH)_2(py)\}_2$-1,n], **9** - **11** (Table 2.6), are virtually identical to those of the analogous monocobaloxime complexes, save for the absence of any methylene bromide signals. A typical spectrum is given in figure 2.2.

It can clearly be seen from Table 2.6 that, as is the case with the monocobaloxime complexes, the signals due to the basal and axial ligands show no sensitivity towards the trans ligand. The methyl peak of the axial ligands of **12**, found at δ 3.94 ppm, is an exception. This represents a shift of about 2.0 ppm from the average position found for this signal in the other complexes. This large downfield shift can be attributed to the Co atom being directly bonded to the benzene ring rather than through a methylene group, as is the case with the other complexes. Complex **12** is furthermore the only one of its type, having the two Co atoms directly linked by a conjugated (benzene ring) system. If one considers the Co atoms to be a source of electrons, the entire molecule becomes conjugated. This conjugation also extends into each of the dimethylgloxime units.

Table 2.6: ^{1}H NMR ($CDCl_3$) data[a] for the dicobaloxime cobaloxime complexes (**9 - 12, 16**)

Compound	pyridine			dimethylglyoxime		
No.	*o*-H	*m*-H	*p*-H	O-H···O	CH_3	Co-CH_2
	d(4H)	t(4H)	t(2H)	bs(4H)	s(24H)	s(4H)
9[b]	8.52	7.26	7.65	18.20	1.90	2.75
10[c]	8.51	7.24	7.64	18.20	1.91	2.75
11[d]	8.52	7.70	8.29	18.20	2.40	2.98
12[e]	8.67	7.15	7.60	18.20	3.94	—
16[f]	8.48	7.70	7.28	18.10	2.21	2.21

[a]: Chemical shifts (δ ppm) are relative to TMS [b]: also a signal for the phenyl protons at δ 6.63 ppm (s, 4H, $C_6\underline{H}_4$) [c]: also a signal for the phenyl protons at δ 6.30 ppm (s, 1H, $1_{equivalent}$ *o*-H), δ 6.83 ppm (d, 2H, $2_{equivalent}$ *o*-H's) and δ 6.35 ppm (t, 1H, *m*-H) [d]: also a signal for the phenyl protons at δ 6.80 ppm (bm, 4H, $C_6\underline{H}_4$) [e]: also a signal for the phenyl protons at δ 8.10 ppm (s, 4H, $C_6\underline{H}_4$) [f]: also a signal for the phenyl protons at δ 4.85 ppm (s, 4H, $C_6\underline{H}_4$)

The integration values of the dimethylglyoxime signals expressed as a ratio relative to those of the benzene ring, provide a useful measure of the nuclearity of the cobaloxime complexes. Thus the ratios obtained for the dinuclear complexes **9 - 11** and **16** are found to be twice as large as those for the the mononuclear analogues derivatives (**6 - 8, 15**).

^{13}C NMR

The ^{13}C resonances of the basal and axial ligands were assigned with reference to the literature values for the free ligands [28] and those of known cobaloxime complexes [12, 27]. The ^{13}C resonances are given in Table 2.7.

Figure 2.2: ^{1}H NMR spectrum of $[C_6H_4\{CH_2Co(DH)_2(py)\}_2\text{-}1,3]$ **10** recorded in $CDCl_3$

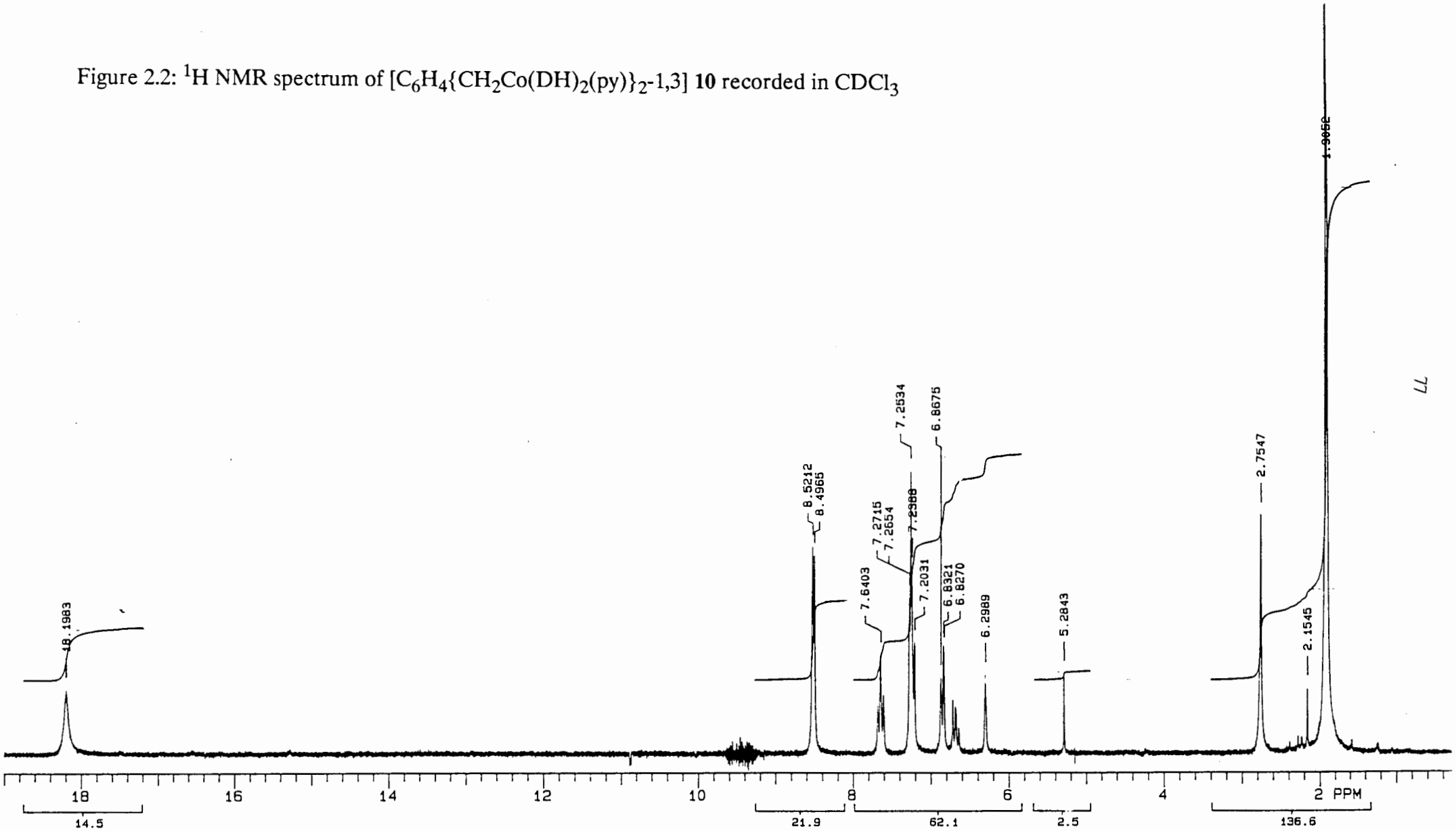


Table 2.7: ^{13}C NMR spectral data[a] for the cobaloxime complexes (**6 - 12, 15** and **16**) recorded in $CDCl_3$

Comp'd	pyridine			dimethylglyoxime		arene			
No.	*o*-C	*m*-C	*p*-C	CH_3	C=N	CH_2	C^{tert}	*o*-C	*m*-C
6	150.3	125.1	137.2	11.8	149.2	[b]	143.4	127.0	—
7	150.1	125.1	137.6	11.8	149.5	29.4	145.3 144.0	129.9 129.8 129.7	130.2
8[c]	150.2	125.1	137.2	11.9	149.5	31.5[d]	143.9	127.9	126.9
9	150.3	125.0	137.3	11.8	149.2	32.5	143.4	128.0	—
10	150.3	125.1	137.2	11.9	149.2	31.0[d]	145.9	125.6 127.9	126.9
11	150.1	125.3	137.6	12.0	149.0	[b]	145.2	124.8	126.1
12	166.3	129.5	127.1	52.4	166.3	—	152.3	133.9	—
15[e,f]	150.0	125.4	137.8	12.2	149.9	[b]	119.3	93.3	92.5
16[e]	150.0	125.2	137.6	12.4	149.9	30.9	115.9	95.7	—

[a]: Chemical shifts (δ ppm) are relative to TMS

[b]: Co-$\underline{C}H_2$ signal not observed

[c]: Spectrum also contains a signal at 125.2 ppm (p-$\underline{C}$)$_{Ph}$

[d]: Very weak signal

[e]: Spectra also contain signals due to Cr-$\underline{C}$O at 234.0 (**15**) and 234.9 ppm (**16**)

[f]: Spectrum also contains a signal at 90.1 (p-$\underline{C}$)$_{Ph}$

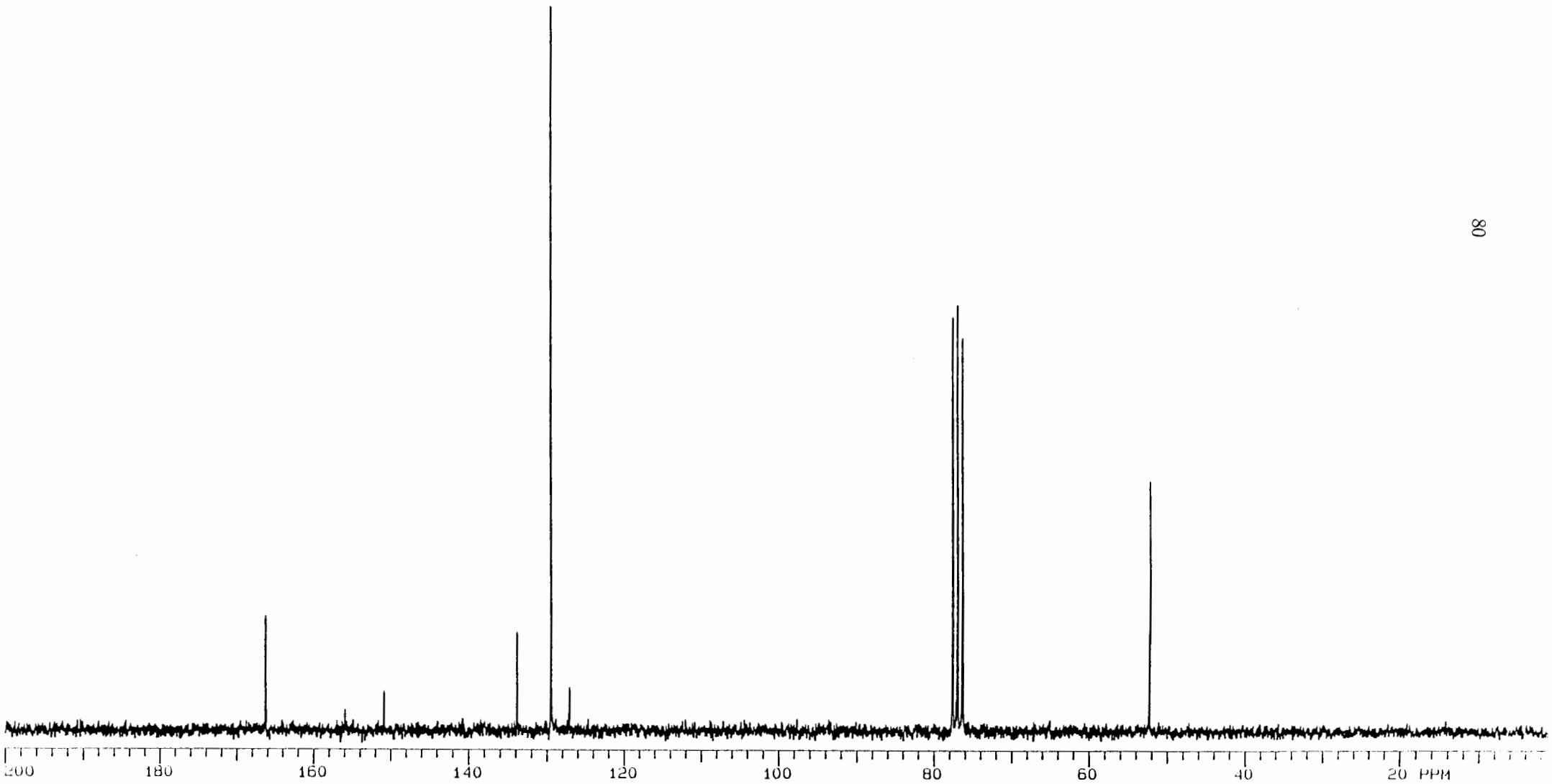
With the exception of complex **12**, the spectra of the cobaloxime complexes are virtually identical. The ^{13}C resonances for the pyridine ligands occur at δ 150.18 ($\pm$0.14), 125.17 ($\pm$0.14) and 137.47 ($\pm$0.24) ppm, assigned to the ortho, meta and para carbon atoms respectively. The signals of the dimethylglyoxime ligands occur at δ 11.98 ($\pm$0.23) and 149.41 ($\pm$0.36) ppm, assigned to the methyl and C=N carbon atoms respectively. It can be seen (from the standard deviations given in parentheses), that these signals do not show much variation. The signals of the basal and axial ligands of other alkyl-cobaloximes of the type $[Co(DH)_2(py)R]$, R = alkyl, show a similar insensitivity to the nature of the alkyl substituents [12].

The ^{13}C resonance of the carbon atom bonded to cobalt was not always detected. In the cases that it was, it was found as a signal of low intensity in the region δ 29 - 30 ppm.

The phenyl signals are all well behaved. The tertiary carbon atoms occur quite far downfield {δ 144.5 ($\pm$1.10) ppm for complexes **6** - **11**}, with the ortho, meta and para carbon atoms being found further upfield (by some 17 - 18 ppm). The phenyl carbons of **15** and **16** are shifted upfield by an average of 30 ppm. This is due to the influence of the "$Cr(CO)_3$" unit attatched to the phenyl ring of these two complexes.

The spectrum of **12** (figure 2.3) deserves a special mention. Except for signal of the *p*-C atom of the pyridine ligands, all the ^{13}C resonances of this complex are found to shift downfield (some more than others) relative to those of the other complexes reported here. The largest downfield shift is experienced by the methyl carbons of the dimethylglyoxime ligands. This signal is found at δ 52.4 ppm, representing a

Figure 2.3: ^{13}C NMR spectrum of $[C_6H_4\{Co(DH)_2(py)\}_2\text{-}1,4]$ **12** recorded in $CDCl_3$



downfield shift of some 40 ppm. The ^{13}C resonance of the C=N group moves downfield by approximately 17 ppm, while the ortho and meta carbon atoms of the pyridine ring are found to shift downfield by 16 and 4 ppm respectively. In contrast, the *p*-C atom of the pyridine ligand moves *upfield* by 10 ppm. This unusual observation, as with the ^{1}H resonances, is attributed to the high degree of conjugation found in the complex arising from the fact that **12** is a *phenylene-bridged* complex.

2.2.2.3 Properties of the monometallic cobalt complexes of the type $(CO)_9Co_3CR$

Some of the physical properties of the two new compounds in this class (**13** and **14**), are listed in Table 2.8. Both compounds were isolated in moderate yields. They are black, air-stable solids possessing moderate solubility in most polar solvents giving dark purple solutions.

Table 2.8: Yield and melting point data for the monometallic tricobalt complexes

Complex No.	Formula	Colour	M.P. (°C)	Yield (%)
13	$PhCH_2OC(O)CCo_3(CO)_9$	black	97	54
14	$Ph\{CH_2OC(O)CCo_3(CO)_9\}_2$-1,4	black	121	51

^{1}H NMR

The ^{1}H NMR spectra of **13** and **14** are virtually identical (see Table 2.9). Their spectra consists of two sets of signals, which differ only in the relative integration values, with only slight chemical shift differences in the corresponding signal

Table 2.9: ^{1}H NMR data[a] for compounds **13** and **14** recorded in $CDCl_3$

Compound	arene			other
No.	*o*-H	*m*-H	*p*-H	CH_2
13	7.64[b]	7.64[b]	7.64[b]	5.36 (s, 2H)
14	7.53(s, 4H)	—	—	5.78 (s, 4H)

[a]: Chemical shifts (δ ppm) are relative to TMS [b]: signals are unresolved and occur as a multiplet integrating for 5H

positions. The phenyl protons of **13** were unresolved and occur as a multiplet integrating for five protons, while those of **14** occur as a sharp singlet integrating for four protons. The only other signal in their spectra is a sharp singlet for the methylene protons (δ 5.36, 2H **13** and δ 5.78, 4H **14**).

^{13}C NMR

As with the ^{1}H NMR spectra, the ^{13}C NMR spectra (see Table 2.10 for data) are virtually identical. These contain three sets of signals. The ^{13}C resonances of the methylene carbons occur around δ 60 - 70 ppm, while the carbonyl resonances occur at δ 198.46 ±0.08 ppm. The peaks for the phenyl carbon atoms all occur in a narrow range of δ 128.1 - 128.6 ppm. Due to the very small chemical shift differences, these signals could not be unambiguously assigned by the methods employed. Table 2.10 thus gives the most likely assignments for the phenyl carbon atoms. These assignments were made by comparison with the spectra of similar complexes (which were completely and unambiguously assigned) reported in this thesis.

Table 2.10: ^{13}C NMR spectral data[a] for compounds **13** - **14** recorded in $CDCl_3$

Compound	arene				other	
	C^{tert}	*o*-C	*m*-C	*p*-C	Co-CO	CH_2
13	128.49[b]	128.40[b]	128.28[b]	128.13[b]	198.52	67.73
14	128.53[b]	128.40[b]	128.35[b]	128.20	198.40	63.20

[a]: Chemical shifts (δ ppm) are relative to TMS [b]: signals not unambiguously assigned (the most likely assignments are given)

Mass Spectral data

The mass spectrum of **13** (Table 2.11) provides the most conclusive evidence for its structure and shows a fragmentation pattern characteristic of $(CO)_9Co_3CR$ complexes [29, 30]. A relatively weak molecular ion peak is observed at m/z 576, followed by peaks showing the stepwise loss of nine carbonyl groups resulting in the formation of the $[Co_3CC(O)OCH_2Ph]^+$ ion (m/z 324). This fragmentation pathway was confirmed by metastable peak analysis. The $[Co_3CC(O)OCH_2Ph]^+$ ion then further fragments in two possible ways:

(i) by losing cobalt successively to form the ions $[Co_2CC(O)OCH_2Ph]^+$ (m/z 265) and $[CoCC(O)OCH_2Ph]^+$ (m/z 206), and

(ii) by loss of a further CO molecule (presumably the acyl CO) to give $[Co_3COCH_2Ph]^+$ (m/z 296), which in turn loses cobalt successively forming the ions $[Co_2COCH_2Ph]^+$ (m/z 237) and $[CoCOCH_2Ph]^+$ (m/z 178).

Table 2.11: Metal fragments in the mass spectrum of $(CO)_9Co_3CC(O)OCH_2Ph$ **13**

	m/z	ion	m/z	ion
A	576	$(CO)_9Co_3CC(O)OCH_2Ph^+$	265	$Co_2CC(O)OCH_2Ph^+$
B	548	$(CO)_8Co_3CC(O)OCH_2Ph^+$	237	$Co_2COCH_2Ph^+$
C	492	$(CO)_6Co_3CC(O)OCH_2Ph^+$	206	$CoCC(O)OCH_2Ph^+$
D	464	$(CO)_5Co_3CC(O)OCH_2Ph^+$	189	Co_3C^+
E	436	$(CO)_4Co_3CC(O)OCH_2Ph^+$	178	$CoCOCH_2Ph^+$
F	408	$(CO)_3Co_3CC(O)OCH_2Ph^+$	177	Co_3^+
G	380	$(CO)_2Co_3CC(O)OCH_2Ph^+$	130	Co_2C^+
H	352	$(CO)Co_3CC(O)OCH_2Ph^+$	118	Co_2^+
I	324	$Co_3CC(O)OCH_2Ph^+$	87	$Co(CO)^+$
	296	$Co_3COCH_2Ph^+$	59	Co^+

Metastable Peaks:

A —> B, B —> C, C —> D, D —> E,

E —> F, F —> G, G —> H, H —> I

2.2.2.4 Properties of the heterobimetallic complexes

Complexes **15** and **16**, like the other cobaloxime **6 - 12**, are air-stable orange solids which decompose at relatively high (>150°C) temperatures. The tricobalt cluster complexes **17 - 20** have properties (Table 2.12) similar to those reported for related complexes of the type $(CO)_9Co_3CR$ [16, 17]. They are purple-black, air-stable crystalline solids, and are soluble in most organic solvents. Solutions of **17** are deep

Table 2.12: Yields and melting points for the heterobimetallic complexes

Complex No.	Formula	Colour	M.P. (°C)	Yield (%)
15	$(\eta^6\text{-}C_6H_5CH_2[Co])Cr(CO)_3$	orange	210(dec.)	72
16	$(\eta^6\text{-}C_6H_4\{CH_2[Co]\}_2\text{-}1,4)Cr(CO)_3$	orange	165(dec.)	77
17	$(\eta^6\text{-}C_6H_5C[Co_3])Cr(CO)_3$	black	120	14[a]
18	$(\eta^6\text{-}C_6H_5CH_2OC(O)C[Co_3])Cr(CO)_3$	purple	163(dec.)	54[a]
19	$(\eta^6\text{-}C_6H_5\{(CH_2)_4OC(O)C[Co_3]\})Cr(CO)_3$	red	71-74	60
20	$(\eta^6\text{-}C_6H_4\{CH_2OC(O)C[Co_3]\}_2\text{-}1,4)Cr(CO)_3$	black	[c]	15[a]

[a]: Based on the amount of cobalt charged [b]: $[Co_3]$ = $(CO)_9Co_3$ unit [c]: not determined

red, while those of **18** - **20** are dark purple. All of them possess moderate to good thermal stability (melting above 100°C). Complex **19** proves an exception, melting at 71 - 74°C. This is expected, however, since it has been observed that complexes of the type $(CO)_9Co_3CR$, bearing long carbon chain substituents, have lowered melting points and can sometimes even exist as oils [17]. Their colour, stability and solubility enabled their detection, purification and isolation to be conveniently carried out by thin-layer and column chromatography.

NMR spectral data

The ^1H NMR spectra of **15** and **16** have been discussed earlier (Section 2.2.2.2). The ^1H NMR spectral data of the heterobimetallic tricobalt cluster type complexes **17** - **20** are given in Table 2.13. The spectra are relatively simple and easy to interpret and will not be discussed further.

Table 2.13: ^{1}H NMR data[a] for compounds **17** - **20** recorded in $CDCl_3$

Compound	arene			other
No.	*o*-H	*m*-H	*p*-H	CH_2
17	5.88	5.19	5.65	—
	(d, 2H)	(t, 2H)	(t, 1H)	
18	5.19	5.45	5.27	2.64
	(d, 2H)	(t, 2H)	(t, 1H)	(s, 2H)
19[b]	5.15	5.36	5.18	2.42
	(d, 2H)	(t, 2H)	(t, 1H)	(s, 2H)
20	5.20	—	—	2.72
	(s, 2H)			(s, 2H)

[a]: Chemical shifts (δ ppm) are relative to TMS [b]: also an unresolved signal at δ 1.78 ppm (m, 4H, $PhCH_2C\underline{H}_2$ and $OCH_2C\underline{H}_2$) and a signal at δ 4.34 ppm (t, 2H, $OC\underline{H}_2$)

The ^{13}C NMR spectra of complexes **17** - **20** are included in Table 2.14. The spectra show two sets of metal carbonyl signals. The ^{13}C resonances for the cobalt carbonyls occur between 190 - 200 ppm, while the chromium carbonyls occur in the narrow range of 232 - 233 ppm. The phenyl signals are found just below 100 ppm. It is noted that the signals for the ortho and meta phenyl carbon atoms of both complexes **18** and **19** were not distinguished. The most probable assignments for these signals are given in Table 2.14. The ^{13}C resonances for the methylene carbons $Ph\underline{C}H_2$ and $\underline{C}H_2O$, were easily identified. The signals for $PhCH_2\underline{C}H_2$ and $\underline{C}H_2CH_2O$ were, however, not unambiguously assigned and the most probable assignments are given.

Table 2.14: ^{13}C NMR spectral data[a] for compounds **17** - **20** recorded in $CDCl_3$

Compound	arene						other	
	C^{tert}	*o*-C	*m*-C	*p*-C	$PhCH_2$	CH_2O	Co-CO	Cr-CO
17	95.4	97.0	87.5	92.7	—	—	199.2	232.1
18[b]	[c]	84.4[d]	83.0[d]	81.2	26.8	—	190.2	233.1
19[e]	113.0	93.7[d]	92.3[d]	90.3	34.7	65.3	198.7	233.0
20[b]	109.1	83.4	—	—	26.4	—	192.0	233.0

[a]: Chemical shifts (δ ppm) are relative to TMS [b]: recorded in CD_2Cl_2 [c]: signal not observed [d]: signals not unambiguously assigned (the most likely assignments are given) [e]: also signals at δ 28.6 and 27.7 ppm assigned to the $PhCH_2CH_2$ and CH_2CH_2O carbons

Mass Spectral data

The class of compounds formulated as $(CO)_9Co_3CR$ is known to fragment *via* fairly well established routes under mass spectral conditions [29, 30] (see also earlier discussion of mass spectrum of **13**). Complexes **17** - **20** can also be classified as $(CO)_9Co_3CR$ compounds. These complexes have, incorporated in the "R" group, a second metal carbonyl unit which is present as (η^6-arene)$Cr(CO)_3$. Accordingly complexes **17** - **20** can also be regarded as belonging to the class of substituted (arene)tricarbonyl chromium complexes, which also fragment *via* well documented pathways under mass spectral conditions. It was of interest to know how these complexes behaved under mass spectral conditions and to see if the presence of the one metal affected the other when the two were present in the same molecule.

The high mass region in the mass spectra of these complexes show twelve evenly spaced peaks corresponding to the sequential loss of all the CO ligands. This

pattern, in conjunction with the metastable peaks observed, was not able to tell us the exact sequence and source of the CO loss. However, from the positions of the lower mass peaks, it *was* possible to conclude that one of the fragmentation pathways involved the sequential loss of the nine CO ligands from the tricobalt cluster. The information available did not preclude a second fragmentation pathway involving the initial loss of the chromium CO ligands. Other pathways of CO loss are also possible.

As a representative example of the complexes discussed here, the mass spectrum of **17** (Table 2.15) is discussed in a little more detail. A weak molecular ion is observed at m/z 654, followed by peaks corresponding to the loss of twelve CO ligands. The presence of the $[\{Co_2CPh\}Cr(CO)_3]^+$ (m/z 343) and $[\{CoCPh\}Cr(CO)_3]^+$ (m/z 284) ions serves to suggest that one of the fragmentation routes is the sequential loss of nine CO ligands from the tricobalt cluster framework. We assume therefore that these ions (m/z 343 and 284) are derived from the ion $[\{Co_3CPh\}Cr(CO)_3]^+$ (m/z 402), since there have been no reports of the loss of cobalt preceding the loss of all the CO ligands from the tricobalt cluster.

The formation of the ion $[\{Co_3CPh\}Cr]^+$ (m/z 318) also proves that another fragmentation pathway which involves the successive loss of all twelve CO ligands, is operative. The $[\{Co_3CPh\}Cr]^+$ ion decomposes further, losing chromium to form $[Co_3CPh]^+$ (m/z 266). This ion then fragments further as reported by Mays and Simpson[1] [30].

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1. Mays and Simpson reported the mass spectrum of $(CO)_9Co_3CPh$. Initial loss of nine CO ligands gave the $[Co_3CPh]^+$ ion. They reported that this ion fragments further *via* two possible pathways. The first involves the sequential loss of two ethylene groups forming $[Co_3C(C_4H_3)]^+$ (m/z 240) and

Table 2.15: Metal containing fragments in the mass spectrum of $[\eta^6\text{-PhCCo}_3(CO)_9]Cr(CO)_3$ **17**

m/z	ion	m/z	ion
654	$Co_3CPhCr(CO)_{12}^+$	343	$Co_2CPhCr(CO)_3^+$
626	$Co_3CPhCr(CO)_{11}^+$	318	Co_3CPhCr^+
598	$Co_3CPhCr(CO)_{10}^+$	284	$CoCPhCr(CO)_3^+$
570	$Co_3CPhCr(CO)_9^+$	266	Co_3CPh^+
542	$Co_3CPhCr(CO)_8^+$	240	$Co_3C(C_4H_3)^+$
514	$Co_3CPhCr(CO)_7^+$	214	$Co_3C(C_2H)^+$
486	$Co_3CPhCr(CO)_6^+$	207	Co_2CPh^+
458	$Co_3CPhCr(CO)_5^+$	155	$Co_3C(C_2H)^+$
430	$Co_3CPhCr(CO)_4^+$	148	$CoCPh^+$
402	$Co_3CPhCr(CO)_3^+$	130	CoC^+
374	$Co_3CPhCr(CO)_2^+$	118	Co_2^+
345	$Co_3CPhCr(CO)^+$	59	Co^+

2.2.2.5 IR spectral data for the new complexes

Infrared spectroscopy has proved a very useful technique in our work. In most cases the IR spectral properties of the complexes were used to monitor the progress of the reactions leading to their formation. The solution IR spectra (in the carbonyl region) of the complexes containing metal carbonyls, were especially useful in this

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$[Co_3C(C_2H)]^+$ (m/z 214). The second pathway involves the sequential loss of cobalt forming $[Co_2CPh]^+$ (m/z 207) and then finally $[CoCPh]^+$ (m/z 148)

regard. In all cases the band patterns were characteristic of the class of compounds concerned.

The metal carbonyl complexes reported here were either of the type $(CO)_9Co_3CR$ (R = alkyl or aryl), or of the type (arene)$Cr(CO)_3$. Both classes of compounds give characteristic and clearly distinguishable metal carbonyl bands. The heterobimetallic complexes belonged to both classes of compounds mentioned. Their IR spectra is thus characterized by carbonyl bands characteristic of complexes of the type $(CO)_9Co_3CR$, as well as carbonyl bands characteristic of (arene)$Cr(CO)_3$ type complexes.

IR Spectra of the cobaloxime complexes (**6 - 12, 15** and **16**)

The complex nature of the infrared spectra of cobaloximes makes assignment of the bands difficult. It is therefore not surprising that this has received considerable attention [31 - 39]. In all the initial studies (up until 1979), band assignments were made almost entirely by empirical methods. It is only recently that debate surrounding many of the initial assignments is being resolved by the isotopic labelling technique [40]. Such a multiple isotopic labelling study by Thornton and Rutherford of the cobaloximes $[Co(DH)_2(py)(X)]$ X = Cl, Br, I, CH_3 [41] and X = NCS and SCN [42] has been reported. They applied three different isotopic labels to the band assignments of the cobaloximes which has to-date provided the most firm assignments of the pyridine ligand and the Co-ligand vibrations. Their assignments were based on ^{15}N-labelling of the dimethylglyoximate, pyridine and thiocyanate nitrogen atoms, as well as deuteration of the pyridine ring and substitution of the ligand X. Their work [41, 42] thus serves

as the main source of reference for assignment of the bands of the new cobaloximes reported hereafter.

The IR spectra of the cobaloximes were determined as Nujol mulls between NaCl plates (4000-600 cm^{-1}) and between caesium iodide plates (600-200 cm^{-1}). We have not attempted to assign all the bands in the spectra; instead only the more prominent bands which could be assigned with the greatest degree of certainty are considered. This is because of the complicating factor presented by the presence of the phenyl rings in our compounds; these were absent from the former IR-studies [41, 42]. The band frequencies are reported in Table 2.16. The spectra of $[Co(DH)_2(py)(X)]$, X = Cl and CH_3, are included for reference. The complex $[Co(DH)_2(py)CH_2C_6H_5]$ [43] is known, but its IR spectrum has not previously been assigned.

In general, there is a band-for-band correspondence between the spectra of the various cobaloxime complexes $[Co(DH)_2(py)R]$. They exhibit a broad band due to the O-H···O bridging group of the dimethylglyoximato ligand, in the region 1715 - 1780 cm^{-1}. This serves to confirm the planar configuration of the $Co(DH)_2$ unit. A weak but sharp band at 1600 cm^{-1} is assigned to the stretching vibration of the pyridine ring. The C=N stretch of the dimethylglyoximate ligand is observed at 1557 cm^{-1} and its position appears to be practically independent of the nature of the alkyl group (R). The bands at 1455 and 1374 cm^{-1} are assigned to the symmetric and antisymmetric deformations of the methyl groups respectively. Uncoupled ν(N-O) bands occur near 970 and 1090 cm^{-1}. The spectra of $[Co(DH)_2(py)R]$ R = Cl and Me, show two bands in the region 1200-1250 cm^{-1}. The band at higher wavenumber (1247 cm^{-1}) is assigned to $\nu(C\text{-}C)_{DH}$ while the lower wavenumber band (1237 cm^{-1}) is assigned to $\delta(C\text{-}H)_{py}$ and ν(N-O) [41]. Except for the spectrum of

Table 2.16: Infrared absorption frequencies[a] for the new cobaloxime complexes $[Co(DH)_2(py)R]$

Complex[b]		$\nu(O\text{-}H\cdots O)$[c]	$\nu(ring)_{py}$	$\nu(C{=}N)_{DH}$	δMe_{sym}	δMe_{anti} + $\nu(ring)_{py}$	$\nu(C\text{-}C)_{DH}$	$\nu(N\text{-}O)$	$\nu(Co\text{-}N)_{DH}$[d]	$\nu(Co\text{-}N)_{py}$	$\gamma(ring)_{py}$ + $m(Co\text{-}N)_{DH}$	$\nu(Co\text{-}C)$
[Co]Cl[e]		1718	1608	1558	1455	1374	1247	1090, 975	511	456	420	
$[Co]CH_3$[e]		1715	1598	1556	1457	1374	1233	1087, 970	515	450	425	319
$[Co]CH_2Ph$[f]		1718	1596	1557	1459	1374	1235	1088, 969	516	449	426	320
$[Co]CH_2PhCH_2Br$-1,4	6	1760	1599	1554	1450	1374	1231	1087, 971	515	448	422	320
$[Co]CH_2PhCH_2Br$-1,3	7	1760	1597	1554	1449	1373	1230	1087, 970	515	450	420	320
$[Co]CH_2PhCH_2Br$-1,2	8	1759	1599	1554	1448	1374	1233	1088, 970	514	449	421	320
$([Co]CH_2)_2Ph$-1,4	9	g	1598	1552	1459	1375	1231	1086, 970	514	449	422	320
$([Co]CH_2)_2Ph$-1,3	10	1774	1602	1558	1459	1374	1231	1088, 972	517	447	423	320
$([Co]CH_2)_2Ph$-1,2	11	1774	1602	1556	1459	1375	1230	1088, 971	515	446	422	320
$([Co])_2Ph$-1,4	12	1724	1600	1557	1458	1374	1278	1106, 953	505	465	433	325
$([Co]CH_2Ph)Cr(CO)_3$	15	h	1600	1556	1457	1374	1236	1088, 972	516	454	429	320
$([Co]CH_2)_2Ph$-1,4$)Cr(CO)_3$	16	h	1600	1556	1459	1375	1231	1087, 971	514	456	426	320

[a]: determined as Nujol mulls
[b]: [Co] = $Co(DH)_2(py)$
[c]: broad band
[d]: also comprises some $\delta(C\text{-}H)_{py}$, $\nu(N\text{-}O)$ and $\delta(C\text{-}H)_{Ph}$ character
[e]: reference [41]
[f]: spectrum not previously assigned although synthesis has been reported [43]
[g]: not seen (masked by nearby strong bands)
[h]: not seen (masked by νCO bands)

$[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **15**, the new complexes show only one band in this region (at 1231 cm^{-1}). This single band is thus assigned to $\nu(C\text{-}C)_{DH}$, $\delta(C\text{-}H)_{py}$ and $\nu(N\text{-}O)$. The spectrum of **15** shows two bands at 1236 and 1217 cm^{-1}. The former is assigned to $\nu(C\text{-}C)_{DH}$ and the latter to $\delta(C\text{-}H)_{py}$ and $\nu(N\text{-}O)$. It is noted that these bands show a small but significant shift (compared to those of the reference complexes $[Co(DH)_2(py)R]$ R = Cl and Me). We have ascribed this shift to the difference in the nature of the R group.

The metal-ligand stretching frequencies, $\nu(Co\text{-}N)_{DH}$, $\nu(Co\text{-}N)_{py}$ and $\nu(Co\text{-}C)$, all occur below 550 cm^{-1}. The band near 515 cm^{-1} is assigned to $\nu(Co\text{-}N)_{DH}$ while the band at 450 cm^{-1} is assigned to $\nu(Co\text{-}N)_{py}$. The out-of-plane vibrations of the pyridine ring appear near 425 cm^{-1}. This band is presumed[1] to comprise some $\nu(Co\text{-}N)_{DH}$ coupling. The $\nu(Co\text{-}C)$ band occurs at 320 cm^{-1} and is practically independent of the nature of the alkyl group, as has been found in earlier work [41].

The new $Co(DH)_2(py)R$ complexes **6 - 12**, **15** and **16**, all contain phenyl rings which have bands in similar positions to those of the pyridine ligands. Since none of the bands associated with the pyridine ligand occur as doublets, one may conclude that they are coupled or coincident with the corresponding phenyl band. Thus, for example, the band at 1600 cm^{-1} is more correctly assigned to $\nu(ring)_{py}$ and $\nu(ring)_{Ph}$.

<u>The carbonyl (Cr-CO) bands of the (η^6-arene)$Cr(CO)_3$ complexes (**1 - 5** and **15 - 20**)</u>

The solution (CH_2Cl_2) IR spectra of all the (η^6-arene)$Cr(CO)_3$ complexes (**1 - 5**, **15 - 20**) show two intense bands in the terminal $\nu(CO)$ region (see Table 2.17). One is

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1. This presumption is also made by the authors of [41]

found in the region 2000 - 1950 cm^{-1} and the other is found in the region 1910 - 1870 cm^{-1}. These bands are a characteristic feature of all (η^6-arene)$Cr(CO)_3$ complexes and prove useful for their rapid identification [44 - 46]. The bands are assigned to a non-degenerate symmetric vibration, A_1 (high frequency band), and a doubly degenerate asymmetric vibration, E (low frequency band). The assignments were done on the basis of local C_{3v} symmetry for the $Cr(CO)_3$ group [47, 48]. Splitting of the (E) band is expected for unsymmetrically substituted [η^6-arene]$Cr(CO)_3$ complexes, resulting from small perturbations of C_{3v} symmetry by arene substituents [49 - 51]. No such splitting was observed however, in the spectra of any of the complexes reported here.

The $\nu(CO)_{Cr\text{-}CO}$ bands are sensitive to the electronic nature of the arene substituent/s, transmitted through the metal to the carbonyls of the "$Cr(CO)_3$" group. They are found to shift to lower frequency as the electron donating power of the substituent increases [52 - 54]. The substituent effects can be seen from Table 2.17 which lists the ν(CO) band positions (A_1 and E) of the new (arene)$Cr(CO)_3$ complexes. Table 2.17 also allows us to compare the electron donating power of the different arene substituents. It is evident that the electron donating power occurs in the order indicated below;

$$CH_2Cl < CCo_3(CO)_9 < (CH_2)_4Cl \approx (CH_2)_4OH < CH_2OC(O)CCo_3(CO)_9 \approx$$
$$2(CH_2OH) < (CH_2)_4OC(O)CCo_3(CO)_9 \approx 2(CH_2OC(O)CCo_3(CO)_9) \approx Me <$$
$$CH_2OH < Me_2 << CH_2Co(DH)_2(py) < PhCH_2NH.$$

Table 2.17: $\nu(CO)_{Cr\text{-}CO}$ frequencies[a] (cm^{-1}) of the substituted (η^6-arene)$Cr(CO)_3$ complexes

Comp'd No.	arene substituent[b]	A_1 ν_{max}	A_1 $\Delta\nu_{max}$[c]	E ν_{max}	E $\Delta\nu_{max}$[c]
	H[d]	1970		1891	
3	$(CH_2Cl)_2$-1,4	1978	+8	1901	+10
17	$CCo_3(CO)_9$	1965	-5	1898	+7
5	$(CH_2)_4Cl$	1965	-5	1895	+4
4	$(CH_2)_4OH$	1966	-4	1884	+3
18	$CH_2OC(O)CCo_3(CO)_9$	1966	-4	1890	-1
2	$(CH_2OH)_2$-1,2	1967	-3	1889	-2
19	$(CH_2)_4OC(O)CCo_3(CO)_9$	1965	-5	1887	-4
20	$(CH_2OC(O)CCo_3(CO)_9)_2$	1963	-7	1887	-4
	Me[d]	1968	-2	1886	-5
	1,2-Me_2[d]	1964	-6	1884	-7
	$(Me)_3$-1,2,3[d]	1958	-12	1877	-14
15	CH_2[Co]	1958	-12	1878	-13
1	$NHCH_2Ph$	1956	-14	1871	-20
16	$(CH_2[Co])_2$-1,4	1947	-23	1870	-21

[a]: measured in CH_2Cl_2; [b]: [Co] = $Co(DH)_2(py)$ [c]: $\Delta\nu_{max} = \nu_{max}(arene) - \nu_{max}(C_6H_6)$
[d]: reference compound [48]

It appears that the electron-donating power of the arene substituents are approximately additive. Thus, for example, the bands of **16** are shifted to lower wavenumber by approximately twice as much as those of **15**. Other workers have found similar results [48].

The carbonyl bands (Co-CO) of the $(CO)_9Co_3CR$ complexes (**13 - 20**)

The solution IR($\nu(CO)_{Co\text{-}CO}$) spectra of the new tricobalt nonacarbonyl complexes **13 - 20** are listed in Table 2.18. The results obtained are consistent with those of other workers [17, 55].

In general, complexes of the type $(CO)_9Co_3CR$ show four bands in the terminal carbonyl region having an intensity pattern; weak, very strong, strong and weak. For all of the complexes reported here (except **13**), the latter band was not resolved and the strong band at 2046 cm^{-1} has a shoulder on the low wavenumber side.

Although the intensity pattern of the carbonyl bands are characteristic of complexes of the type $(CO)_9Co_3CR$, the band positions are not sensitive to the nature of the R group. Thus these bands are not diagnostic for the R group.

Table 2.18: ν(CO) frequencies[a] (cm^{-1})for the complexes $RCCo_3(CO)_9$

Complex	ν(CO)	
No.	Co-CO	acyl CO
13	2109w, 2064vs, 2046s, 2020vw	1688br
14	2109w, 2064vs, 2046s	1709br
17	2103w, 2057vs, 2047s	—
18	2110w, 2066vs, 2046s	1640br
19	2109w, 2062vs, 2045s	1673br
20	2109w, 2065vs, 2046s	1645br

[a]: recorded in CH_2Cl_2

Since most of the complexes reported here are of the type $(CO)_9Co_3CC(O)OR$, Table 2.18 also gives the position of the acyl band which appears characteristically as a broad signal of low intensity around 1650 cm^{-1}.

2.2.3 X-ray crystallographic study of $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$

Complexes containing the $Co(DH)_2$ system are generically known as cobaloximes. Such complexes have been used extensively as models for the vitamin B_{12} complexes [56 - 59]. Alkyl cobaloximes have also been proposed as models for alkylcobalt intermediates in catalytic reactions [60].

The equatorial positions of cobaloximes are occupied by two monodeprotonated dimethylglyoxime ligands H-bonded to each other. This results in four equatorial N atoms which are virtually co-planar. The axial coordination sites are usually occupied by a basal donor ligand such as pyridine, H_2O, PR_3 (R = alkyl or aryl).

The reaction product (equation 14) was subjected to various spectroscopic analyses. The results of the analyses (discussed earlier), and the reaction route used, suggested that the complex could be formulated as $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **15**. That is, it consists of a distinct cobaloxime unit and (arene)tricarbonyl chromium unit. Proof of its heterobimetallic structure was sought by x-ray crystallography.

The molecular structure of **15** is now reported. This complex is the first heterobimetallic complex of cobalt and chromium derived from a cobaloxime to be structurally characterized.

X-ray diffraction studies

A suitable single crystal was selected from a batch prepared by the method described in the experimental section and subjected to a x-ray diffraction study. The structure was solved by conventional Patterson and Fourier methods. The complex crystallizes in the triclinic P1 space group with Z = 2. Crystal data are given in Table 2.19. The structure was refined to give a final conventional R factor of 0.042. Final positional parameters are given in the appendix. The structure factors have been included in a copy of this thesis kept at the library of the University of Cape Town. The bond distances are listed in Table 2.20, while selected bond angles are given in Table 2.21.

Results and discussion

The molecular structure of **15** is shown in figure 2.4. Packing is affected by van der Waal forces and by an extensive system of hydrogen bonds (see figure 2.5). The general features of the molecular structure of **15** are consistent with those suggested by its spectroscopic data (discussed earlier). All the hydrogen atom positions were located. As expected the Co···Cr distance of 5.246(1)Å is too long for any metal-metal interaction. The compound can be regarded either as a monosubstituted (arene)tricarbonyl chromium complex or as an alkyl(pyridine)cobaloxime(III) complex.

Table 2.19: Crystal data for $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **15**

Crystal data	
Molecular formula	$C_{23}H_{26}CoCrN_5O_7$
Formula weight	595.418 g. mol^{-1}
Space group	$P\bar{1}$
a, Å	8.437(2)
b, Å	12.202(2)
c, Å	13.235(2)
α, (°)	71.17(1)
β, (°)	83.44(1)
γ, (°)	83.01(1)
V($Å^3$)	1275.9(4)

Table 2.20: Bond lengths (Å) with e.s.d's in parentheses for the complex $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$

Co-N(1)	1.876(4)	C(1)-C(2)	1.467(7)
Co-N(2)	1.870(3)	C(1)-C(11)	1.490(10)
Co-N(3)	1.886(4)	C(3)-C(4)	1.458(8)
Co-N(4)	1.885(3)	C(3)-C(31)	1.490(10)
Co-C(8)	2.044(4)	C(4)-C(41)	1.499(8)
Co-N(91)	2.038(4)	C(8)-C(81)	1.472(7)
Cr-C(81)	2.280(4)	C(81)-C(82)	1.399(5)
Cr-C(82)	2.222(5)	C(81)-C(86)	1.409(6)
Cr-C(83)	2.194(5)	C(82)-C(83)	1.403(9)
Cr-C(84)	2.195(7)	C(83)-C(84)	1.354(10)
Cr-C(85)	2.229(4)	C(84)-C(85)	1.389(8)
Cr-C(5)	1.800(9)	C(85)-C(86)	1.412(9)
Cr-C(6)	1.822(7)	N(91)-C(92)	1.338(7)
Cr-C(7)	1.830(5)	N(91)-C(96)	1.340(5)
N(1)-C(1)	1.305(6)	C(92)-C(93)	1.362(7)
N(1)-O(11)	1.336(4)	C(93)-C(94)	1.377(7)
N(2)-C(2)	1.294(7)	C(94)-C(95)	1.365(8)
N(2)-O(21)	1.339(5)	C(95)-C(96)	1.378(7)
N(3)-C(3)	1.295(6)	C(5)-O(5)	1.138(11)
N(3)-O(31)	1.350(4)	C(6)-O(6)	1.165(9)
N(4)-C(4)	1.288(7)	C(7)-O(7)	1.142(7)
N(4)-O(41)	1.357(5)		

Table 2.21: Selected bond angles (degrees) with e.s.d.'s in parentheses

C(8)-Co-N(91)	176.2(2)
N(4)-Co-N(91)	90.4(2)
N(4)-Co-C(8)	90.3(2)
N(3)-Co-N(91)	90.5(2)
N(3)-Co-C(8)	85.9(2)
N(3)-Co-N(4)	80.8(2)
N(2)-Co-N(91)	90.6(2)
N(2)-Co-C(8)	88.7(2)
N(2)-Co-N(4)	178.9(2)
N(2)-Co-N(3)	98.6(2)
N(1)-Co-N(91)	90.4(2)
N(1)-Co-C(8)	93.2(2)
N(1)-Co-N(4)	98.9(2)
N(1)-Co-N(3)	179.0(2)
N(1)-Co-N(2)	81.7(2)

Figure 2. 4: Molecular structure of $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ showing the numbering system used

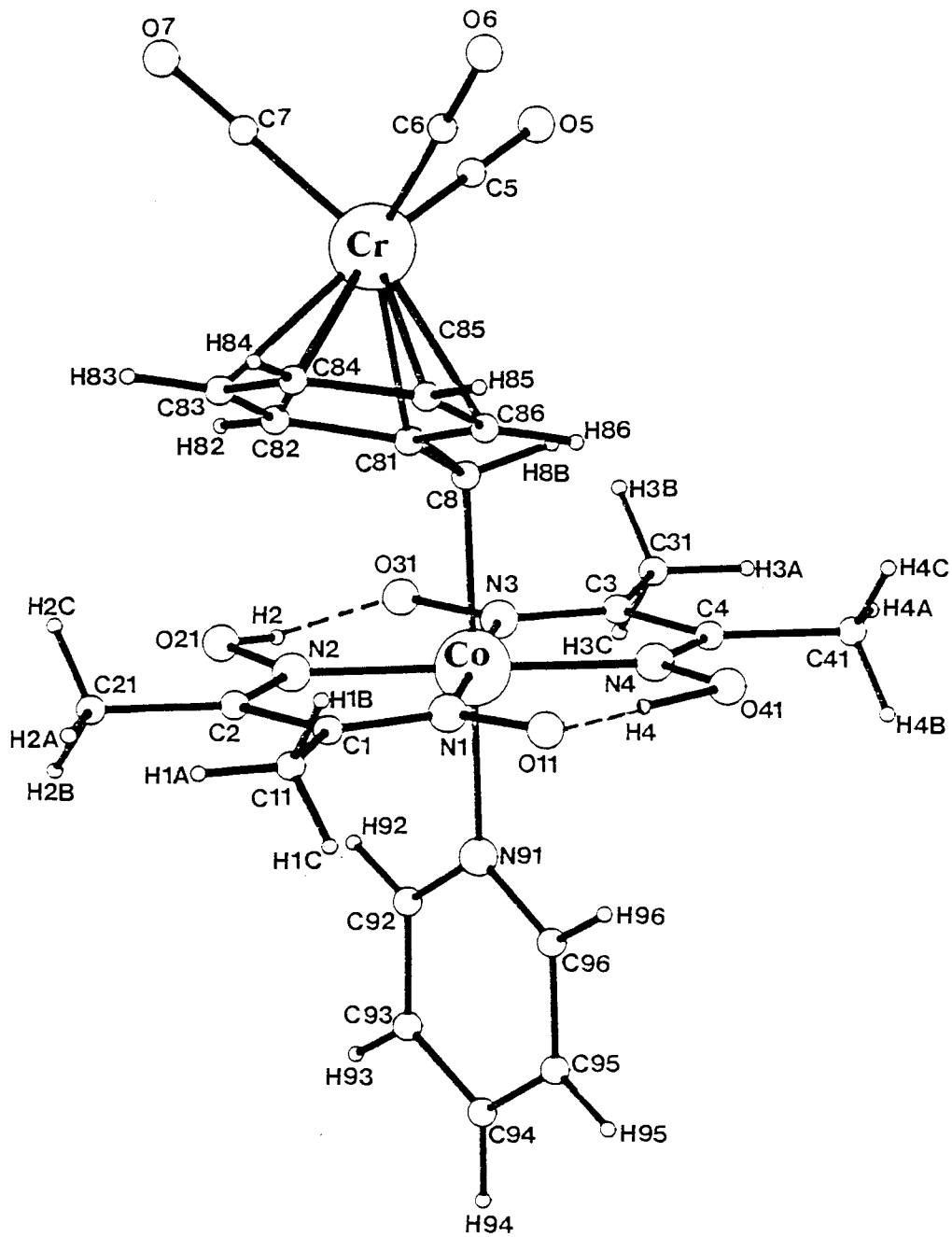
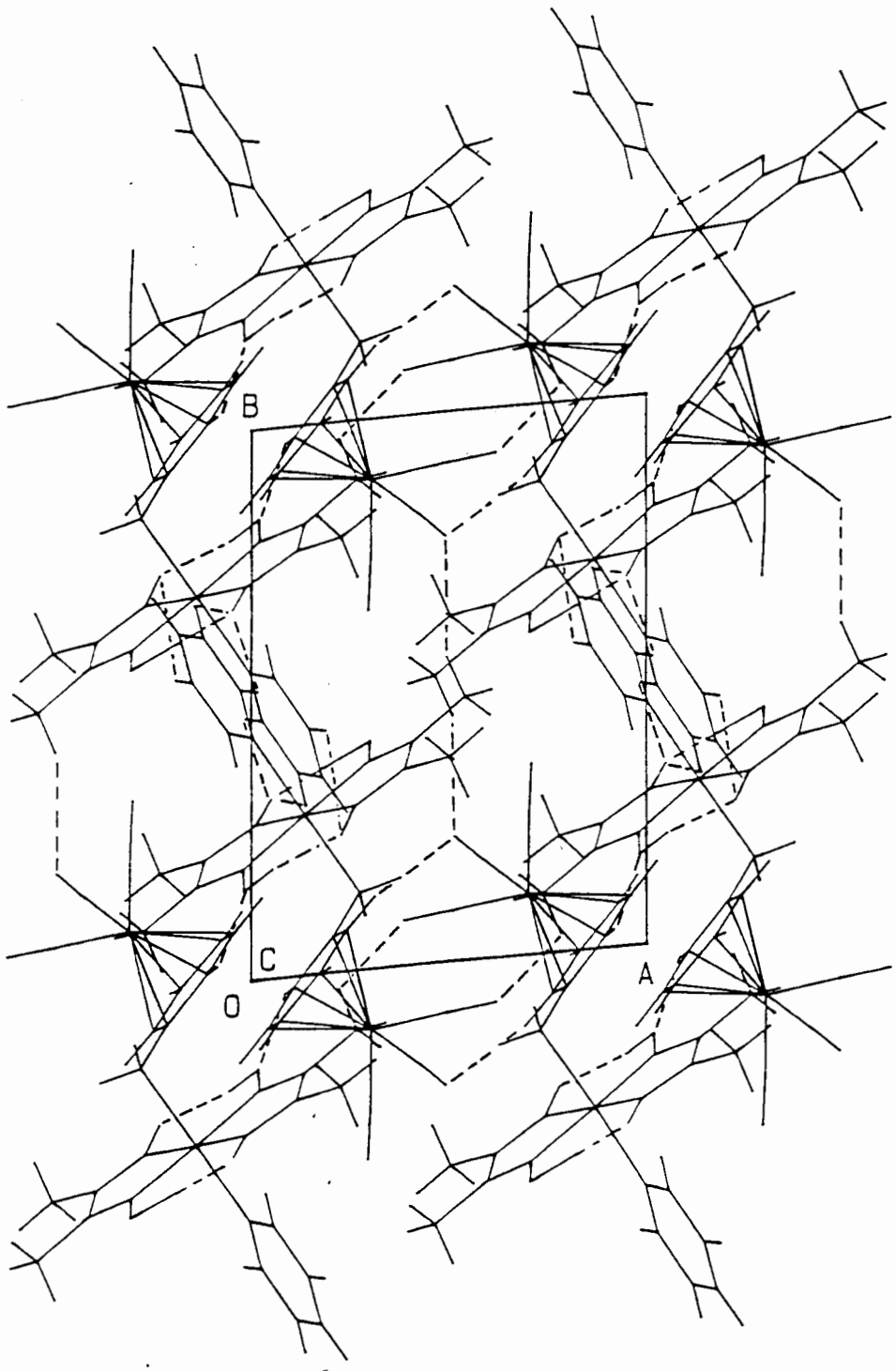


Figure 2. 5: Packing diagram viewed down Z0; hydrogen bonds are indicated by broken lines



Considering the complex as a cobaloxime, we see that compound has a structure typical of complexes of the type $[Co(DH)_2(py)R]$. Table 2.22 compares some of the more relevant bond angles of the cobaloxime unit with some typical related cobaloximes. The cobalt end of the molecule has a distorted octahedral geometry

Table 2.22: Comparison of some bond angles of the "$Co(DH)_2(py)$" unit of **15** with some related cobaloxime complexes {e.s.d.'s are given in parentheses}

Complex	N_{eq}-Co-C	N_{eq}-Co-N_{py}	Reference
15	90.3(2), 90.3(2) 85.9(2), 88.7(2)	176.2(2)	a
[Co]-Me	88.5(2), 89.3(2) 87.4(2), 88.3(2)	178.0(2)	61
[Co]-Et	85.9 - 93.0	177.1(2)	62
[Co]-Pr^i	86.4 - 92.2	175.4(1)	63
[Co]-$CF(CF_3)_2$	90.3(1), 94.3(1)	177.5(2)	64

[a]: present work

with the DH ligands occupying the equatorial positions. The four equatorial N atoms of the DH units are effectively coplanar.

Table 2.23 compares some of the more important bond distances of **15** with those of some typical cobaloxime complexes of the type $[Co(DH)_2(py)R]$. Of the complexes noted in Table 2.23, it can be seen that the Co-N_{eq} bond lengths do not show any appreciable differences. Brescianni-Pahor and co-workers found [27] this to be the case for cobaloxime type complexes in general. They found the Co-N_{eq} bond distance to be independent of both the basal ligand and the substituent on the C bonded to cobalt.

Table 2.23: Comparison of some of the more important bond lengths (Å) of **15** with those of some reported cobaloxime complexes of the type [Co]-R, [Co] = $Co(DH)_2(py)$ {e.s.d.'s are given in parentheses}

Complex	Co-C	Co-N_{eq}	Co-N_{py}	Reference
15	2.044(4)	1.876(4), 1.886(4) 1.870(3), 1.815(3)	2.038(4)	present work
[Co]-Me	1.99(8)(5)	1.877, 1.887 1.918, 1.905	2.068(3)	61, 65
[Co]-Et	2.035(5)	1.884(4)[a]	2.081	62
[Co]-$CH(Me)_2$	2.085(3)	1.887(2)[a]	2.099(2)	63
[Co]-$CF(CF_3)_2$	2.084(5)		2.037(3)	64
[Co]-N_3		1.896(5), 1.896(5) 1.908(5), 1.913(5)	1.973(5)	66
[Co]-CH_2CO_2Me	2.033	1.883, 1.885 1.896, 1.892	2.043	67

[a]: Average bond length

The Co-N(py) bond length is however found to be influenced by the nature of the trans ligand. When one compares the data for the complexes $[Co(DH)_2(py)\{CH_2R\}]$ {R = $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ **15**; H and CO_2Me}, it becomes evident that the Co-N(py) bond length is sensitive to the electronic nature of the R substituent. For complex **15** (R = electron withdrawing group), the Co-N(py) bond distance is significantly shorter than that of 2.099(2) Å for the complex having R = Me.

The Co-CH_2 bond length displays a similar sensitivity towards the nature of the substituent on the C bonded to the cobalt atom. The slightly longer Co-C bond lengths of **15** and $[Co(DH)_2(py)\{CH_2CO_2Me\}]$, relative to those for the complex $[Co(DH)_2(py)CH_3]$ undoubtedly reflects the greater electron withdrawing character of the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ and CO_2Me groups over that of a H atom.

Complex **15** possesses the usual "piano-stool" structure typical of (arene)tricarbonyl chromium derivatives. The Cr atom is approximately equidistant from each ring carbon except the C(81) atom. The Cr-CO bond distances (1.800(9) - 1.830(5) Å) fall within the range of 1.77 - 1.85 Å published for other (arene)$Cr(CO)_3$ complexes [68 - 71]. All the other bond lengths and angles are quite normal.

2.3 CONCLUSIONS

This chapter has reported results of a study which investigated the high yield synthesis of new stable heterobimetallic complexes containing only the elements Co, Cr, C, H, O and N. The new complexes **15** and **16** were successfully synthesised and were isolated in analytically pure form as air-stable solids. They were formed in greater than 70% yields and decompose above 160°C. The air-stable complexes **18** and **19**, having Co:Cr atomic ratio of 3:1, were formed in 54 - 60% yields. Complex **18** is thermally stable up to temperatures of 163°C, while **19** is found to melt at 71°C. Complex **20** isolated in 15% yield contains the highest ever reported Co:Cr atomic ratios. Future studies will include investigations leading to the high yield synthesis of **20**, as well as new complexes having Co:Cr ratios greater than 6.

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CHAPTER 3

USE OF THE NEW HETEROBIMETALLIC COMPLEXES AS PRECURSORS TO SUPPORTED METAL CATALYSTS

3.1 INTRODUCTION

Supported multimetal catalysts have been the object of intense study in recent years. Many such catalytic systems have demonstrated higher activities and selectivities than their homonuclear counterparts [1 - 3]. Similar studies into the activity of catalysts containing both cobalt and chromium have not been carried out.

We now report the results of some preliminary studies of supported catalysts, containing both cobalt and chromium, for the CO hydrogenation reaction. Our aim was to introduce the metals onto the support in the form of a heterobimetallic complex. In this way the supported material was assured to have a uniform dispersion of metal atoms, as well as having metal centers in close proximity.

We have investigated the potential use of some of the new heterobimetallic complexes reported in Chapter 2 as catalyst precursors for the CO hydrogenation reaction. The catalyst precursors were derived by loading the heterobimetallic complexes (which are denoted by the same index numbers as used in the previous chapter), onto an inorganic oxide support[1]. The final catalyst was formed after reduction and sintering at high temperatures, which would be expected to remove the ligands. The term "supported complex" is loosely used to refer to the material formed after loading the complexes onto the inorganic oxide support.

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1. Common industrial supports include titania, alumina, silica or mixtures thereof. The exact nature of the support used in the present work has not been divulged due to commercial confidence. It is however noted that the same support material was used for all the preparations.

3.2 RESULTS AND DISCUSSION

Complexes **15**, **16** and **19** were loaded onto a previously calcined and pelleted inorganic oxide support (particle size 1.0 - 1.7 mm), using the incipient wetness technique [4, 5], to give a 5% cobalt loading. The supported complexes were studied by diffuse reflectance FT-IR spectroscopy and differential scanning calorimetry (DSC). It was hoped that the FT-IR studies would shed some light on the mode of interaction between the complexes and the oxide support. DSC studies were used to investigate the thermal properties of the supported complexes. Supported **15** was also studied by scanning electron microscopy (SEM).

3.2.1 STUDIES ON THE SUPPORTED COMPLEXES

FTIR studies

The FT-IR spectra of each of the supported complexes showed no change in the positions of the metal carbonyl bands suggesting the absence of strong metal-support interactions through the carbonyl groups.

DSC studies

The DSC curve of **15** shows one sharp endothermic peak[2] (T_{max} = 222°C). Compound **15** was found to decompose at temperatures greater than 210°C, indicated by darkening of the crystals when heated under a hotstage microscope. The DSC peak at 222°C thus corresponds to decomposition of the complex. The decomposition temperature was more accurately determined from the DSC peak to

2. Pure samples often give sharp endotherms while impure samples give broad endotherms [6]

be 216°C. The DSC curve of supported **15** shows two broad endothermic peaks centered at 229°C (T_{onset} = 199°C)and 363°C (T_{onset} = 308°C). The endotherm at 229°C is associated with a species derived from weakly adsorbed **15**. The peak at 363°C is suggested to be associated with a highly stabilised species arising from the strong interacting of the complex and the support material.

The DSC curve (25 - 400°C) of supported **19** shows only a sharp (endothermic) peak at 120°C. Since the complex melts at 71°C, this peak is attributed to a species derived from a strong complex-support interaction.

Investigation of supported **15** by SEM

Scanning electron micrographs (figure 3.1), were taken of;

- pure crystals of the complex **15**
- the pelleted inorganic support
- the supported complex
- the supported complex which had been decomposed by heating to 400°C

Crystals of **15** are formed as oblique plates. The morphology of the supported complex is very different to that of the pure, crystalline complex. It appears that cubic crystals have been deposited onto the surface of the oxide support. These cubic crystals are easily distinguished from the bulk support matrix and appear to be weakly physisorbed. Electron micrographs of particles removed from the surface of the supported complex show some amorphous material clinging to relatively large cubic crystals, whose sides are approximately 8 μM long. An electron

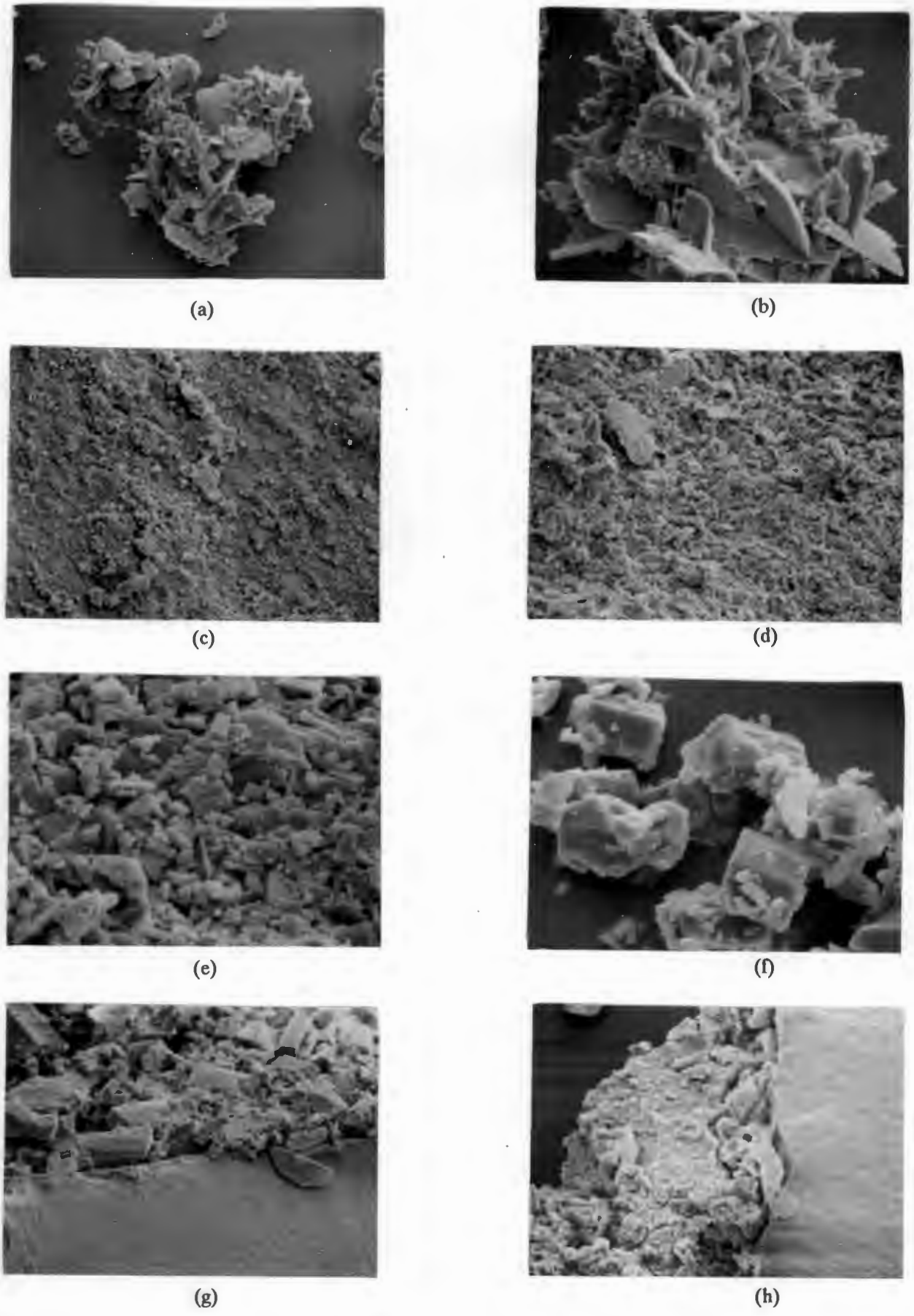

Figure 3.1: Electron micrographs (magnification shown in brackets) of: crystalline **15** (a) and (b) (900X); the pelleted oxide support (c) (950X); supported **15** (d) (950X) and (e) (3000X); particles obtained from the outer surface of supported **15** (f) (30 000X): a cross-section through particle of supported **15** (g) (530X); a cross-section through a decomposed particle of the supported **15** (400°C) (h) (950X).

micrograph of a cross-section through a pellet of the supported complex shows different morphologies for the inner bulk matrix and outer surface. There appears to have been no penetration of the complex into the inner bulk matrix of the oxide support.

A cross-section through a decomposed sample of the supported complex shows virtually no change in appearance of the inner bulk matrix, while the outer surface material shows no crystalline shapes.

When this information is combined with the information of the FT-IR spectroscopic results, it strongly suggests that there is no strong interaction between the **15** and the oxide support material. This result is surprising, in view of the fact that many metal carbonyl complexes loaded onto inorganic oxide supports show strong metal-support interactions [7].

3.2.2 Use of the supported heterobimetallic complexes as catalyst precursors for the CO hydrogenation reaction

Evaluation of supported **15** as a CO hydrogenation catalyst precursor

Supported **15** was loaded into a fixed-bed microreactor and activated by reduction under a hydrogen atmosphere, followed by sintering at elevated temperatures. The resulting material was found to be an active CO hydrogenation catalyst. The preliminary results of the catalyst testing are shown in Table 3.1.

Table 3.1: Preliminary results for the catalyst system derived from supported **15**

%CO conversion	3.13	
%(CO + CO_2) conversion	2.92	
Selectivities (Mass %)	C_1	4.17
	C_2	4.17
	C_2 alkene/alkane	1.00
	C_3 and greater	91.65

The low methane selectivity of 4.17% is a paricularly significant result, since for most practical purposes, methane is an undesirable product, being the most unreactive of the alkanes. There is currently no commercial process which converts methane directly into useful organic products. The result becomes even more significant if one considers that methane and light hydrocarbons (C_2 - C_3) are the major products of many CO hydrogenation catalyst systems [8 - 11]. For example, decomposed samples of supported iron complexes $[Cp(CO)_2Fe]_2[\mu\text{-}(CH_2)_n]$ (n = 0, 3, 5), gave methane, C_2 and C_3 hydrocarbons as the major reaction products when tested for CO hydrogenation activity under similar reaction conditions [9]. The reverse selectivity is observed for our system, with more than 90% of the reaction products having a chain length of 3 or greater.

The result becomes even more significant when compared to those obtained for catalyst systems derived from simple salts of cobalt and chromium. When cobalt chromate was supported on the inorganic oxide, and tested in a similar manner, the resulting species was found to be inactive in the CO hydrogenation reaction. Similarly, a supported catalyst, derived from a 1:1 mixture of cobalt nitrate and

chromium nitrate, was also found to have no catalytic activity in the CO hydrogenation reaction.

The CO conversion of 3.1% is, however, very low when compared to other systems. For example, catalyst systems derived from supported complexes of the type $[Cp(CO)_2Fe]_2[\mu\text{-}(CH_2)_n]$ (n = 0, 3, 5), were found to exhibit CO conversions of between 10 and 15% [9]. It was however believed that the activity of the catalyst could be improved by increasing the ratio of the active metal (Co) relative to the promoter metal (Cr). In order to prove this hypothesis, the activity of two similarly derived catalytic systems having Co:Cr atomic ratios of 1:1 and 2:1, were evaluated. In order to allow for meaningful comparison, the two systems had to be tested under identical reaction conditions. The results of such a study are now reported.

Comparative study of supported metal catalysts having different Co:Cr ratios

Supported catalysts having Co:Cr atomic ratios of 1:1 and 2:1 were prepared from activated samples of supported **15** and supported **16**, respectively. Their activity in the CO hydrogenation reaction was determined under identical reaction conditions (19 Bar, 250°C, GHSV = 800 hr^{-1}). The results obtained are shown in Table 3.2, along with those obtained (under similar reaction conditions), for a catalyst derived in a similar manner from supported $[\eta^6\text{-}C_6H_4\{CH_2OCCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$ (representing a catalyst system having a Co:Cr atomic ratio of 6:1) [12].

Table 3.2: Relative CO hydrogenation activities of supported metal catalysts having different Co:Cr atomic ratios

Co:Cr atomic ratio	1:1	2:1	6:1
metal complex	15	16	[a]
activity	1	3.1	18.7

[a]: $[\eta^6\text{-}C_6H_4\{CH_2OCCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$ [12]

Table 3.2 shows that the catalyst activity does indeed increase with increasing Co:Cr atomic ratios. We see that doubling the Co:Cr atomic ratio results in a three-fold increase in the activity, while increasing the Co:Cr ratio to 6:1, leads to a 19-fold increase of activity. These results serve to demonstrate the effect of varying Co:Cr atomic ratios on the activity (at least at low ratios), while also proving the superior CO hydrogenation activity of cobalt over that of Cr.

A plot of the olefin-to-paraffin ratios versus carbon number is shown in figure 3.1. This shows the greater olefin selectivity of the 2:1 catalyst over that of the 1:1 and 6:1 systems. The 6:1 catalyst produces primarily paraffins over the C_3 - C_9 range.

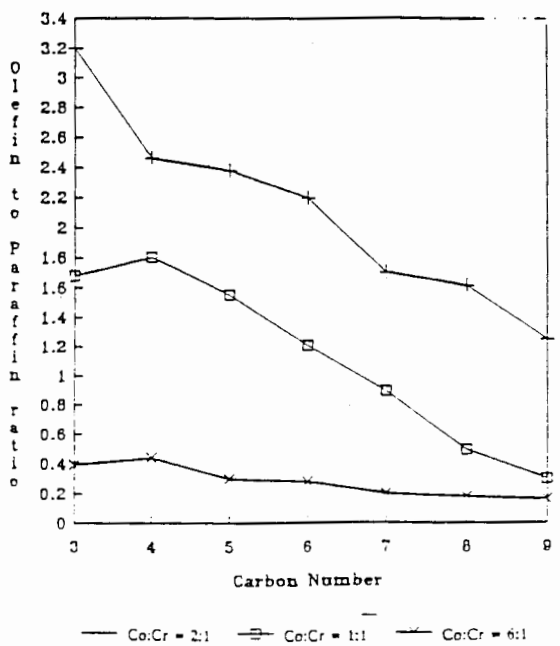

Figure 3.1: Plot of olefin-to-paraffin ratio vs carbon number

3.3 CONCLUDING REMARKS

We have reported the preliminary results of the use of supported heterobimetallic complexes of cobalt and chromium, having Co:Cr atomic ratios of 1:1 and 2:1, as catalyst precursors in the CO hydrogenation reaction. Both supported complexes were shown to yield active hydrogenation catalysts superior to catalytic systems derived from the monometallic constituents. The results presented, together with those reported for a similarly derived 6:1 catalyst, show an increase in activity as the Co:Cr ratio increases from 1:1 to 2:1 to 6:1.

Future work will include similar studies on heterobimetallic complexes having Co:Cr atomic ratios greater than 6:1. In this way we hope to delineate the effect of the Co:Cr atomic ratio on the product distribution of the hydrocarbon products and determine the optimum Co:Cr ratio.

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CHAPTER 4

EXPERIMENTAL

4.1 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 2

General

All reactions were carried out using standard Schlenk tube techniques under an atmosphere of nitrogen with continuous stirring, unless otherwise stated.

The solvents used were generally analytical grade and were purified as follows: THF and diethylether were dried over Na/benzophenone and distilled prior to use; dichloromethane was distilled from anhydrous $CaCl_2$. Methanol[1] and benzene (A.R) were used without further purification.

The following starting compounds were prepared by literature methods; $[Co(DH)_2(py)Cl]$ [1], $[\eta^6\text{-}C_6H_5CH_2OH]Cr(CO)_3$ [2], $[\eta^6\text{-}C_6H_5CH_2Cl]Cr(CO)_3$ [3], $(CO)_9Co_3CCl$ [4], $(CO)_9Co_3CH$ [5], $(CO)_9Co_3CPh$ [6] and $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ [7].

The following chemicals were purchased from Aldrich and used without further purification; $Cr(CO)_6$, $Co_2(CO)_8$, $[C_6H_4(CH_2OH)_2\text{-}1,4]$, $[C_6H_5\{(CH_2)_4OH\}]$, $[C_6H_4(CH_2Br)_2\text{-}1,4]$, $[C_6H_4(CH_2Br)_2\text{-}1,3]$, $[C_6H_4(CH_2Br)_2\text{-}1,2]$ and $[C_6H_4(COCl)_2\text{-}1,4]$. Benzyl alcohol was purchased from SAARCHEM, and $[\eta^6\text{-}C_6H_6]Cr(CO)_3$ was purchased from Strem Chemicals Inc.

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1. Methanol was saturated with nitrogen immediately prior to use

Final purification of the reaction products was achieved either by column chromatography (Silica Gel 60[2]/hexane) or recrystallization (CH_2Cl_2/hexane served well in most cases), or by a combination of the two.

Except for the reactions involving the substituted cobaloxime complexes $[Co(DH)_2(py)R]$, the progress of the reactions was monitored by TLC (Silica Gel 60) and/or IR spectroscopy {ν(CO), CH_2Cl_2}.

IR spectra were recorded on a Perkin Elmer 983 spectrophotometer using solution cells (NaCl windows), or as Nujol mulls between NaCl or CsI plates.

^1H and ^{13}C NMR spectra were recorded on a Varian VXR 200 or a Bruker WH 90 NMR spectrometer. Unless otherwise stated, the spectra were recorded in $CDCl_3$, using tetramethylsilane as an internal standard (δ 0.0 ppm).

Low resolution E. I. mass spectra (70 eV, 4 kV) were recorded on a VG Micromass 16 F spectrometer at the laboratories of the University of Cape Town by Ms H. Von Straaten

Melting points were determined with a Kofler Hotstage Microscope (Reichart Thermovar) and are uncorrected.

Microanalyses were determined at the microanalytical laboratories of the University of Cape Town, by Mr G. P. Benin-Casa.

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2. Obtained from Merck

Preparation of (N-benzylaniline)chromium tricarbonyl **1**.

A 100 ml 2-necked flask fitted with a reflux condenser, was charged with N-benzylaniline (1.65 g, 9.00 mmol), $Cr(CO)_6$ (2.00 g, 9.00 mmol), di-n-butyl ether (60 ml) and THF (5 ml). The mixture was refluxed for 24 hrs. The resultant yellow solution was then cooled to RT and filtered through a sintered glass funnel containing a pad of silica gel. The silica gel was washed with small amounts of THF. The solvents were then removed from the filtrate and the crude product recrystallized from CH_2Cl_2/hexane to give pure **1** as bright yellow crystals (1.93 g, 67%).

Anal. Calcd. for $C_{16}H_{13}CrNO_3$: C 60.2, H 3.9, N 4.4%; mw 319.29 g. mol^{-1}

Found: C 60.5, H 4.1, N 4.3%; M^+ 319

Preparation of $[\eta^6\text{-}C_6H_4(CH_2OH)_2\text{-}1,4]Cr(CO)_3$ **2**.

Complex **2** was prepared by the same method described above for **1** with the following quantities of reagents: $[C_6H_4(CH_2OH)_2\text{-}1,4]$ (4.0 g, 28.9 mmol); $Cr(CO)_6$ (6.40 g, 28.9 mmol); di-n-butyl ether (190 ml); THF (16 ml). The mixture was refluxed for 26 hrs after which it was cooled in an ice bath. The resulting yellow crystals were then filtered off and recrystallized from CH_2Cl_2/hexane to give yellow crystals of **2** (7.0 g, 90%).

Anal. Calcd. for $C_{11}H_{10}CrO_5$: C 48.2, H 3.7; mw 274.19 g. mol^{-1}

Found: C 48.4, H 3.6; M^+ 274

Preparation of $[\eta^6\text{-}C_6H_5\{(CH_2)_4OH\}]Cr(CO)_3$ **3**.

Complex **3** was prepared by the same method described for **1** above with the following quantities of reagents: $[C_6H_5\{(CH_2)_4OH\}]$ (1.0 ml); $Cr(CO)_6$ (1.48 g, 6.49 mmol); di-n-butyl ether (45 ml); THF (4.0 ml). The reaction mixture was refluxed for 21 hrs, afterwhich

it was cooled to RT. Hexane (5 ml) was added and the solution cooled in an ice bath. The resulting precipitate was filtered and washed with cold hexane to yield **3** (1.5 g, 81%) as a bright yellow crystalline solid.

Anal. Calcd. for $C_{11}H_{10}CrO_5$: C 54.5, H 4.93; mw 286.25 g. mol^{-1}

Found: C 54.4, H 4.95; M^+ 286

Preparation of $[\eta^6\text{-}C_6H_4(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$ **4**.

$[\eta^6\text{-}C_6H_4(CH_2OH)_2\text{-}1,4]Cr(CO)_3$ **2** (3.5 g, 12.8 mmol) in benzene (80 ml), was shaken up with concentrated HCl (125 ml) for 15 min in a separatory funnel. After separation of the phases, the organic layer was washed with distilled water (2 x 80 ml) and dried over $MgSO_4$. The solution was then filtered through a pad of silica gel and the solvent evaporated. The crude product was recrystallised from CH_2Cl_2/hexane to yield pure yellow crystals of **4** (3.2 g, 80%).

Anal. Calcd. for $C_{11}H_8Cl_2CrO_3$: C 42.47, H 2.59; mw 311.074 g. mol^{-1}

Found: C 42.1, H 2.5; M^+ 311

Preparation of $[\eta^6\text{-}C_6H_5\{(CH_2)_4Cl\}]Cr(CO)_3$ **5**.

Complex **5** was prepared by the same method described above for the synthesis of **4** with the following quantities of reagents: $[\eta^6\text{-}C_6H_5\{(CH_2)_4OH\}]Cr(CO)_3$ **3** (0.5 g, 1.75 mmol); HCl(conc.)(9 ml); benzene (15 ml). After the organic layer was separated, dried and evaporated, **5** was isolated as a yellow oil (0.32 g, 60 %).

Anal. Calcd. for $C_{13}H_{13}ClCrO_3$: C 51.2 , H 4.3 ; mw 304.684 g. mol^{-1}

Found: C 51.0 , H 4.4; M^+ 304

Preparation of [{(py)(DH)$_2$CoCH$_2$}C$_6$H$_4${CH$_2$Br}-1,4] **6**

[Co(DH)$_2$(py)Cl] (0.50 g, 1.24 mmol) was added to nitrogen-saturated methanol (10 ml) and the slurry stirred for 5 min. [C$_6$H$_4$(CH$_2$Br)$_2$-1,4] (0.34 g, 1.28 mmol) was added and the mixture stirred for a further 5 min. NaBH$_4$(0.25 g, 6.60 mmol) was then added portionwise over a period of 10 min. The resulting orange solution was stirred for a further 1 hr. The orange product was filtered off and washed with diethyl ether (5 ml). The crude product was then recrystallized from CH$_2$Cl$_2$/hexane to give **6** (0.33 g, 48%) as an orange crystalline solid

Anal. Calcd. for $C_{21}H_{27}BrCoN_5O_4$: C 45.7, H 4.9, N 12.7; mw 552.316 g. mol^{-1}

Found: C 45.5, H 4.8, N 12.9

Preparation of [{(py)(DH)$_2$CoCH$_2$}C$_6$H$_4${CH$_2$Br}-1,3] **7**

Compound **7** was prepared by the method described above for **6** with the following amounts of reagents: [Co(DH)$_2$(py)Cl] (0.50 g, 1.24 mmol); [C$_6$H$_4$(CH$_2$Br)$_2$-1,3 (0.34 g, 1.28 mmol); NaBH$_4$(0.25 g, 6.60 mmol). Complex **7** was isolated (0.34 g, 50%) as a light orange-yellow solid.

Anal. Calcd. for $C_{21}H_{27}BrCoN_5O_4$: C 45.7, H 4.9, N 12.7; mw 552.316 g. mol^{-1}

Found: C 46.0, H 4.8, N 14.0

Preparation of [{(py)(DH)$_2$CoCH$_2$}C$_6$H$_4${CH$_2$Br}-1,2] **8**

Compound **8** was prepared by the method described above for **6** with the following amounts of reagents: [Co(DH)$_2$(py)Cl] (0.50 g, 1.24 mmol); [C$_6$H$_4$(CH$_2$Br)$_2$-1,2] (0.34 g,

1.28 mmol); $NaBH_4$(0.25 g, 6.60 mmol). Complex **7** was isolated (0.34 g, 50%) as a light orange-yellow solid.

Anal. Calcd. for $C_{21}H_{27}BrCoN_5O_4$: C 45.7, H 4.9, N 12.7; mw 552.316 g. mol^{-1}

Found: C 45.2, H 5.0, N 14.1

Preparation of $[C_6H_4\{CH_2Co(DH)_2(py)\}_2$*-1,4]* **9**.

Method (i) $[Co(DH)_2(py)Cl]$ (1.00 g, 2.48 mmol) was added to nitrogen-saturated methanol (15 ml) and the slurry stirred for 5 min. $[C_6H_4(CH_2Br)_2$-1,4] (0.34 g, 1.28 mmol) was added and the mixture stirred for a further 5 min. $NaBH_4$(0.5 g, 13.2 mmol) was then added portionwise over a period of 5 min and the resulting orange solution was stirred for a further 1 hr. The crude product was filtered off and recrystallized from CH_2Cl_2/hexane. Orange crystals (1.7 g, 79%) of **9** were isolated.

Method (ii) Compound **9** was also prepared by the method described above for **6** with the following amounts of reagents: $[Co(DH)_2(py)Cl]$ (0.08 g, 0.20 mmol); $[\{(py)(DH)_2CoCH_2\}C_6H_4\{CH_2Br\}$-1,4] **6** (0.10 g, 0.18 mmol); $NaBH_4$(0.05 g, 1.32 mmol). Complex **9** was isolated in 50% (0.08 g) yield.

Anal. Calcd. for $C_{34}H_{46}Co_2N_{10}O_8$: C 48.6, H 5.5, N 16.6; mw 840.668 g. mol^{-1}

Found: C 48.4, H 5.1, N 16.5

Preparation of $[C_6H_4\{CH_2Co(DH)_2(py)\}_2$*-1,3]* **10**.

Method (i) Compound **10** was prepared by the first method described above for **9** with the following quantities of reagents: $[Co(DH)_2(py)Cl]$ (2.00 g, 4.96 mmol);

$[C_6H_4(CH_2Br)_2$-1,3] (0.68 g, 2.56 mmol); $NaBH_4$ (1.0 g, 26 mmol). This gave **10** (1.78 g, 44%) as orange crystals which was recrystallized from CH_2Cl_2/hexane.

Method (ii) Compound **10** was also prepared by the method described for **6** above with the following quantities of reagents: $[Co(DH)_2(py)Cl]$ (0.08 g, 0.20 mmol); **7** (0.10 g, 0.18 mmol); $NaBH_4$ (0.05 g, 1.32 mmol). Compound **10** was isolated in 33% (0.05 g) yield.

Anal. Calcd. for $C_{34}H_{46}Co_2N_{10}O_8$: C 48.6, H 5.5, N 16.6; mw 840.668 g. mol^{-1}

Found: C 48.6, H 5.4, N 13.3

Preparation of $[C_6H_4\{CH_2Co(DH)_2(py)\}_2$*-1,2]* **11**.

Method (i) Compound **11** was prepared by the method described for **9** above with the following quantities of reagents: $[Co(DH)_2(py)Cl]$ (1.00 g, 2.48 mmol); $[C_6H_4(CH_2Br)_2$-1,2] (0.34 g, 1.28 mmol); $NaBH_4$ (0.50 g, 13.2 mmol). This gave orange crystals of **11** (0.43 g, 40%) which were recrystallized from CH_2Cl_2/hexane.

Method (ii) Compound **11** was also prepared by the method described for **6** above with the following quantities of reagents: $[Co(DH)_2(py)Cl]$ (0.16 g, 0.40 mmol); **7** (0.20 g, 0.36 mmol); $NaBH_4$ (0.10 g, 2.64 mmol). This gave 0.08 g (26%) of **11**.

Anal. Calcd. for $C_{34}H_{46}Co_2N_{10}O_8$: C 48.6, H 5.5, N 16.6; mw 840.668 g. mol^{-1}

Found: C 49.0, H 5.7, N 14.4

Preparation of $[C_6H_4\{Co(DH)_2(py)\}_2\text{-}1,4]$ **12.**

Compound **12** was prepared by the method described above for **9** with the following amounts of reagents: $[Co(DH)_2(py)Cl]$ (1.00 g, 2.48 mmol); $[C_6H_4(C(O)Cl)_2\text{-}1,4]$ (0.25 g, 1.23 mmol); $NaBH_4$ (0.50 g, 13.2 mmol). This gave **12** as a beige solid in 32% (0.32 g) yield.

Anal. Calcd. for $C_{32}H_{42}Co_2N_{10}O_8$: C 47.3, H 5.2, N 17.2; mw 812.616 g. mol^{-1}

Found: C 47.3, H 5.1, N 18.2

Preparation of $(CO)_9Co_3CC(O)OCH_2C_6H_5$ **13.**

Preparation of the acylium cation, $[(CO)_9Co_3CCO]^+[AlCl_4 \cdot AlCl_3]^-$ The tricobaltcarbon decacarbonyl cation was prepared by the method of Seyferth [8] as follows; An R.B. flask was charged with $(CO)_9Co_3CCl$[3] (0.5 g, 1.1 mmol) and CH_2Cl_2 (25 ml). The solution was stirred to produce a purple homogeneous solution and $AlCl_3$ (0.48 g, 3.1 mmol) was then added. The solution was stirred (30 min) until the starting material was converted to the $(CO)_9Co_3C(CO)^+$ cation. This was indicated by a single brown spot (R_f = 0) on a TLC (Silica Gel/hexane) plate. The solution had also become brown and somewhat heterogenous.

Addition of the nucleophile Benzyl alcohol (25 ml) was then added and the reaction mixture stirred for approximately 2 hrs, until TLC shows the consumption of the cation and only spots due to the reaction products. The mixture was then poured over cold 10% HCl (50 ml). The organic layer was then separated and dried over anhydrous magnesium sulphate. The solvent was then removed under reduced pressure. The solid

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3. Prepared by the method of Booth and co-workers by heating $Co_2(CO)_8$ and CCl_4 in hexane for 7 hrs [4]

residue was then purified by column chromatography (Silica Gel/Hexane). A fast moving purple band ($(CO)_9Co_3CCl$, 60 mg, 11%) was eluted first with hexane. A second (slow moving) dark-purple band was eluted with CH_2Cl_2 to give **13** as a black solid in 54% (0.34 g) yield.

Anal. Calcd. for $C_{18}H_7Co_3O_{11}$: C 37.5, H 1.2; mw 576.026 g. mol^{-1}

Found: C 38.4, H 1.4; M^+ 576

Preparation of $[C_6H_4\{CH_2OC(O)CCo_3(CO)_9\}_2\text{-}1,4]$ **14.**

Compound **14** was prepared by the same method described above for **13**, except that the nucleophile was reacted with two molar equivalents of the cation. The following quantities of reagents were used to prepare the acylium cation : $(CO)_9Co_3CCl$ (0.33 g, 0.69 mmol); $AlCl_3$ (0.32 g) and CH_2Cl_2 (25 ml). After the formation of the cation was complete, the diol $[C_6H_6(CH_2OH)_2\text{-}1,4]$ (0.05 g, 0.35 mmol), was added. After the standard workup procedures were followed, column chromatography gave $(CO)_9Co_3CCl$ (40 mg) (eluted first with hexane) followed by **14** which was isolated as a black solid in 51% (0.18 mmol) yield.

Anal. Calcd. for $C_{30}H_8Co_6O_{22}$: C 33.5, H 0.75; mw 1073.94 g. mol^{-1}

Found: C 34.0, H 0.8

Preparation of $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **15.**

Complex **15**, was prepared by a modification of the method used by Nash and Moss [9]. $[Co(DH)_2(py)Cl]$ (8.83 g, 21.86 mmol) was slurried with methanol (90 ml) for 5 min. after which time $[\eta^6\text{-}C_6H_5CH_2Cl]Cr(CO)_3$ (5.74 g, 21.86 mmol) was added and the mixture stirred for 5 min. Portions of $NaBH_4$ (1.65 g, 43.72 mmol) were then added over a period of 25 min and the resulting orange solution stirred for a further 1 hr. The solution was then

cooled at -15°C for 20 hrs. The orange crystalline product was then filtered off and washed with cold hexane (3 x 3 ml). The complex was recrystallized from CH_2Cl_2/hexane and 9.20 g (70%) of solid isolated.

Anal. Calcd. for $C_{23}H_{26}CoCrN_5O_7$: C 46.4, H 4.4, N 11.8; mw 595.418 g. mol^{-1}

Found: C 46.2, H 4.1, N 11.7

Preparation of $[\eta^6\text{-}C_6H_4\{CH_2Co(DH)_2(py)\}_2\text{-}1,4]Cr(CO)_3$ **16**

Compound **16** was prepared by the method described for **15** above but the following quantities of reagents were used: $[Co(DH)_2(py)Cl]$ (7.82 g, 19.36 mmol); $[\eta^6\text{-}C_6H_4\text{-}(CH_2Cl)_2\text{-}1,4]Cr(CO)_3$ (3.01 g, 9.68 mmol); $NaBH_4$ (3.78 g, 26.4 mmol). The reaction mixture was stirred for 1 hr after the last portion of $NaBH_4$ was added and cooled at -15°C for 20 hrs. The crude product was then filtered and washed with distilled water (5 ml) and diethyl ether (5 ml). The product was then recrystalized from CH_2Cl_2/hexane and isolated in 77% yield.

Anal. Calcd. for $C_{37}H_{46}Co_2CrN_{10}O_{11}$: C 45.5, H 4.7, N 14.4; mw 976.698 g. mol^{-1}

Found: C 45.4, H 4.6, N 14.4

Preparation of $[\eta^6\text{-}C_6H_5CCo_3(CO)_9]Cr(CO)_3$ **17**.

Method (i) A R.B. flask was flushed with N_2 and charged with $(CO)_9Co_3CH$[4] (0.141 g, 0.318 mmol), bis(phenyltricarbonylchromium)mercury[5] (0.200 g, 0.318 mmol) and THF (15 ml). Carbon monoxide gas was then bubbled through the reaction mixture for 30 min,

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4. Prepared by heating (50°C) a mixture of $Co_2(CO)_8$ and $CHBr_3$, in THF, for 6 hrs [5].

5. Prepared by the thermal reaction between $(C_6H_6)_2Hg$ and $Cr(CO)_6$, in a refluxing mixture of diglyme and octane [7]

thereafter it was refluxed for 4 hrs. The solution was then cooled to RT, filtered through glass frit and washed with acetone. The solvents were removed from the filtrate and the resulting solid was column chromatographed (silica gel/hexane). A purple band containing $(CO)_9Co_3CH$ (0.03 g, 6%) followed by a yellow band of $[\eta^6\text{-}C_6H_6]Cr(CO)_3$ (trace amounts, identified by IR spectroscopy, and M. P.) was eluted with hexane. The reddish-purple product containing band (0.1 g, 14%) was eluted with 10% diethyl ether in hexane.

Method (ii) Compound **17** was also synthesized by the following method; $Cr(CO)_3(py)_3$ was first prepared by the method suggested by Cargamano [10] as follows: $[\eta^6\text{-}C_6H_6]Cr(CO)_3$ (0.74 g, 3.48 mmol) and pyridine (8 ml) was refluxed, with stirring, for 2 hrs. The reaction mixture was then cooled to RT and anhydrous diethyl ether (30 ml) was added to precipitate the product. Red crystals of $Cr(CO)_3(py)_3$ (0.77 g, 60%) were filtered under nitrogen.

A R. B. flask was then charged with $(CO)_9Co_3CPh$[6] (0.25 g, 0.48 mmol), anhydrous diethyl ether (20 ml), $Cr(CO)_3(py)_3$ (0.18 g, 0.48 mmol) and $BF_3 \cdot Et_2O$ (0.177 ml, 1.44 mmol). The reaction mixture was then refluxed for 3 hrs and allowed to cool to RT. The solution was then diluted with diethyl ether (20 ml), filtered and washed with an equal volume of distilled water. The product was then extracted with diethyl ether (until the extracts were colourless) and dried over magnesium sulphate. The solvents were then evaporated to yield a brown-purplish solid which was then column chromatographed (Silica Gel/ hexane). An unidentified brown band was eluted first which had ν(CO) bands at 2100m, 2053vs, 2039s, 2020m and 1979w cm^{-1}. The second product-containing band on

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6. Prepared by the method of Dolby and Robinson by refluxing benzene solution of $(CO)_9Co_3CCl$ in the presence of $AlCl_3$ for 6 hrs [6]

the top of the column was then eluted with CH_2Cl_2/hexane (50%) to yield **17** in 10% yield.

Anal. Calcd. for $C_{19}H_5Co_3CrO_{12}$: C 34.9, H 0.8; mw 654.02 g. mol^{-1}

Found: C 35.1, H 1.1; M^+ 654

Preparation of $[\eta^6\text{-}C_6H_5CH_2OC(O)CCo_3(CO)_9]Cr(CO)_3$ **18**.

As described in the preparation of **13** above, the cation $(CO)_9Co_3C(CO)^+$ was formed from $(CO)_9Co_3CCl$ (0.8 g, 1.7 mmol), CH_2Cl_2 (42 ml) and $AlCl_3$ (0.68 g, 5.1 mmol). $[\eta^6\text{-}C_6H_5CH_2OH]Cr(CO)_3$ (0.42 g, 1.7 mmol) was then added and the solution stirred (2 hrs) until TLC shows the abscence of the $(CO)_9Co_3C(CO)^+$ cation. The reaction mixture was then poured into cold 5% HCl (200 ml). The organic layer was then separated, dried over anhydrous magnesium sulphate, and evaporated to dryness to yield 0.82 g of dark purple solid. Column chromatography (silica gel/hexane) yielded a purple band ($(CO)_9Co_3CCl$, 80 mg) and a brown band of unknown composition. CH_2Cl_2 was then used to elute a brown band of unknown composition and a third brown band containing **18** (0.156 g, 13%)

Anal. Calcd. for $C_{21}H_7Co_3CrO_{14}$: C 35.4, H 1.0: mw 712.056

Found: C 36.2, H 1.2

Preparation of $[\eta^6\text{-}C_6H_5\{(CH_2)_4OC(O)CCo_3(CO)_9\}]Cr(CO)_3$ **19**.

Complex **19** was prepared by the same method as described for **13** above, with the following amounts of reagents: $(CO)_9Co_3Cl$ (0.50 g, 1.01 mmol); $[\eta^6\text{-}C_6H_5\{(CH_2)_4OH\}]$-$Cr(CO)_3$ **3** (0.30 g, 1.01 mmol); $AlCl_3$ (0.48 g, 3.05 mmol) and CH_2Cl_2 (25 ml). After the standard reaction procedure and workup (as detailed previously for the synthesis of **13**), the crude product was purified by column chromatography. Eluting with a 50%

CH_2Cl_2/hexane mixture gave an initial brown band (unidentified) in trace amounts. This band was followed by a purplish-brown product containing band. The product was isolated as a dark-red solid in 60% (0.5 g) yield.

Anal. Calcd. for $C_{24}H_{13}Co_3CrO_{14}$: C 38.2, H 1.7: mw 754.134 g. mol^{-1}

Found: C 39.0, H 1.8; M^+ 754

Preparation of $[\eta^6\text{-}C_6H_4\{CH_2OOCCCo_3(CO)_9\}_2\text{-}1,4]Cr(CO)_3$ **20**.

Complex **20** was prepared by the same method described for **13** above except that a cation/nucleophile molar ratio of 2:1 was employed. The following quantities of reagents were used: $(CO)_9Co_3Cl$ (0.50 g, 1.06 mmol); $[\eta^6\text{-}C_6H_4(CH_2OH)_2\text{-}1,4]Cr(CO)_3$ **2** (0.145 g, 0.53 mmol); $AlCl_3$ (0.42 g, 3.1 mmol) and CH_2Cl_2 (26 ml). The standard reaction and workup procedures (as detailed previously for the synthesis of **13**), were followed. Final purification was achieved by column chromatography. The product containing band (purple) was eluted with CH_2Cl_2. The product was isolated as a dark solid in 15% (0.074 g) yield.

Anal. Calcd. for $C_{33}H_8Co_6CrO_{25}$: C 32.8, H 0.7: mw 1209.974 g. mol^{-1}

Found: C 33.0, H 0.7

Growing crystals of $[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ **15** *suitable for x-ray diffraction studies.*

A dilute methylene chloride solution of **15** (prepared as detailed above) was prepared. Hexane was then added until the solution went cloudy. More methylene chloride was then added dropwise until the cloudiness just dissappeared. The solution, contained in a vessel which allowed for slow evaporation of CH_2Cl_2, was then stored in the dark. After 2 - 3

days, air-stable orange-brown platelets of **15** suitable for x-ray diffraction studies were recovered.

Details regarding the X-ray structural determination of **15**

The data collection was performed by Dr. M. Niven at the University of Cape Town on an Enraf-Nonius CAD4 diffractometer, at 293 K, using graphite-monochromated Mo K_α radiation (λ = 0.7107 Å) and the ω - 2θ mode. During the data collection, 3 reference reflections were monitored periodically to check stability. Data reduction included Lorentz and polarisation corrections. The structure was solved by Dr. A. Irving[7], using the SHELX76 program system [11].

4.2 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 3

General

Differential scanning calorimetry was performed by Ms S. Bourne, on a Perkin Elmer Series 7 DSC instrument, using a heating rate of 10°C/min., under a N_2 flow of 40 ml/min. Scanning electron micrographs were recorded by Mr D. Gerneke[8], in a Cambridge S180 scanning electron microscope. The support material consisted of pellets of an inorganic oxide[9] (particle size of 1.0 - 1.7 mm), that had been previously calcined in air at 400°C.

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7. Department of Chemistry, University of Cape Town, Private Bag, Rondebosch, 7700

8. Electron Microscope Unit, University of Cape Town, Private Bag, Rondebosch, 7700

9. The same oxide support was used throughout our work

The catalyst testing was performed in a Fixed-Bed, stainless steel microreactor at the laboratories of Sasol[10]. Reagent grade dichloromethane was used.

Preparation of the supported complexes

Complexes **15**, **16** and **19**, were loaded onto pellets of the inorganic oxide support, using the incipient wetness technique [12, 13]. Dichloromethane was used as the solvent in all the preparations to give supported samples having 5% cobalt loading.

Evaluation of the activity of supported **15**

Supported **15** (4 cm^3) was loaded into the reactor chamber and reduced under an atmosphere of hydrogen (H_2 SV = 15000 hr^{-1}) at 350°C for 16 hrs at a pressure of 3 Bar. The resulting material was sintered at elevated temperatures and tested for its CO hydrogenation activity. The reaction was performed at 220°C at a pressure of 10 Bar using a H_2/CO molar ratio of 2 and a GHSV of 2500 hr^{-1}. The hydrocarbon products were analysed by chromatography.

A comparative study of the catalytic activity, and olefin/paraffin ratios of supported **15**, *and* **16**

The activity of the two catalyst systems derived from supported **15** and **16** were evaluated under identical reaction conditions (19 Bar, 250°C, GHSV = 800 hr^{-1}) for their activity in the CO hydrogenation reaction. The olefin/paraffin ratios of the hydrocarbon products having chain lengths of 3 and greater were also determined.

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APPENDIX

POSITIONAL PARAMETERS FOR THE COMPLEX

$[\eta^6\text{-}C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$

Table of fractional atomic coordinates ($x10^4$) with e.s.d.'s in parentheses for [η^6-$C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$

Atom	x/a	y/b	z/c
Co	1357(1)	2918(0)	2737(0)
Cr	3023(1)	1114(1)	2115(1)
N(1)	128(4)	2820(3)	1679(3)
N(2)	-213(4)	2032(3)	3636(3)
N(3)	2620(4)	3000(3)	3793(3)
N(4)	2970(4)	3787(3)	1842(3)
C(1)	-1158(5)	2268(4)	2019(4)
C(2)	-1356(5)	1792(4)	3190(4)
C(3)	3867(5)	3582(4)	3471(4)
C(4)	4053(5)	4059(4)	2307(5)
O(11)	527(5)	3288(3)	633(2)
O(21)	-183(5)	1638(3)	4703(3)
O(31)	2267(4)	2483(3)	4849(2)
O(41)	2992(5)	4145(3)	758(3)
C(11)	-2255(8)	2107(7)	1282(6)
H(11)	-3122(8)	1681(7)	1694(6)
H(12)	-1675(8)	1684(7)	838(6)
H(13)	-2675(8)	2853(7)	840(6)
C(21)	-2667(7)	1080(5)	3810(6)
H(21)	-3384(7)	1008(5)	3326(6)

(continued...)

Table of fractional atomic coordinates ($x10^4$) with e.s.d.'s in parentheses for [η^6-$C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ (...continued)

Atom	x/a	y/b	z/c
H(22)	-3244(7)	1451(5)	4297(6)
H(23)	-2217(7)	321(5)	4205(6)
C(31)	4986(7)	3719(6)	4206(6)
H(31)	5821(7)	4181(6)	3794(6)
H(32)	5450(7)	2967(6)	4607(6)
H(33)	4410(7)	4096(6)	4689(6)
C(41)	5377(8)	4788(6)	1713(7)
H(41)	6044(8)	4882(6)	2215(7)
H(42)	4927(8)	5536(6)	1296(7)
H(43)	6008(8)	4412(6)	1247(7)
C(8)	2736(5)	1408(3)	2780(4)
H(81)	2880(5)	977(3)	3516(4)
H(82)	3757(5)	16073()	2406(4)
C(81)	2076(4)	650(3)	2296(3)
C(82)	1082(5)	-203(4)	2908(4)
H(82)	852(5)	-307(4)	3659(4)
C(83)	415(6)	-911(4)	2449(5)
H(83)	-271(6)	-1485(4)	2888(5)
C(84)	725(7)	-794(5)	1395(6)
H(84)	244(7)	-1271(5)	1085(6)
C(85)	1744(7)	19(5)	765(4)
H(85)	1991(7)	86(5)	23(4)

(continued...)

Table of fractional atomic coordinates ($x10^4$) with e.s.d.'s in parentheses for [η^6-$C_6H_5CH_2Co(DH)_2(py)]Cr(CO)_3$ (...continued)

Atom	x/a	y/b	z/c
C(86)	2420(6)	749(4)	1205(3)
H(86	3114(6)	1313(4)	760(3)
N(91)	31(4)	4413(3)	2791(3)
C(92)	-578(5)	4552(4)	3725(4)
H(92)	-377(5)	3926(4)	4370(4)
C(93)	-1466(6)	5531(4)	3813(4)
H(93)	-1860(6)	5594(4)	4503(4)
C(94)	-1790(6)	6429(4)	2895(5)
H(94)	-2427(6)	7124(4)	2933(5)
C(95)	-1186(6)	6311(4)	1930(4)
H(95)	-1393(6)	6923(4)	1277(4)
C(96)	-277(5)	5301(4)	1906(4)
H(96)	157(5)	5231(4)	1224(4)
H(3)	542(91)	1980(65)	4795(60)
H(4)	1835(89)	3738(58)	666(54)
C(51)	4919(9)	-933(5)	2513(8)
C(61)	4175(7)	-1808(5)	1200(5)
C(71)	3004(7)	-2566(5)	3100(4)
O(51)	6150(7)	-829(5)	2724(8)
O(61)	4886(7)	-2267(4)	618(4)
O(71)	2940(6)	-3484(4)	3687(4)