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HOMO- AND HETERO-DINUCLEAR COMPLEXES OF COBALT

by

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Submitted in partial fulfilment
of the requirement for the degree of
Doctor of Philosophy

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ABSTRACT

The work presented in this thesis concerns the synthesis and characterization of a series of novel phosphine-carbonyl complexes of cobalt. Chapters 2 and 3 outline mononuclear and homodinuclear cobalt complexes, chapters 4 and 5 discuss heterobimetallic complexes $[CoM(CO)_n(\mu\text{-dppm})_2]$ (M=Rh,n=3; M=Mn or Re,n=5), and finally chapters 6 and 7 discuss complexes containing the μ-PPh_2 group and the complex $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$, respectively.

Introduction of CO into Co(II)/phosphine/$NaBH_4$ reaction systems, previously shown to produce a number of interesting complexes, has provided a novel approach to the synthesis of phosphine-carbonyl complexes of cobalt. A number of complexes were isolated including the previously known $[CoH(CO)(PPh_3)_3]$ and also $[Co(CO)(PP)_2]^+$ (PP = dppm or dppe). In addition isomers of $\{Co(CO)_2(dppm)\}_2$, were prepared by this method. By introduction of $RhCl_3 \cdot (H_2O)_n$ into the reaction system, the heterobimetallic complex $[CoRh(CO)_3(\mu\text{-dppm})_2]$ was isolated. Complexes $[M(CO)(dppm)_2][Co(CO)_4]$, isolated for M = Co, and observed by ^{31}P and ^{13}C in the case of M = Rh, were observed to lose CO in the formation of complexes $[CoM(CO)_n(\mu\text{-dppm})_2]$ (M=Co,n=4; M=Rh,n=3). Similarly the $[Co(CO)(dppm)_2]^+$ cation reacted with other metal carbonyl anions $[M(CO)_5]^-$ (M=Mn or Re) to give the complexes $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})M(CO)_4]$ and $[CoM(CO)_5(\mu\text{-dppm})_2]$.

The fluxionality of $[CoM(CO)_n(\mu\text{-dppm})_2]$ (M=Co,n=4; M=Rh,n=3; M=Mn,n=5) and protonated derivatives $[Co_2(\mu\text{-}H)(CO)_4(\mu\text{-dppm})_2]^+$ and $[CoRh(\mu\text{-}H)(CO)_3(\mu\text{-dppm})_2]^+$ was investigated by variable temperature ^1H, ^{13}C and ^{31}P NMR and four types of fluxionality were observed.

The reactivity of complexes $[CoM(CO)_n(\mu\text{-dppm})_2]$ (M=Co,n=4; M=Rh,n=3) was investigated with a range of inorganic oxidizing agents and complexes $[CoM(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-dppm})_2(CO)_2]^{n+}$ (M=Co or Rh; X=Cl,n=1; X=Br,n=1; X=I,n=1; X=S,n=0) and $[CoRh(\mu\text{-}H)(CO)_n(\mu\text{-dppm})_2]^+$ (M=Co,n=4; M=Rh,n=3) were characterized. The reactivity of $[CoM(CO)_n(\mu\text{-dppm})_2]$ towards olefins was demonstrated to be limited.

Surprising results from the Co(II)/dppm/$NaBH_4$/CO reaction systems were the isolation of complexes $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-dppm})_n(CO)_{6-2n}]$ (n=1 or 2) and $[Ni_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2(CO)_2]^+$, resulting from the cleavage of a P-C bond in dppm under very mild conditions, and the isolation of $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$ containing the first structurally characterized simple metal-BH_2 linkage.

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KEY ABBREVIATIONS

Å = Angstrom
Anal. calc. = analysis calculated
COD = cyclooctadiene
Cp = cyclopentadiene
diars = 1,2-bis(dimethylarsino)benezene
depe = bis(diethylphosphino)ethane
depm = bis(diethylphosphino)methane
dmpe = bis(dimethylphosphino)ethane
dmpm = bis(dimethylphosphino)methane
dpam = bis(diphenylarsino)methane
dppb = bis(diphenylphosphino)butane
dppe = bis(diphenylphosphino)ethane
dppm = bis(diphenylphosphino)methane
dppp = bis(diphenylphosphino)propane
FAB = fast atom bombardment
EtOH = ethanol
$f_4$fars = $Me_2As(CF_2C=CCF_2)AsMe_2$
$f_4$fos = $Ph_2P(CF_2C=CCF_2)PPh_2$
HOAc = acetic acid
IR = infrared
ν = frequency
L = two electron donating ligand
L_3 = tridentate ligand
LL = bidentate ligand
M = metal centre
Me = methyl
MS = mass spectrum
NMR = nuclear magnetic resonance
δ = chemical shift
s = singlet
d = doublet
t = triplet
quart. = quartet
quint. = quintet
br = broad
J = coupling constant
OAc = acetate
Ph = phenyl
PP = bidentate phosphine
R = alkyl or aryl
TBP = trigonal bipyramid
THF = tetrahydrofuran
X = halogen

Chapter 1 : Introduction

This thesis concerns the synthesis, characterization and chemistry of a series of novel metal-phosphine-carbonyl complexes. The diagnostic use of ν(CO) from IR spectra and the diversity of types of carbonyl ligands found in the complexes synthesized in this work necessitates a brief discussion of modes of CO binding in metal complexes (sections 1.1, 1.1.1, 1.1.2, 1.1.2.1). Also ^{13}C NMR was used to assign structures to complexes with respect to carbonyl ligands and fluxionality was observed in a number of complexes. Thus a review of the scrambling processes of metal carbonyl clusters elucidated by ^{13}C NMR is included (section 1.1.3). The phenomenon of quadrupolar broadening in both the ^{31}P and ^{13}C NMR of complexes containing cobalt is evident and was useful in assigning ^{13}C and ^{31}P resonances where both quadrupolar and non-quadrupolar nuclei are present. The phenomenon of "thermal decoupling" is discussed (section 1.1.3.1).

The unique synthetic methods employed to prepare many of the complexes described in this thesis prompts a discussion of conventional methods of synthesis of phosphine-carbonyl complexes of transition metals; namely phosphine substitution of metal carbonyls (section 1.1.4). The chemistry of a series of complexes $[CoM(CO)_n(\mu\text{-dppm})_2]$ (M=Co,n=4; M=Rh,n=3; M=Mn,n=5) is reported in this thesis. To place this work in context, the chemistry observed for related $M_2(\mu\text{-dppm})_2$ and $MM^1(\mu\text{-dppm})_2$ complexes is also discussed (sections 1.1.5 and 1.1.6.1).

1.1. M-CO bonding in metal carbonyls

As well as being able to stabilize metals in low oxidation states, carbon monoxide is also a versatile ligand which can coordinate terminally or can bridge two or more metals in a variety of ways (Figure 1.1). In terminal carbonyl complexes, two components to the bonding are present. A metal-carbon σ bond is formed by the interaction of the 5σ electrons of CO with an empty d orbital of the metal[1]. This raises the CO bond order slightly as the 5σ orbital is slightly antibonding in nature. CO can also π bond to a metal by overlap of a filled d metal orbital with the $2p\pi^*$ orbital on CO. The net effect of this type of synergistic bonding is a drift of electrons from the metal to antibonding orbitals of CO resulting in a reduced C-O bond order. The net effect is a reduction of CO bond strength in most complexes.

1.1.1. IR spectroscopy and C-O bond order

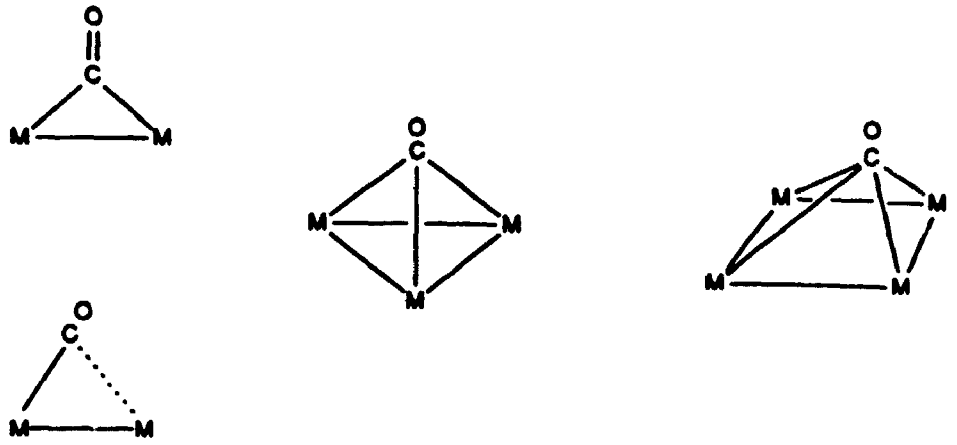
Vibrational spectroscopy, particularly infrared, is useful in determining the electronic nature of the M-CO interaction as the IR absorption frequency of the carbonyl group, $\nu(CO)$, is a measure of the C-O force constant or bond order. Thus most terminal complexes have a $\nu(CO)_{max}$ in the 1900 to 2100 cm^{-1} region, below $\nu(CO)$ for free CO at 2155 cm^{-1} [1]. If the metal is in a high oxidation state or there

Figure 1.1: Modes of bonding of CO in metal-carbonyl complexes

terminal CO $M-C\equiv O$

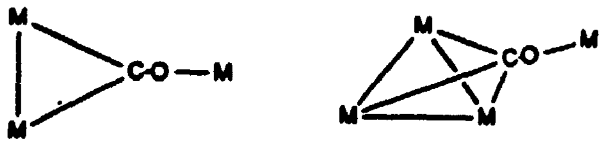
bridging CO

i. u-CO



ii. π-CO

iii. Σ-CO $M-C\equiv O-M$



are electron withdrawing groups on the metal, the back donation of electrons from the metal to the carbonyl group is minimized and the ν(CO) approaches or exceeds that of free CO. For example, $[PbF_2(CO)]$ has been isolated in an argon matrix and has ν(CO) at around 2175 cm^{-1}. At the other extreme, where the metal is in a low oxidation state and contains good σ-donors/poor π-acceptors, the ν(CO) can be found in a region associated with bridging carbonyl. For example, the terminal carbonyls in the complexes $[(C_4H_4)Fe(dppe)(CO)]$ and $[(dien)Mo(CO)_3]$ have IR absorptions at 1880 cm^{-1} for the former and 1883 and 1723 cm^{-1} for the latter. When CO bridges, it receives electron density into an antibonding orbital from more than one metal centre and hence the the C-O bond order is reduced relative to that in a terminal CO complex. This results in a value of ν(CO) between 1600 and 1900 cm^{-1}. It is apparent from the iron and molybdenum examples given above that a signal below 1900 cm^{-1} cannot always be interpreted as being due to a μ-CO. If, however, two sets of well separated signals appear in the regions designated above then it is likely that both modes of CO coordination are present[2].

Several studies have been conducted to determine the effect of the metal oxidation state, degree of substitution, and the nature of the substituents on the ν(CO) in mononuclear complexes. For example, the IR spectra of two series of isoelectronic metal carbonyl complexes; $[V(CO)_6]^-$, $[W(CO)_6]$, $[Re(CO)_6]^+$, and $[Fe(CO)_4]^{2-}$, $[Co(CO)_4]^-$ and

$[Ni(CO)_4]$ were compared and it was found that, in both series, the $\nu(CO)_{max}$ of the complexes shifts to a higher frequency as the oxidation state of the metal increases[2,3]. This is expected for an increase in CO bond order corresponding to decreasing electron density on the metal available for backbonding to the $2p\pi^*$ orbital on CO.

1.1.2. Bridging CO groups

Three types of bridging carbonyl have been distinguished and designated as μ-CO, π-CO, and Σ-CO[4] (Figure 1.1). X-ray diffraction, more so than IR spectroscopy, has allowed for the distinction between the bridging modes. The μ-CO complexes which contain metal-CO bonding strictly through the carbon atom, are the most common and there is much diversity among them. The asymmetric bridges are often referred to as semibridging. These systems, including those bonded through the oxygen as well as the carbon, will be discussed in some detail in a later section. $[Rh_6(CO)_{16}]$, which contains four triply bridging carbonyls on alternate faces of the metal octahedron, provided the first example of a μ_3-CO ligand[3]. In the complex $[Fe_4(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)_4]$, there are also four face bridging carbonyl ligands. Complex $[Mo_2Ru_5(CO)_{14}(\mu_4\text{-}CO)_2Cp_2(\mu_4\text{-}S)]$, structurally characterized by X-ray diffraction, provides the first example of a quadruply bridging carbonyl ligand[5].

There are also a number of possibilities for the interaction of a metal and the C-O bond in a π-CO complex[4,6]. Direct side-on coordination of the C≡O unit has not yet been identified but a bridging CO containing a linear M-C-O array suggestive of a π-CO bridge has been identified in $[Mn_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$[7]. When counting electrons, it is apparent that in order to achieve the desired 18 electron count on each metal an additional two electrons must be accounted for and these are presumably taken from the C-O triple bond, as suggested by the geometry of the C-O unit. Thus a bridging π-CO ligand acts as a four electron donor. Another possibility for four electron donation exists in a trimeric system where the CO bridges two metal atoms symmetrically and the whole bridge is bent toward a third metal so that a metal π-CO interaction can occur[4].

A few types of Σ-CO bonding have been proposed where an interaction occurs between a basic oxygen of a carbonyl group and a Lewis acid[4]. They are generally referred to as iso-carbonyls. An example is provided by the 1:1 adduct of $[Ni_2(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$ with AlR_3 in which the AlR_3 unit binds to the μ-CO group[8]. There is a significant shift of the bridging CO signal in the IR spectrum to a lower frequency accompanying the coordination to the Lewis acid. The basicity of the oxygen atom increases as the carbonyl goes from terminal to bridging to triply bridging which reflects the tendency of these species to complex with Lewis acids to form Σ-CO complexes.

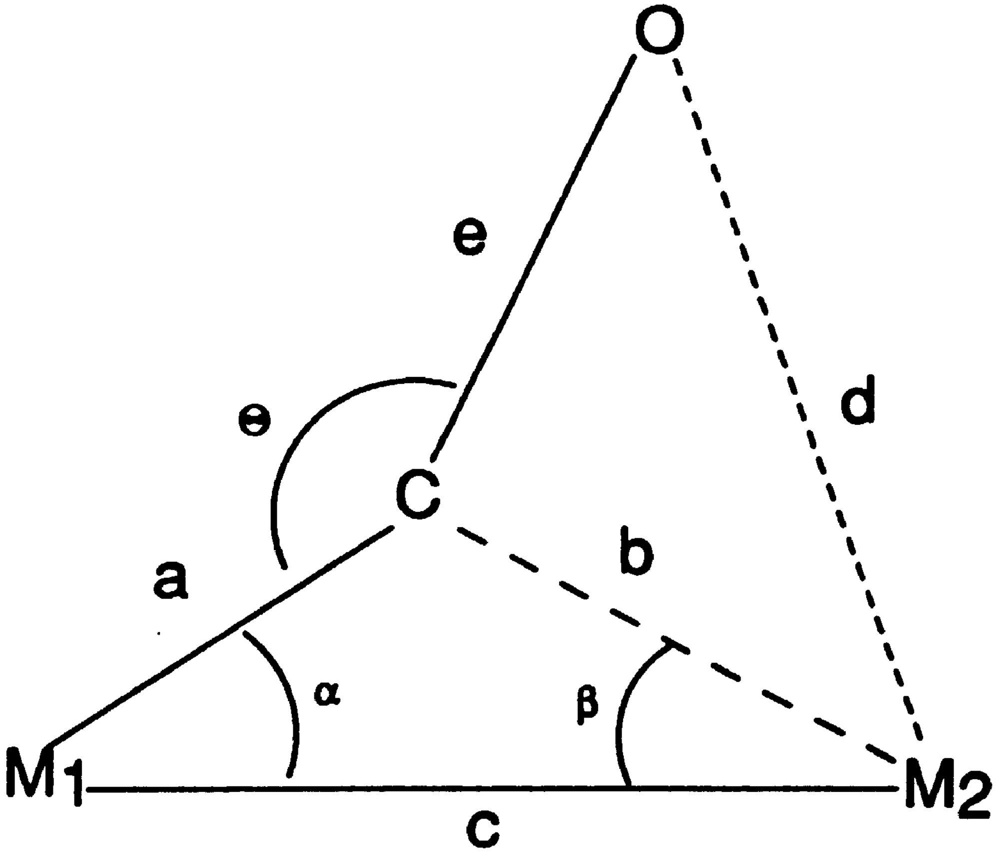
1.1.2.1. Semibridging carbonyls

The term "semibridging carbonyl" denotes an unsymmetrical carbonyl brid with different M-CO lengths, a and b, and M-C-O angles, α and β (Figure 1.2)[9]. There is also a distinction made between bent and linear bridging carbonyls. Cotton and Wilkinson[6] recognize three sets of circumstances under which the asymmetric bridges form. One explanation for the formation of a semibridged carbonyl is that it may be a way for a complex to "fine tune" delocalization of negative charge.

A review by Crabtree and Lavin[9] states "semibridging CO groups can be thought of as a structural continuum that leads from terminal to symmetrical arrangements". A model (Figure 1.2) labelled with appropriate M-C and C-O bond lengths and bond angles was used to explore this concept by compiling these data for a large number of structurally characterized complexes. From a correlation of these data a reaction trajectory for the terminal-bridge-terminal carbonyl exchange was constructed (Figure 1.3). There are many examples where a low energy fluxional process involving CO exchange has been established in carbonyl complexes in both solution and the solid state (section 1.1.3).

They found several examples of μ-CO ligands which do not fit into the continuum of terminal-bridging CO exchange in that they contain a linear M-C-O bridge. By plotting θ vs α, a vs α and b vs α, Crabtree and Lavin were able to distinguish three types of linear semibridged species from

Figure 1.2: Model for a semibridging carbonyl ligand



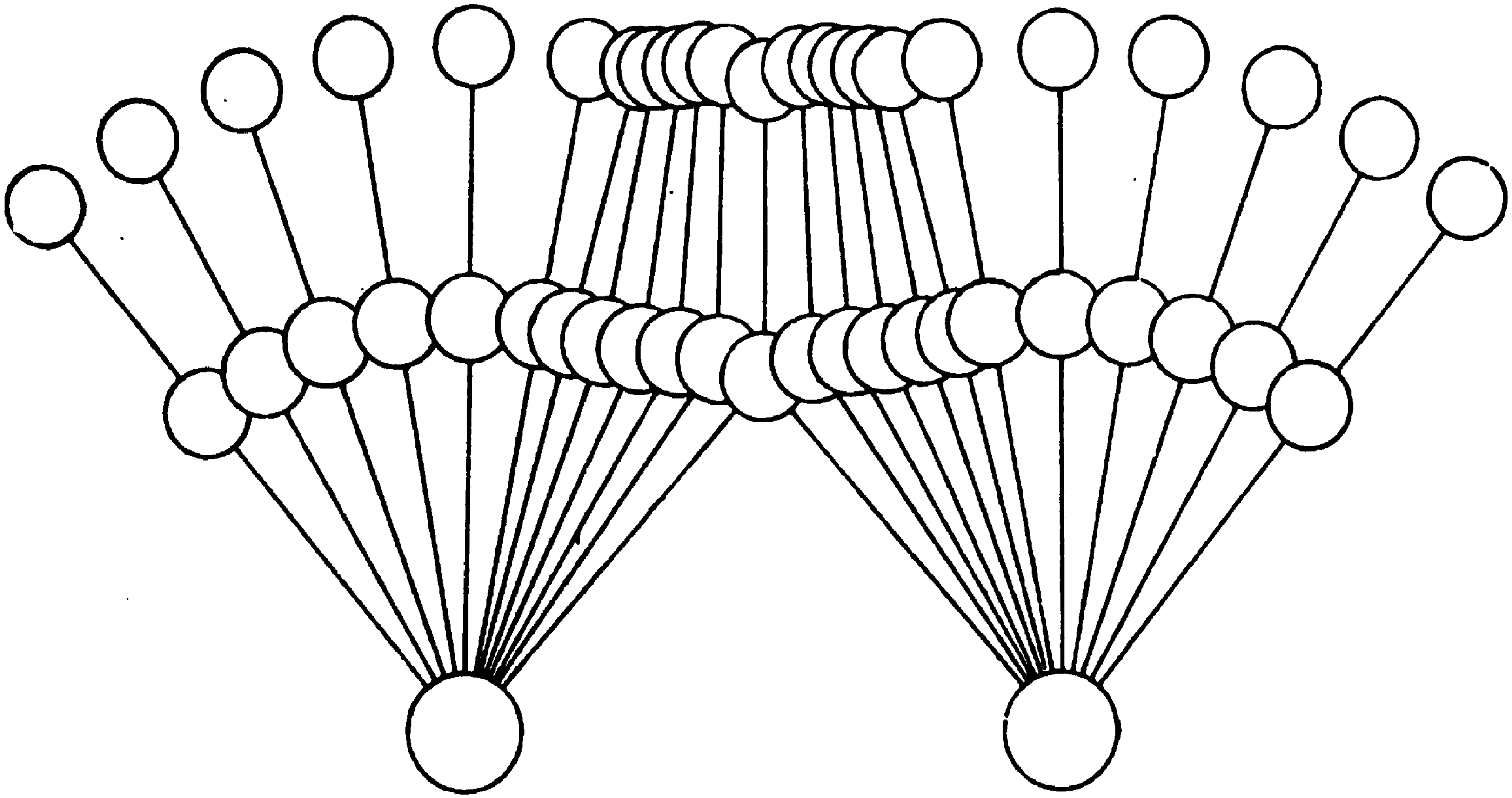


Figure 1.3: Reaction trajectory for terminal-bridge-terminal carbonyl exchange

the three distinct clusters of data points found around certain values of a, θ, and ●. Each cluster was represented by a specific combination of metals M(1) and M(2) from different parts of the periodic table. One example, $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, emerged from this study that did not conform to any of these three types. This exception was rationalized by the presence of a four electron donating linear carbonyl bridge.

1.1.3. Scrambling of CO ligands in metal-carbonyl clusters

The mobility of CO in polynuclear metal complexes is well known and is likened to movement of adsorbed CO on metal surfaces which is not readily studied by direct experimentation. Fortunately the advent of routine dynamic ^{13}C NMR techniques has allowed for the investigation of CO scrambling in clusters with sophisticated pulse sequences and computer aided line shape analysis. In this way four different scrambling processes have been distinguished[10,11].

a. Localized exchange, of which there are two types, refers to exchange of carbonyl ligands on a single metal atom. Turnstile rotation is observed in $[M_3(\mu\text{-}X)(\mu\text{-}Y)(CO)_{10}]$ (M=Os,X=H,Y=H,CR or NO; M=Ru,X=halide,Y=H) complexes[10] at $M(CO)_3$ sites and at the two different $M(CO)_3$ sets within the $M(CO)_4$ group. The net result is exchange of axial/equatorial sites. Alternatively pairwise exchange can occur between two carbonyl ligands. The distinction between turnstile rotation and pairwise exchange is retention of the configuration at the metal in the latter process.

b. Delocalized exchange refers to the scrambling of CO ligands between two or more metals and two types are distinguishable. A polytopal rearrangement mechanism was deduced for the fluxionality of $[Fe_3(CO)_{12}]$ in the solid state[12] by "magic angle spinning" solid state ^{13}C nmr spectroscopy. The 12 carbonyls can be thought of as occupying vertices of a distorted icosahedron surrounding the Fe_3 triangle and rotation of the Fe_3 triangle in e the polyhedron makes all the carbonyls equivalent. Conversely discrete delocalized exchange occurs between the tautomers of $[Ir_4(CO)_{11}(\mu\text{-}SO_2)]$[10] which represents the other type of delocalized exchange.

c. The third type of fluxionality involves the oscillation of an asymmetric bridge. An example is provided by $[Mn_2(CO)_5(dppm)_2]$[13] which contains a $\mu\text{-}\eta^2\text{-}CO$ four electron donating ligand. In addition to $\mu\text{-}\eta^2\text{-}CO$ ligands, asymmetric RNC, CN^-, and C_2R^- bridges have been found to oscillate readily between two metals when this is a degenerate process.

d. The final type of CO scrambling mechanism distinguished by ^{13}C NMR involves rotation of an entire $M(CO)_n$ moiety. For example, in $[Os_3Pt(\mu\text{-}H)_3(CO)_{10}(PCy_3)]^+$ the $Pt(CO)PCy_3$ function was found to rotate above the Os_3 triangle[14]. In $[Re_3(CO)_{10}H_3]^{2-}$ four separate processes were found to occur[11]. One of these was the rotation of the $ReH(CO)_4$ unit about the axis perpendicular to and bisecting the $[(CO)_3Re(\mu\text{-}H)_2Re(CO)_3]^{2-}$ unit. The dimer anion is isolobal with an acetylenic unit and this motion is reminiscent of acetylene rotation in a side-on η^2-RC≡CR complex.

1.1.3.1 Thermal decoupling

Several transition metals possess quadrupolar moments and there is an associated problem with the evaluation of the ^{13}C NMR of their carbonyl complexes[15]. For example, the elements $^{55}Mn(I=5/2)$, $^{59}Co(I=7/2)$, $^{155}Re(I=5/2)$ and $^{191}Ir(I=3/2)$ are all of nearly 100% natural abundance. As a result of this property, quadrupolar coupling between the metal and ^{13}C nuclei can cause significant broadening of the ^{13}C resonance. Fortunately, a solution to this problem is provided using a technique known as "thermal decoupling" which simply involves running the spectra at low temperatures. The reason for low temperature sharpening as a result of this thermal decoupling phenomenon is evident from the expression for the nuclear spin-lattice relaxation time $_MT_1$ of a metal M (equation 1.1), where I is the spin number, eq is the electric field gradient, eQ is the electric quadrupole moment and τ_c is the molecular correlation time [16].

$$_MT_1^{-1} = 3(2I+3)(e^2Qq)\tau_c/40I_2(2I-1)h \qquad (1.1)$$

When the quadrupole induced relaxation of M, R_q, is sufficiently low due to a low electric field gradient or due to rapid molecular tumbling, a well resolved multiplet due to M-^{13}C coupling can be observed. A low electric field gradient is the result of high molecular symmetry. For example, in the ^{13}C NMR spectrum of $[Co(CO)_4]^-$, which has tetrahedral symmetry, the coupling is evident as an eight line multiplet with a ^{59}Co-^{13}C coupling of 287 Hz[17]. Conversely, if the electric field gradient is sufficiently high and/or the molecular tumbling rate is low, a sharp singlet is observed. Frequently the situation lies somewhere between the two extremes just discussed and a broad resonance appears which can be confused with broadening due to stereochemical non-rigidity. For a given molecule, the electric field gradient is more or less constant. However, the τ_c value can be altered by decreasing temperature and increasing solvent viscosity, each of which cause a decrease in the rate of molecular tumbling. This technique is known as thermal decoupling.

The effects of quadrupolar broadening have also been noted in the ^{31}P NMR spectra of cobalt-phosphine complexes such as $[(\mu_3\text{-}CCH_3)Co_3(CO)_9\{\eta^1\text{-}PPh_2CH_2P(O)Ph_2\}]$[18].

1.2 Synthesis of metal-phosphine-carbonyls

The most common method of synthesizing metal-phosphine-carbonyl complexes has been the substitution of CO ligands in binary carbonyls by phosphines, particularly with complexes of Group VIIIb metals. There is a large number of binary carbonyl compounds of the transition elements representing a wide range of structural types and nuclearities. The significance of this type of compound to inorganic and organometallic chemistry and to the understanding of bonding in atomic clusters is well recognized as reflected by the large number of reviews published annually concerning this chemistry[19].

The substitution of carbonyl complexes by phosphines is also the subject of many comprehensive reviews[20] and the discussion of this chemistry will be brief and will focus on recent and interesting examples from each metal triad and syntheses of phosphine bridged metal carbonyl dimers. In addition to substitution of binary carbonyls, other methods of synthesis of metal-phosphine-carbonyl complexes are included at the end of each section.

1.2.1 Group IVb

While there are no binary carbonyl complexes of the Group IV metals some metal-phosphine-carbonyl derivatives have been synthesized. For example, $[TiCl_4(THF)_2]$ reduced by sodium naphthalenide in the presence of $Me_2PCH_2CH_2PMe_2$ (dmpe) followed by carbonylation produces $[Ti(CO)_3(dmpe)_2]$ in a high yield[21]. Further carbonylation occurs to provide $[Ti(CO)_5(dmpe)]$, a bis substituted derivative of the hypothetical binary carbonyl $[Ti(CO)_7]$.

1.2.2 Group Vb

The anionic carbonyls $[M(CO)_6]^-$ (M=V,Nb,Ta) and derivatives, are well known and have been used to synthesize phosphine complexes. For example, the compound $NEt_4[V(CO)_5(\eta^1\text{-dppm})]$ is prepared by the reaction of $[V(CO)_5NH_3]^-$ with an equivalent of ligand[22]. The only neutral carbonyl from this family is the paramagnetic $[V(CO)_6]$. Derivatives of this unusual species have not been prepared by direct substitution but the complexes cis-$[V(CO)_4PP]$ (PP=dppm,dppe,dppp,dppb), $[V(CO)_5PPh_3]$ and $[\{V(CO)_5\}_2\{\mu\text{-p-}C_6H_4(PPh_2)_2\}]$ were prepared by the oxidation of the corresponding anionic complexes with tropylium tetrafluoroborate[23].

1.2.3 Group VIb

Thermally induced substitution of two carbonyl ligands in $[M(CO)_6]$ complexes yields $[M(CO)_4(PP^1])$ where PP^1 is a chelating unsymmetrical bis-phosphine[24]. Complexes of the type $[M_2(\mu\text{-PP})_n(CO)_{8-2n}]$ are produced from the treatment of the corresponding carbonyl with a bidentate phosphine. For example, at elevated temperatures such complexes with $M{=}Cr,Mo;n{=}2;PP{=}trans\text{-}Ph_2PCH{=}CHPPh_2$[25] and $M{=}Cr,Mo,W;n{=}2;(PP)_2{=}eHTP$[26] $\{eHPT{=}(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2\}$ are produced. The ambient temperature TMNO induced decarbonylation of $[Mo(CO)_6]$ followed by addition of dppm or dppe produces the n=1 derivative[27].

1.2.4 Group VIIb

Binary carbonyls, $[M_2(CO)_{10}]$ are known for all three metals, manganese, technetium and rhenium, of Group VIIb and in the case of manganese and rhenium the complexes have been used to prepare metal-phosphine-carbonyl complexes[28]. Few derivatives of $[Tc_2(CO)_{10}]$ are known due to the radioactivity of technetium.

$[Mn_2(CO)_{10}]$ reacts with tertiary phosphines PR_3 to give complexes $[Mn_2(CO)_{10-n}(PR_3)_n]$ (n=1 or 2)[28]. Further substitution generally leads to paramagnetic mononuclear complexes $[Mn(CO)_3(PR_3)_2]$; or in the case of $P(OCH_2)_3CEt$, the complexes $[Mn_2(CO)_{10-n}(L)_n]$ (n=3 or 4) have been isolated[28]. In general, $[Re_2(CO)_{10}]$ reacts with monodentate phosphines to give complexes of the type $[Re_2(CO)_{10-n}(PR_3)_n]$[28].

$[Mn_2(CO)_{10}]$ reacts with bidentate phosphines and arsines to give complexes $[Mn_2(CO)_{10-2n}(\mu\text{-}LL)_n]$. Complexes with n=1 are known for dppm, dppe, dpam and diars[28]. Complexes with n=2 include the dppm, dppe, dpam, diars[28], depe[29] and dmpm[30] derivatives. With dppe, in addition to the dimers described above, a mononuclear complex [Mn(CO)$_3$(dppe)] was isolated[28]. An equivalent of CO can be expelled from the dppe, dppm[28] and depm[31] complexes $[Mn_2(CO)_6(PP)_2]$ to give $[Mn_2(CO)_5(\mu\text{-}PP)_2]$ which contain a four electron donating $\mu\text{-}\eta^2\text{-}CO$ ligand.

Alternative methods to substitution of the binary carbonyl have been used to prepare phosphine bridged rhenium dimers. An exception is provided from the reaction of

$[Re_2(CO)_{10}]$ with dmpm in refluxing xylene to give $[Re_2(CO)_6(\mu\text{-dmpm})_2]^{32}$. Reductive elimination of $CH_2CHC_4H_9$ from $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-CH=CHC}_4H_9)]$ in the presence of phosphines PP (PP= dmpm, dppm, dppe, dmpe) provides complexes $[Re_2(CO)_8(\mu\text{-PP})]^{33}$. Thermal or photochemical substitution of two carbonyls from complexes $[Re_2(CO)_8(\mu\text{-PP})]$ by dppm or dmpm gives $[Re_2(CO)_6(\mu\text{-PP})(\mu\text{-P}^1P^1)]^{34}$. Carbonylation of $[Re_2(\mu\text{-dppm})Cl_4]$, which contains a rhenium-rhenium triple bond, provides $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_3(CO)]^{35}$ and in the presence of H_2, gives $[Re_2(\mu\text{-H})(\mu\text{-Cl})(\mu\text{-dppm})_2(CO)_2Cl_2]^{36}$. In a multistep reaction $[Re_2(\mu\text{-X})_2(\mu\text{-dppm})_2(CO)_4]$ (X=Cl,Br) is produced by refluxing $[ReX(CO)_5]$ in the presence of dppm[28].

Reaction of $[Mn_2(CO)_{10}]$ with tridentate phosphines $MeC(CH_2PPh_2)_3$ or $C(CH_2PPh_2)_4$ leads to a disproportionation and $[Mn(CO)_3(L_3)]^+[Mn(CO)_5]^-$ complexes are formed[28].

1.2.5 Group VIIIb

1.2.5.1 Iron Triad

Binary carbonyl compounds of the iron family can be formulated as $[M(CO)_5]$, $[M_2(CO)_9]$ and $[M_3(CO)_{12}]$ (M=Fe,Ru,Os)[28]. Higher nuclearity clusters of osmium such as $[Os_5(CO)_n]$ (n=16 or 19), $[Os_6(CO)_n]$ (n=18 or 20), $[Os_7(CO)_{21}]$ and $[Os_8(CO)_{24}]$ are also known[37,38]. An oligomeric complex of formula $[Ru(CO)_4]_n$ has been identified but its structure is unknown[28].

An enormous number of phosphine and arsine substituted carbonyl complexes of iron and ruthenium and to a lesser extent osmium have been prepared by substitution of the corresponding binary carbonyls[28]. Substituted derivatives of $[Fe(CO)_5]$ are generally obtained under thermal or photochemical conditions that promote CO dissociation and both mono and disubstituted products are obtained. It is usually found that substitution occurs at axial positions first and that disubstitution gives trans diaxial species. Bidentate ligands which form four membered chelate rings with metals, cannot span the axial sites to provide the trans species and instead substitution occurs at both axial and equatorial sites to give $[Fe(CO)_{5-2n}(L-L)_n]$ type complexes as in $[Fe(CO)(dmpm)_2]$[39].

The reaction of $[Ru(CO)_5]$ and $[Os(CO)_5]$ with phosphines proceeds with formation of primarily monosubstituted products and mixtures of $[Os(CO)_{5-n}(PR_3)_n]$ respectively[28]. Reaction of $[Ru(CO)_5]$ with bidentate ligands has led to disubstitution but harsh conditions are required. An exception to this limitation on the degree of substitution of complexes $[M(CO)_5]$ is provided with PF_3 with which complexes $[M(CO)_{5-n}(PF_3)_n]$ (n=1-5) (M=Fe or Ru) have been isolated[28].

The number of substituted di- and trinuclear complexes derived from $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ respectively is small due to the tendency of the clusters to fragment during the reaction with phosphines. For example, The reaction of $[Fe_2(CO)_9]$ with trialkyl phosphines in nonpolar solvents leads to products of the type $[Fe(CO)_{5-n}(PR_3)_n]$ (n=0,1,2)[28]. The dinuclear frame is retained in complexes of the type $[Fe_2(CO)_{9-2n}(L-L)_n]$ and $[Fe_2(CO)_{10-2n}(L-L)_n]$. The $[Fe_2(\mu-CO)(CO)_{8-2n}(L-L)_n]$ complexes contain a metal-metal bond and are essentially derivatives of the $[Fe_2(CO)_9]$ dimer. The structures of $[Fe_2(CO)_6(\mu-PP)_2]$ **(a)** and $[Fe_2(CO)_4(\mu-CO)(\mu-PP)_2]$ **(b)** {PP= $CH_3N(PF_2)_2$}, prepared by the reaction of PP with $[Fe_3(CO)_{12}]$ and subsequent loss of CO from $[Fe_2(CO)_6(\mu-PP)_2]$, respectively have been determined[40]. The geometry about each metal atom in **(a)** is distorted square based pyramidal while in **(b)** the geometry about each iron is approximately trigonal bipyramidal with the phosphorus atoms of the bridging ligands occupying the axial sites. $[Fe_2(CO)_{10-2n}(\mu-LL)_n]$ complexes contain no metal-metal bond and can be considered as two substituted $Fe(CO)_5$ units joined by bridging ligand(s).

The chemistry of $[Ru_2(CO)_9]$ and $[Os_2(CO)_9]$ towards phosphine substitution has not been as well explored as that of the iron dimer, but some reactions of the osmium dimer have been documented[28]. $[Os_2(CO)_9]$ reacts with ER_3 (E=P or As), for example, to give the monosubstituted product $[Os(CO)_4L]$.

Treatment of $[Fe_3(CO)_{12}]$ with dppm results in the formation of complexes $[Fe(CO)_4(\eta^1\text{-dppm})]$, $[Fe_2(\mu-CO)(CO)_6(\mu\text{-dppm})]$ and $[Fe_2(\mu-CO)(CO)_4(\mu\text{-dppm})_2]$[41].

$[Ru_3(CO)_{12}]$ tends to fragment upon reaction with phosphines but not to the same extent as the iron trimer[28].

Reaction with PR_3 ligands provides $[Ru_3(CO)_{12-n}(PR_3)_n]$ under various conditions. Fragmentation occurs in some cases to give $[Ru(CO)_{5-n}L_n]$ (n=1 or 2) species. Treatment of $[Ru_3(CO)_{12}]$ with bidentate phosphines leads to the formation of $[Ru_3(CO)_{10-2n}(L\text{-}L)_n]$, $[Ru_3(CO)_{11}]_2(\mu\text{-}L\text{-}L)]$, $[Ru_2(CO)_7(L\text{-}L)]$ and $[Ru(CO)_3(L\text{-}L)]$ complexes depending on the phosphine and the reaction conditions. $[Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})]$[41] and $[Ru_3(CO)_{11}(\eta^1\text{-dppe})]$ have also been made in this way.

Reactions of ligands with $[Os_3(CO)_{12}]$ is not a good route to mononuclear complexes, in contrast to the iron and ruthenium analogues, due to the high Os-Os bond strength[28]. $[Os_3(CO)_{12-n}L_n]$ (n=1-3) have been prepared with higher degrees of substitution observed for some bidentate phosphines. Reactions with bis-phosphines resemble those of $[Ru_3(CO)_{12}]$ as $[Os_3(CO)_{12-2n}(L\text{-}L)_n]$ (n=1-3) and $[Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})]$[41] have been made.

1.2.5.2. Cobalt Triad

Binary carbonyls of the cobalt family can be generalized as $[M_2(CO)_8]$, $[M_4(CO)_{12}]$ and $[M_6(CO)_{16}]$ (M=Co,Rh,Ir)[42]. Differences in the stability of the compounds for each metal are observed. For example, the $[M_2(CO)_8]$ complexes decompose with the loss of CO to give the tetranuclear carbonyls with the rate of decomposition increasing in the order Co<<Rh<Ir. $[Rh_2(CO)_8]$, which has the same solid state structure, $[M_2(\mu\text{-}CO)_2(CO)_6]$, as the cobalt analogue and the corresponding iridium complex has only been prepared at very low

temperatures in a CO matrix.

Generally, reactions of [$Co_2(CO)_8$] with tertiary phosphines and arsines lead to substituted products of the type [$Co(CO)_{5-n}L_n$][$Co(CO)_4$] or [$Co_2(CO)_{8-n}L_n$] depending on the reaction conditions[42]. Disproportionation to provide the ionic complexes is generally promoted by polar solvents while nonpolar solvents or polar solvents at high temperature facilitate substitution with retention of the dinuclear unit.

The structures of the cations [$Co(CO)_{5-n}(L)_n$]$^+$, in the disproportionation products are based on a five coordinate TBP diamagnetic Co(I) atom. The arrangements of the carbonyl and phosphine ligands are dependent on n and the nature of the phosphine or arsine.

[$Co_2(CO)_8$] also reacts with many bidentate phosphines L-L and species of the type [$Co(CO)_3(LL)$][$Co(CO)_4$] and [$Co_2(CO)_4(LL)_3$][$Co(CO)_4$]$_2$ are generally formed[42]. The dicationic complex $[(CO)_2(\eta^2\text{-PP})Co(\mu\text{-PP})Co(\eta^2\text{-PP})(CO)_2]^{2+}$ has an unusual non metal-metal bonded structure with two $[(CO)_2Co(\eta^2\text{-LL})]^+$ units bridged by a diphosphine.

Under certain circumstances the metal-metal bonded dinuclear structure is retained upon substitution of CO ligands in [$Co_2(CO)_8$] by bidentate phosphines and complexes of the type [$Co_2(CO)_{8-2n}(L\text{-}L)_n$] (n=1,2,3) have been identified. If the bridged structure of [$Co_2(CO)_8$] is considered as a template for these substitutions then several possibilities exist for the coordination of a single

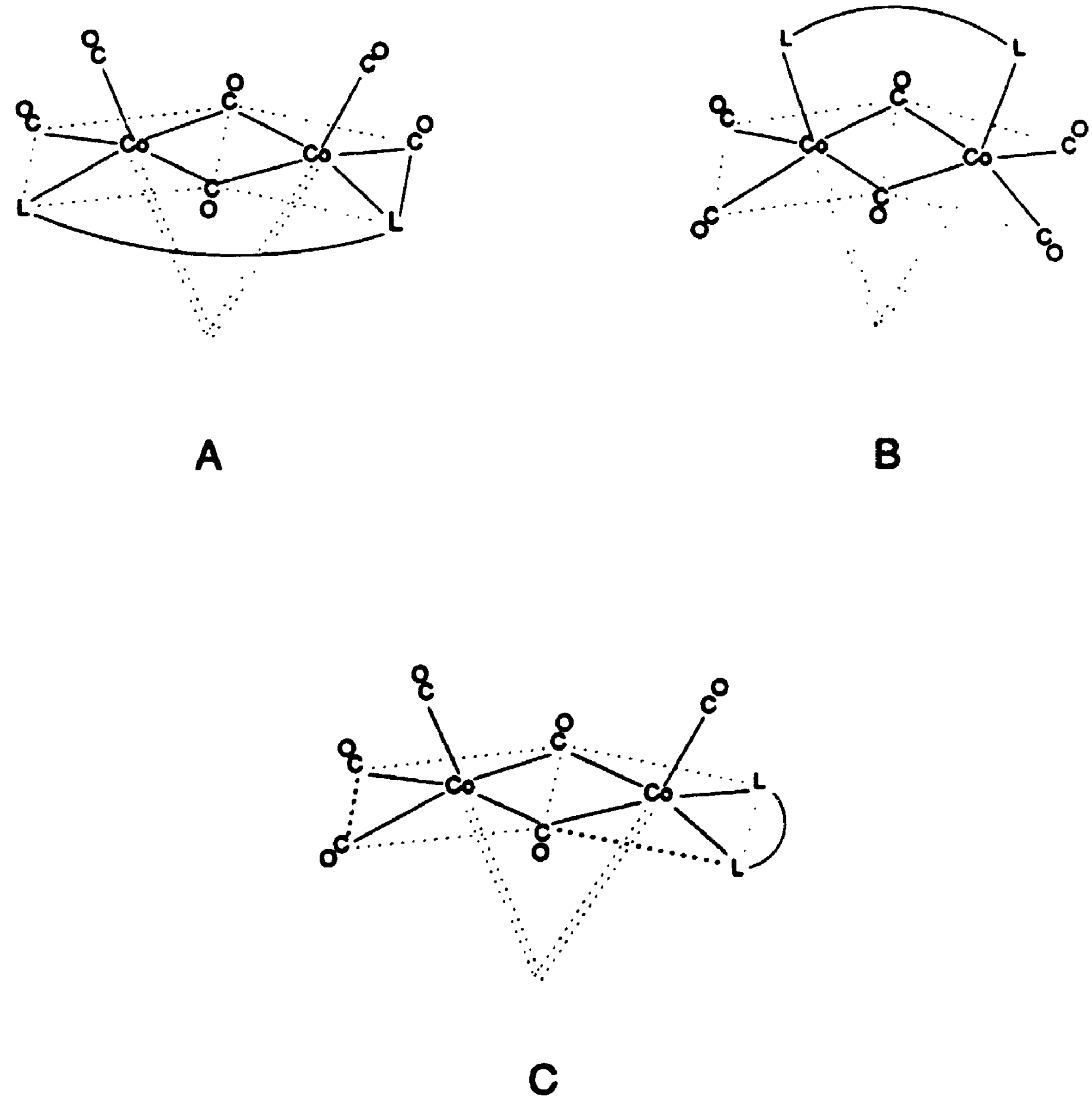
L-L ligand in these complexes as illustrated in Figure 1.4[43]. Other structural types are possible as reflected by the existence of two other non bridged isomers of $[Co_2(CO)_8]$. The complex with L-L=$f_4$fars and n=1 has been structurally characterized and contains the framework given in **c**[43]. The solid state structure of $[Co_2(CO)_6(\mu\text{-}Ph_2PNHPPh_2)]$ on the other hand has been determined to be of type **b**[44]. The dppe complex of the same formula has a structure determined by X-ray diffraction to most closely resemble **a** [44]. Complexes with L-L=diars, dmpa,dmph and dmpo have also been assigned a structure of type **a**[45].

Complexes of the type $[Co_2(CO)_4(LL)_2]$ have been obtained in one case by the further substitution of carbonyl ligands in $[Co_2(CO)_6(L\text{-}L)]$ complexes where L-L=dppe,(p-tolyl)$_2$(CH$_2$)$_2$(p-tolyl)$_2$[46]or $f_4$fos[43]. These complexes have been assigned an **a** type structure with two chelating ligands. The synthesis of three isomers of formula $[Co(CO)_2(dppm)]_2$ from the reaction of $[Co(CO)_4]^-$ with thallium(I) compounds has been reported[47]. However no structural assignments were made and the complexes were characterized solely on the basis of elemental analysis.

Solutions of $[Co_2(CO)_8]$ and $MeN(PF_2)_2$ irradiated with U.V. light lead to substitution of six or all eight carbonyl ligands and isolation of $[Co_2[\mu\text{-}MeN(PF_2)_2]_3(CO)_2]$ and $[Co_2(PF_2MeNH)_2\{\mu\text{-}MeN(PF_2)_2\}_3]$ respectively[48].

Bis(diphenylphosphino)maleic anhydride, reacts with $[Co_2(CO)_8]$ to give a very unusual paramagnetic 19 electron

Figure 1.4: Possible structures of complexes [$Co_2(CO)_6(LL)$]



monomeric Co(0) species[49]. The structure of the $[Co(CO)_3(LL)]$ species resembles a square base pyramid with the phosphine chelating in the square base. The odd electron is thought to be delocalized in the conjugated π system on the ligand and it can be considered a Co(I) system with an anionic ligand with an unpaired electron.

$[M_4(CO)_{12}]$ complexes are much more stable to fragmentation than $[Co_2(CO)_8]$ and the nuclearity of the cluster is usually retained upon substitution with phosphines[42]. Reaction of these complexes with phosphines and arsines normally provides complexes of the type $[M_4(CO)_{12-n}L_n]$. In some cases, however fragmentation can occur giving substituted dinuclear species. For example, in n-heptane $[Co_4(CO)_{12}]$ reacts with PPh_3 to give $[Co_4(CO)_8(PPh_3)_4]$ but in dichloroethane $[Co_2(CO)_6(PPh_3)_2]$ is formed[50]. Also, $[CoRh(CO)_5(PEt_3)_2]$ is isolated as the main product from the reaction between $[Co_2Rh_2(CO)_{12}]$ and the phosphine although tetranuclear substituted products were suspected as intermediates[51].

Treatment of $[Rh_4(CO)_{12}]$ with phosphines under CO pressure produces unstable $[Rh_2(CO)_6L_2]$ dimers which readily lose CO to give tetranuclear species[42]. Direct substitution occurs on $[Rh_4(CO)_{12}]$ by monodentate phosphines and the degree of substitution is enhanced by the decreasing basicity of the phosphine.

Substitution by bidentate ligands generally occurs without cluster fragmentation. $[M_4(CO)_{10}(dppe)]$ and

$[(M_4(CO)_{11})_2(\mu\text{-dppe})]$ have been isolated in this way[42]. $[M_4(CO)_{12}]$ species also react with tridentate ligands by substitution of three carbonyls to give $[M_4(CO)_9(P_3)]$.

The substitution of ligands in carbonyl derivatives of the cobalt triad has also provided a route to metal-phosphine-carbonyl complexes. With the absence of stable dimeric binary carbonyls of rhodium this has proven a particularly important method of synthesizing dinuclear rhodium-phosphine-carbonyls. $[RhCl(CO)_2]_2$ is very reactive towards bidentate phosphines and arsines to produce bridged Rh(I) dimers. It also reacts with tertiary phosphines PR_3 to provide $[RhCl(CO)PR_3]_2$ or trans-$[RhCl(CO)(PR_3)_2]$ complexes depending on the conditions[42]. $[IrCl(C_8H_{12})]_2$ and $[Rh(CO)_2Cl_2]^-$ react with dppm in the presence of CO to give complexes $[M_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]^+$ (M=Ir or Rh)[52].

Another common method of synthesizing metal-phosphine-carbonyls involves carbonylation of metal phosphine complexes. For example, reaction of $CoCl_2$ with the tetradentate phosphine eHPT provides $[Co_2Cl_4(eHPT)]$ which subsequently reacts with more $CoCl_2$ in a CO/H_2 atmosphere to provide $[Co_2(CO)_4(eHPT)][CoCl_4]$[53]. Reaction of $[CoBr(PMe_3)_3]$ with CO in the presence of $NaBPh_4$ proceeds with displacement of the halide by carbon monoxide to give $[Co(CO)_2(PMe_3)_3]BPh_4$[54].

1.2.5.3 Nickel Triad

$[Ni(CO)_4]$ is the only stable binary carbonyl of the nickel triad at room temperature[55]. It is formed readily by the passage of CO over nickel metal. Substitution reactions of $[Ni(CO)_4]$ with tertiary phosphines and arsines have been well studied whereas phosphine substituted palladium and platinum carbonyls are generally prepared by indirect methods[55]. Complexes formed from $[Ni(CO)_4]$ with monodentate phosphines are generally of the type $[Ni(CO)_{4-n}(PR_3)_n]$ (n=1-3). As the extent of phosphine substitution increases the number of compounds isolable decreases. This can be rationalized by the fact that the more basic phosphines build up charge on the metal which can be transferred to the remaining CO groups, building the Ni-CO bond strength and making further substitution more difficult. A steric factor is also introduced as the cone angle of the ligand will affect the degree of substitution possible. Ligands of lower basicity such as halide substituted phosphines, phosphites and chelating ligands can effect higher degrees of substitution. For example, complete displacement of the carbonyls in $[Ni(CO)_4)]$ is observed for PF_3 and $[Ni(PF_3)_4]$ is formed.

$[Ni(CO)_4]$ has been treated with tridentate phosphines $(Me_2PCH_2)_2PMe$[56] and $(PPh_2)_3CH$[57] to afford complexes $[Ni(CO)_3]_3(Me_2PCH_2)_2PMe]$ and $[Ni_3(\mu\text{-}CO)_3(CO)_3\{(PPh_2)_3CH\}_2]$ respectively. Decomposition of $[Ni_3(\mu\text{-}CO)_3(CO)_3\{(PPh_2)_3CH\}_2]$[57] via cleavage of a P-C bond in the ligand, provides $[Ni_2(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$ which has also been synthesized by other routes. For example, reduction of

Ni(II) salts with $NaBH_3X$ (X=H or CN) in the presence of dppm and CO also provides $[Ni_2(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$ among other complexes[58]. This complex, which is a derivative of the hypothetical binary carbonyl $[Ni_2(CO)_7]$, is also prepared from the reaction of $[Ni_2(\mu\text{-}CNMe)(\mu\text{-}dppm)_2(CNMe)_2]$ with CO_2, from the treatment of $[Ni(COD)_2]$ with dppm and CO[59], or from the reduction of $[NiCl_2(\eta^1\text{-}dppm)_2]$ with zinc powder in a CO atmosphere[60]. Other $[Ni_2(CO)_3(\mu\text{-}PP)_2]$ complexes with PP= $F_2PN(Me)PF_2$, $(CF_3)_2PXP(CF_3)_2$ (X= NH, NMe or S)[55] have been prepared. Complexes $[Ni_2(\mu\text{-}cyclo\text{-}P_3Pr^i{}_3)_2(CO)_4]$[56] and $[Ni_2(\mu\text{-}dmpm)_3(CO)_2]$[32], made from the reaction of $[(C_5H_5)Ni(CO)_2]_2$ with dmpm, do not contain a metal-metal bond or a μ-CO function as in the $[Ni_2(CO)_3(\mu\text{-}PP)_2]$ complexes described above. The metal-metal bond in $[Ni_2(CO)_3(dppm)_2]$ can be reversibly cleaved by CO to give $[Ni_2(CO)_4(dppm)_2]$[57].

Preparation of phosphine substituted palladium and platinum carbonyls is generally performed by reduction of M(II) salts in the presence of CO and phosphine. One exception is the reaction of the oligomeric $[Pt(CO)_2]_n$ with phosphines to give complexes of the type $[Pt_3(PR_3)_4(CO)_3]$ and $[Pt_5(PR_3)_4(CO)_6]$[61]. Complexes $[Pt_4(PP)_3(CO)_3]$ (PP= $R_2P(CH_2)_nPR_2$, n=2;R=Et,Ph,$CHMe_2$; n=1,3,4, R=Ph) are obtained from the reduction of $[PtCl_2L]$ with $NaBH_4$ in a CO atmosphere[62]. Reaction of $Pd(OAc)_2$ with CO and phosphines PR_3 in the presence of a NaOAc/HOAc mixture provides complexes $[Pd_4(CO)_5(PR_3)_4]$[55]. Treatment of $[M(O_2CCF_3)_2(\eta^2\text{-}dppm)]$ (M=Pt or Pd) with CO in aqueous methanol provides complexes $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ [56]. Dimeric carbonyl complexes of palladium and platinum containing bridging dppm are obtained by carbonylation of such complexes as $[M_2(\mu\text{-dppm})_3]$ and $[M_2Cl_2(\mu\text{-dppm})_2]$ (M=Pd or Pt)[55].

1.3 Chemistry of complexes containing the $M_2(\mu\text{-dppm})$ unit

Oxidative addition and reductive elimination reactions are common among organometallic complexes and reversible oxidative addition is often a necessity for complexes to be active in homogeneous catalysis. An oxidative addition involves heterolytic or homolytic cleavage of a species XY with addition of both X and Y to the metal centre(s). For this reason, dinuclear complexes are common substrates for oxidative addition as it can occur with a resulting increase in the oxidation state of each metal by only one. Bridging ligands are often incorporated into these systems in order to maintain the integrity of the dinuclear unit during the addition, which can occur with cleavage of a metal-metal bond. Bridging phosphines of the type $R_2P(CH_2)_nPR_2$ are particularly effective at this as they are flexible, accommodate a wide range of metal-metal distances and are also good at stabilizing various oxidation states of a particular metal. Carbon monoxide ligands are also commonly found in these systems as their π-bonding ability and various coordination modes (section 1.1) allow them to adapt to changes arising from metal oxidation.

XY species commonly observed to add oxidatively to metal complexes include dihalogens, alkyl halides, hydrogen halides, water, elemental sulphur, olefins and acetylenes, and primary and secondary phosphines. In some instances, additions to metal dimers are not always oxidative but may proceed by insertion of ligands into a metal-metal bond, by ligand substitution, or simply by addition to an electronically unsaturated centre. Carbon monoxide, nitriles and isonitriles are most often associated with this type of addition. Because of the similar chemistry within a transition metal triad the reaction chemistry of the $M_2(\mu\text{-P-P})_n$ unit will be discussed for each metal triad in turn where there is significant representation of this type of complex.

1.3.1. Group VIb

Of the Group VIb metals, molybdenum and tungsten have been found in complexes of the type $[M_2X_4(\mu\text{-P-P})_2]$ which contain quadruple metal-metal bonds[63,64]. There are few examples of addition reactions involving these complexes, probably owing to the already high coordination number and oxidation state of the metals. However, the oxidative addition chemistry of complexes $[M_2X_4(\mu\text{-dppm})_2]$ towards Ph_2R_2 (R=S or Se), CH_2Cl_2 and Cl_2 has been studied[65].

1.3.2 Group VIIb

There are a few examples of phosphine bridged dimers from Group VIIb. $[Mn_2(CO)_6(\mu\text{-tepid})_2]$

{tepid=$(EtO)_2POP(OEt)_2$} reacts with I_2 or Br_2 in CH_2Cl_2 to provide the complexes $[Mn_2(\mu\text{-}I)(CO)_6(\mu\text{-tepid})_2]^+$ and $[Mn_2Br_2(CO)_6(\mu\text{-tepid})_2]$ respectively[66]. $[Mn_2(\mu\text{-}I)(CO)_8(\mu\text{-dppm})]I$ is formed from the reaction of $[Mn_2(CO)_8(\mu\text{-dppm})]$ with I_2[66]. $[Mn_2(CO)_5(\mu\text{-dppm})_2]$ contains an unusual four electron donating $\eta^2\text{-}\mu_2$ carbonyl bridge which forms a symmetrically bridging two electron donor carbonyl when small molecules are added to the dimer[67]. A number of species formulated as $[Mn_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-X})]$ have been made in this way. The addition of SO_2 can be reversed by heating the SO_2 adduct under reflux for several hours.

Reaction of $[Mn_2(CO)_5(\mu\text{-dppm})_2]$ with CO or isonitriles has led to complexes of the type $[Mn_2(CO)_5L(\mu\text{-dppm})_2]$ (L=CO,MeNC,$PhCH_2NC$,p-MeC_6H_4NC)[28]. Carbonylation also occurs when $[Mn_2(CO)_5(\mu\text{-dppm})_2]$ is treated with BF_3 to afford the intermediate $[Mn_2(CO)_5(BF_3)(\mu\text{-dppm})_2]$ which quickly decomposes to give $[Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-dppm})_2]BF_4$[67]. This complex can also be directly prepared by the reaction of $[Mn_2(CO)_5(\mu\text{-dppm})_2]$ with HBF_4 under a CO atmosphere.

Other examples of phosphine bridged manganese dinuclear complexes include $[Mn_2H(CN)(CO)_5(dppm)_2]$ and also $[Mn_2H(\mu\text{-}\eta^2\text{-CN})(CO)_4(dppm)_2]$ which contains a four electron donor cyanide ligand[68]. The latter complex was made by the protonation of $[Mn_2(CO)_5(dppm)_2]$ by HBF_4 in acetonitrile[31].

There are several known rhenium dimers with bridging phosphines derived from the reactions of $[Re_2X_4(\mu\text{-dppm})_2]$ (X=Cl,Br),which contain metal-metal triple bonds, with CO and isonitriles[35,69].

$[Re_2(CO)_6(\mu\text{-PP})(\mu\text{-P}^1P^1)]$ (PP=dppm, P^1P^1=dppm or dmpm) form complexes $[Re_2(\mu\text{-H})(\mu\text{-X})(\mu\text{-PP})(\mu\text{-P}^1P^1)(CO)_4]$ (X= C≡CPh,OH,OMe or H) when reacted with phenylacetylene, water, MeOH, or refluxing 1,2,4-trimethylbenzene respectively[34].

1.3.3 Group VIIIb

1.3.3.1 Iron triad

Examples of $M_2(\mu\text{-P-P})_n$ units that are substrates for addition reactions in the iron triad include $[M_2(CO)_5(\mu\text{-P-P})_2]$ species. For instance, $[Fe_2(\mu\text{-CO})(CO)_4(\mu\text{-dmpm})(\mu\text{-dppm})]$ reacts with HBF_4 to afford $[Fe_2(\mu\text{-H})(\mu\text{-CO})(CO)_4(\mu\text{-dmpm})(\mu\text{-dppm})]BF_4$[70]. Analogous products are formed with substrates where the phosphine is $(RO)_2PN(Et)P(OR)_2$ (R=Me,Et,Pr,Ph) or $R_2PCH_2PR_2$ (R=Me,Ph)[70]. In all cases, the single hydride bridge necessitates the retention of a metal-metal bond in order to retain an 18 electron count on each Fe(I) atom. With the $R_2PCH_2PR_2$ adducts, the protonation is reversible only in the presence of a strong base while, with the $(RO)_2PN(Et)P(OR)_2$ complexes, deprotonation occurs by solvent molecules in the absence of an excess of acid. Complexes $[Ru_2(CO)_5(\mu\text{-PP})_2]$ (PP= dmpm[71] or dppm[70]) react with acids HX ($X=BF_4^-,PF_6^-$) to provide $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_4(\mu\text{-dppm})_2]X$ in which the metal-metal bond is retained. $[Ru_2(CO)_5(\mu\text{-dmpm})_2$ was also demonstrated to form complexes $[Ru_2(CO)_4(\mu\text{-}R_2C_2)(\mu\text{-dmpm})_2]$ (R= Ph or CO_2Me) when treated with the appropriate acetylene[71].

1.3.3.2 Cobalt triad

A large number of phosphine bridged dimers of the cobalt triad have been characterized. The metal(0) dimers $[M_2(CO)_3(\mu\text{-}PP)_2]$ (M=Co,PP=dppm or dmpm[72];M=Rh,PP=dppm[73];M=Ir,PP=dppm[74]), $[M_2(CO)_4(\mu\text{-}PP)_2]$ {M=Co[75];M=Ir,PP=dppm[74]}, $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$[76] and $[Co_2(CO)_6(\mu\text{-}dppm)]$[72] are good candidates for addition reactions. For example, $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(\mu\text{-}dppm)(\mu\text{-}PP)]I$ (PP= dppm or dmpm) is formed by the reaction of $[Co_2(CO)_3(dppm)(PP)]$ or of $[Co_2(CO)_6(\mu\text{-}dppm)]$ with I_2 in the presence of one equivalent of dppm or dmpm[72]. $[Co_2(CO)_3(dppm)_2]$ is reported to be paramagnetic and is tentatively characterized by a poor elemental analysis. $[Co_2(CO)_6(\mu\text{-}dppm)]$, in the presence of dppm also reacts with S_8 to give $[Co_2(\mu\text{-}S)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$[72].

$[Rh_2(\mu\text{-}dppm)_2(CO)_3]$ reacts with acids HX to give Rh(I) dimers $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]X$ ($X=PF_6^-$,$p\text{-}CH_3C_6H_4SO_3^-$), $[Rh_2(CO)_2(\mu\text{-}H)(dppm)_2]BF_4$ and $[RhX(CO)(dppm)]_2$ (X=Cl,Br)[77,78]. It also reacts with MeI under a H_2 atmosphere to afford methane plus $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}I)(dppm)_2]$[78]. $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$ also reacts with acids HX to give $[Rh_2(\mu\text{-}H)(CO)_2(dppm)_2]X$ ($X=PF_6^-$ or $p\text{-}C_6H_6SO_3^-$)[77]. Other A-frames are formed with the cleavage of the Rh-Rh bond in the reaction of $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$ with ligands such as acetylenes HCCR (R=H,Ph) and carboxylates RCO_2^- ($R=H,CH_3$)[77]. One equivalent of CO will add to $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$ to provide the complex $[Rh_2(CO)_3(\mu\text{-}$

dppm)$_2$] already mentioned.

Both [$Ir_2(CO)_3(\mu$-dppm)$_2$] and [$Ir_2(CO)_4(\mu$-dppm)$_2$] are protonated by acids giving complexes [$Ir_2(\mu$-H)(μ-CO)$(CO)_2$(dppm)$_2]^+$ and [$Ir_2(\mu$-H)$(CO)_4$(dppm)$_2]^+$, respectively, which are interconvertible by a reversible addition of CO[79]. [$Ir_2(CO)_4$(dppm)$_2$] adds two equivalents of H_2 to provide [$Ir_2(\mu$-H)$_2$(H)$_2$(CO)$_2$(dppm)$_2$]. Under a CO atmosphere a reductive elimination of H_2 restores [$Ir_2(CO)_4(\mu$-dppm)$_2$].

SO_2, CO and ^{t}BuNC react with [$Rh_2(\mu$-Cl)$(CO)_2(\mu$-dppm)$_2]^+$ non oxidatively by forming [$Rh_2(\mu$-Cl)(μ-SO_2)$(CO)_2(\mu$-dppm)$_2]^+$, [$Rh_2(\mu$-Cl)(μ-CO)$(CO)_2(\mu$-dppm)$_2]^+$ and [$Rh_2(\mu$-Cl)(μ-CO)(CO)(^{t}BuNC)(μ-dppm)$_2]^+$ respectively [80,81]. Similarly, CO adds to in [$Rh_2(\mu$-Cl)$(CO)_2$(dppm)$_2]^+$ to give [$Rh_2(\mu$-Cl)(μ-CO)$(CO)_2$(dppm)$_2]^+$ with formation of a metal bond[80].

There are a number of trimeric complexes where an essentially linear array of metal atoms is held together by a tridentate ligand of type $(R_2XCH_2)_2XR$ where X=P or As[82]. These complexes contain two M(μ-P-P)M units which share a common metal atom and hence they exhibit the same kind of reactivity as the analogous dimers. For example, [Rh_3(dpmp)$_2(CO)_3I_2$]BPh_4 {dpmp=$(Ph_2PCH_2)_2PPh$} reversibly adds one equivalent of CO[78]. Further decarbonylation occurs with prolonged refluxing in acetone and [$Rh_3(CO)_2I_2$(dpmp)$_2$]BPh_4 is formed. [Rh_3(dpmp)$_2(CO)_3I_2$]BPh_4 also reacts with I_2 to give [$Rh_3I_4(CO)_3$(dpmp)$_2$]BPh_4 which loses two carbonyls, the last one reversibly.

1.3.3.3 Nickel triad

An abundance of complexes of the type $M_2(\mu\text{-PP})_n$ can be found in the nickel family with representatives from oxidation states from zero to four. There are a few metal(0) dimers in this family which act as substrates for addition reactions. Recently the rich reaction chemistry of $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ has been established[8,83,84]. One of the most interesting of these is the reversible addition of CO. The resulting complex, formulated as $[Ni(CO)_2(dppm)]_2$, was postulated as the result of low temperature solution ^{31}P NMR and IR data. A solid can be precipitated from solution but it decomposes rapidly when brought to room temperature. Other M(0) dimers, namely $[M_2(\mu\text{-dppm})_3]$ (M=Pd,Pt), oxidatively add alkyl halides to give metal(II) A-frame adducts $[M_2(\mu\text{-}X)R_2(\mu\text{-dppm})_2]^+$ (M=Pt,R=Et,X=I,Br,R=Me,X=I;M=Pd,R=Me,X=I,Br)[85,86]. The intermediate species $[Pt_2Me(\eta^1\text{-dppm})(\mu\text{-dppm})_2]I$ has been isolated from the addition of one equivalent of MeI to $[Pt_2(\mu\text{-dppm})_3]$. $[Pd_2(\mu\text{-dppm})_3]$ also reacts with dihalomethanes to yield A-frame complexes $[Pd_2(\mu\text{-}CH_2)(X)_2(dppm)_2]$[87].

1.3.3.3.1 Metal(I) dimers

There are a large number of M(I) dimeric complexes in the nickel family that can be formulated as $[M_2XY(\mu\text{-P-P})_2]^{n+}$. This type of complex and particularly $[MCl(dppm)]_2$ (M=Pd or Pt), is a good substrate for the study of reactions of the Pt-Pt or Pd-Pd bond[88]. The approximately planar structures allow easy access to the metal atoms and the low oxidation state makes it susceptible to oxidative addition reactions. A characteristic reaction of these complexes is the addition of small molecules across the metal-metal bond to form A-frame complexes. The addition is often reversible and does not necessarily involve the oxidation of the metal. For example, SO_2 will insert into the metal-metal bonds of $[Pd_2Cl_2(\mu\text{-dppm})_2]$[89] and $[ClPt(dppm)_2Pd(C_6F_5)]$[90]. CO will add to complexes $[Pt_2X_2(\mu\text{-dppm})_2]$ (X=Cl or Me) by insertion into the metal-metal bond to give A-frames[91]. The metal-metal bond in $[Pt_2Cl_2(\mu\text{-dppm})_2]$ can be protonated to give the $[Pt_2(\mu\text{-H})Cl_2(\mu\text{-dppm})_2]^+$ cation[92].

1.4 $MM^1(\mu\text{-PP})_n$ heterobimetallics

The division of the discussion of $M_2(\mu\text{-PP})_n$ systems into the metal triads necessitates a separate discussion of heterobimetallics of the type $MM^1(\mu\text{-PP})_n$. Dppm is commonly found in these systems and therefore the discussion will focus on the synthesis and properties of $MM^1(\mu\text{-dppm})_2$ complexes. The two main systematic approaches to the synthesis of these complexes involve a reaction of a monodentate dppm complex or a ring opening reaction of a chelated dppm in the presence of another metal species. The reactions of $[MX_2(\eta^1\text{-dppm})_2]$ complexes of the nickel family with various species, for example, have produced numerous $MM^1(\mu\text{-dppm})_2$ dimers. The crystal structure of

$[NiPtCl_2(CO)_2(dppm)_2]$, obtained from the reaction of $[Ni(CO)_2(\eta^1\text{-}dppm)_2]$ with $PtCl_2$, has been determined[93]. The nickel and platinum atoms retain their respective tetrahedral and square planar geometries associated with their original (0) and (II) oxidation states. $[Ni(CO)_2(\eta^1\text{-}dppm)_2]$ is so reactive that at room temperature it dimerizes in solution with loss of CO and dppm to give $[Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2]$.

The ring strain associated with chelating dppm has provided a method of producing heterobimetallic complexes via ring opening reactions. A few reactions of this type are illustrated in Table 1.1. Ring opening of one of the diphosphine ligands in the complexes $[M(CO)_3(\eta^1\text{-}dppm)(\eta^2\text{-}dppm)]$ (M=Cr,Mo,W) in the presence of CuX (X=Cl or I), $[RhCl(CO)_2]_2$ or [IrCl(CO)$_2$(p-toluidine)] produces complexes $[(CO)_3M(dppm)_2CuX]$[94] and $[(CO)M(dppm)_2M^1(CO)X]$[78] (M=Rh,Ir) respectively. Similar reactions are observed for mer-cis-$[MnX(CO)_2(\eta^1\text{-}dppm)(\eta^2\text{-}dppm)]$[95].

1.4.1 Chemistry of $MM^1(\mu\text{-}dppm)$ complexes

As expected heterobimetallics containing bridging phosphines exhibit a reaction chemistry similar to that of related homobinuclear species. For example, $[MoRu(CO)_6(dppm)_2]$ will lose CO under vacuum, isomerizes to a CO bridged structure, and will add H_2 to give $[(CO)_2Ru(\mu\text{-}H)_2(dppm)_2Mo(CO)_2]$[96]. A-frames $[XPt(\mu\text{-}Y)(dppm)_2Pd(C_6F_5)]$ ($Y=CO,CS_2,SO_2$) are formed from $[XPt(dppm)_2Pd(C_6F_5)]$ in

Table 1.1: $M(\mu\text{-dppm})_2M^1$ heterobimetallics from η^2-dppm complexes

$M(\eta^2\text{-dppm})_2$ complex	M^1 complex	$M(\mu\text{-dppm})_2M^1$ complex	Ref.
$[RuH_2(dppm)_2]$	$[Mo(CO)_6]$	$[MoRu(CO)_6(dppm)_2]$ (3 interconvertable forms)	96
$[Pt(dppm)_2]Cl$	$[Hg(C\equiv CR)_2]$	$[(RC\equiv C)_2Pt(dppm)_2HgCl_2]$	97
$[Ir(CO)(dppm)_2]Cl$	$[M(C\equiv CPh)]$ (M=Cu,Ag,Au)	$[(PhC\equiv C)(CO)Ir(dppm)_2MCl]$	99
	$[AuCl(PPh_3)]$	$[(CO)ClIr(dppm)_2Au]Cl$	
	$[AgCl(PPh_3)]_4$ or CuCl	$[(CO)ClIr(dppm)_2MCl]$ (M=Cu,Ag)	
	$[RhCl(CO)_2]_2$	$[RhIr(CO)_3Cl(dppm)_2]Cl$	
$[Rh(CO)(dppm)_2]Cl$	$[AgCl(PPh_3)]_4$	$[Cl(CO)Rh(dppm)_2AgCl]$	
$[RhCl(dppm)_2]$	$Na[Co(CO)_4]$	$[CoRh(CO)_3(dppm)_2]$	100
	$Na[M(CO)_5]$ (M=Mn,Re)	$[RhM(CO)_4(dppm)_2]$	
	$[HM(CO)_4]^-$ (M=Fe,Ru,Os)	$[(CO)Rh(\mu\text{-H})(dppm)_2M(CO)_2]$	
	$[HM(CO)_5]^-$ (M=Cr,W)	$[(CO)Rh(\mu\text{-H})(dppm)_2M(CO)_3]$	
$[RuCl_2(dppm)_2]$	$Na[Mn(CO)_5]$	$[(CO)_3Mn(\mu\text{-CO})(dppm)_2RuCl_2]$	101

reactions that resemble those of the homonuclear $[ML(dppm)]_2$ species[90].

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Chapter 2 : Reaction of Co(II) Halide Salts with $NaBH_4$ or $NaBH_3CN$ in the Presence of Phosphines and Carbon Monoxide

2.1 Introduction

The use of $NaBH_4$ in synthetic organic chemistry is well known and is largely due to the efforts of Brown[1]. Its use in synthetic inorganic chemistry has been fairly limited until recently. One early application was the reduction of metal salts with $NaBH_4$ to give metal borides of unknown composition[2]. Many of these borides were found to be catalytically active in the hydrogenation of alkenes[3]. It was thought that to isolate intermediates in the formation of the metal borides might reveal clues as to the composition of the catalytically active borides. In order to obtain "freeze frame" pictures of the fast reduction process, phosphines were added to the reaction system[4]. Numerous interesting phosphine complexes of various metals were isolated in this way. The general solubility of the phosphine complexes, as opposed to the insolubility of the borides, made it possible for characterization by NMR techniques. With the borohydride anion being a potential ligand through the formation of metal-hydride-boron bridges, it was not surprising that a whole range of metal-phosphine-borohydride complexes were also identified (section 7.1.3.1).

The next step in the slowing down of the reduction process came with the recognition that replacement of a hydride in $NaBH_4$ with an electron withdrawing group diminished the reducing power of the species. Thus $NaBH_3CN$ was used in the metal/phosphine reaction system with similar results[5]. The CN substituent makes the reagent a versatile ligand as well as a reducing agent and numerous coordination modes have been identified in products resulting from such reaction systems.

Some interesting cobalt phosphine complexes have been identified as products in Co(II)/phosphine/$NaBH_3Y$ (Y=H or CN) reaction systems. For example, with the homologous series of $Ph_2P(CH_2)_nPPh_2$ phosphines, the type of product isolated was dependent on the chain length, or value of n, in the phosphine. Thus, with the n=2 (dppe) ligand and $NaBH_3CN$ as a reducing agent, complexes isolated include $[Co(BH_3CN)_2(dppe)_2]$, $[Co(BH_3CN)(dppe)_2]X$, $[Co(CN)(dppe)_2]ClO_4$ and $[Co(CN)_2(dppe)_2]X$ [6]. With dppm (n=1) however, with both $NaBH_3CN$ and $NaBH_4$ a series of complexes $[CoH(\eta^2\text{-dppm})X]Y$ (X=Cl,Y=Cl or BPh_4; X=Y=Br; X=Y=I; X=BH_3CN, Y=BH_3CN,ClO_4 or BPh_4) have been isolated[7]. The appearance of a Co(III) complex from such a strongly reducing environment is surprising but isolation of intermediates in the reaction has given clues about the mechanism of their formation. A dark green paramagnetic complex formulated as $[Co_2X_3(dppm)_2]$ was isolated from the early stages of reactions leading to the Co(III) complexes. This intermediate was shown to react further under the reaction conditions described to form the

Co(III) species along with a complex identified as $[CoX(\eta^1\text{-}dppm)_3]$. $[Co_2X_3(dppm)_2]$ is thought to have a bis(μ-dppm) A-frame structure containing a Co(I)-Co(II) core. This type of phosphine bridged, mixed oxidation state formulation has been confirmed in other complexes such as $[Co^ICo^{II}(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)Cl_3]$ and $[Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl]$[8]. The formation of a Co(III)-hydride complex from $[Co_2X_3(dppm)_2]$ could follow from oxidative addition of H_2 generated from the reducing agent or some other HX species across the Co(I)-Co(II) centres. Subsequent dimer degradation could provide the $[CoH(dppm)_2X]^+$ cation.

The tendency of higher n value phosphines in the homologous series $Ph_2P(CH_2)_nPPh_2$ to chelate rather than bridge, due to their larger "bite" may preclude the formation of a phosphine bridged complex like $[Co_2X_3(dppm)_2]$ which is postulated as an intermediate in the formation of Co(III) species. The complex $[CoX(\eta^1\text{-}dppm)_3]$ is also paramagnetic but the complex was characterized by elemental analysis and a single crystal X-ray diffraction study[9]. The structure contains a tetrahedrally coordinated cobalt atom with the halide at one site and the phosphorus donors of the three monodentate phosphines at the remaining sites. The coordination mode of the dppm in this complex also emphasizes the difference in the ligating properties of the n=1 vs the higher n value phosphines. Dppm does not have a large enough "bite" to span the tetrahedral angle of 109° and thus no tetrahedral complexes containing (η^2-dppm) ligands are known. This trend is also evident in Ni(0) sytems where complexes $[Ni(CO)_2(\eta^2\text{-PP})]$ are isolated for n=2-4 whereas $[Ni(CO)_2(\eta^1\text{-dppm})_2]$ is produced under similar conditions when n=1[10,11].

The reluctance of dppm and ligands with similar bites to chelate can be explained on the basis of ring strain as illustrated in the complexes $[PdCl_2(\eta^2\text{-PP})]$ for n=1-3[12]. The crystal structures of all three have been determined and the P-Pd-P bond angles are 72.7°, 85.80° and 90.58° for the n=1,2 and 3 derivatives respectively. In the dppm complex there is considerable distortion from the ideal bond angle of 90° expected for square planar geometry and thus ring strain is introduced. Ring strain in dppm chelate complexes is also observed in complexes $[M(CO)(dppm)_2]^+$ (M=Co,Rh,Ir), a property capitalized upon in the synthesis of dppm bridged heterobimetallic complexes as discussed in section 1.4.

The introduction of carbon monoxide into the metal-halide/phosphine/$NaBH_3Y$ (Y=H or CN) reaction systems was a logical development and has provided a unique approach to the synthesis of metal-phosphine-carbonyl complexes. For example, a series of reduced nickel complexes of this type were produced by reaction of $NaBH_3CN$ or $NaBH_4$ with of $NiX_2\cdot 6H_2O$ and the bidentate phosphine with a continual stream of CO being passed through the solution[10,11]. The type of complex(es) isolated from a particular reaction was found to depend on the nature of the bidentate phosphine and the reducing agent and the rate of addition of the reducing agent. For dppm, $[Ni(\eta^1\text{-dppm})_2(CO)_2]$ and $[Ni_2(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]$ were identified while, with the larger bite phosphines, complexes of the type $[Ni(CO)_2(\eta^2\text{-PP})]$, $[Ni_2(CO)_2(\eta^2\text{-PP})_2(\mu\text{-PP})]$ and $[Ni(CO)(\eta^1\text{-PP})(\eta^2\text{-PP})]$ have been isolated. Other groups have used this approach to synthesize metal-phosphine-carbonyl complexes. Reduction of $PtCl_2/R_2P(CH_2)_nPR_2$ (n=2,R=Et,Ph,$CHMe_2$; n=1,3,4, R=Ph) mixtures with $NaBH_4$ under a CO atmosphere provides complexes $[Pt_4(PP)_3(CO)_3]$[13].

The following text describes the synthesis and characterization of a number of Co(I) and Co(0) phosphine carbonyl complexes isolated from $CoX_2\cdot6H_2O$/phosphine/$NaBH_3Y$ (X=Cl or Br; Y=H or CN) reaction systems under a CO atmosphere.

2.2 $Co(II)/PPh_3/CO/NaBH_3CN$ reaction systems

2.2.1 $CoH(CO)(PPh_3)_3$ **2.1**

2.1 is isolated in acceptable yields as a crystalline solid from reactions involving addition of EtOH solutions of $NaBH_3CN$ to a solution of $CoBr_2\cdot6H_2O/PPh_3$ through which a continuous stream of CO is bubbling. The complex has also been synthesized by CO induced elimination of H_2 from $CoH_3(PPh_3)_3$ [14]. The significance of the $NaBH_3CN$ route is that it is a "one pot" reaction whereas the other route is a multistep reaction.

The spectroscopic data collected for the samples of **2.1** prepared by the $NaBH_3X$ (X=H,CN) route are consistent with that reported for **2.1** in the literature[14]. The structure of **2.1**[14] has been determined crystallographically. It contains a nearly regular TBP geometry about the cobalt atom with three phosphines occupying equatorial sites and the hydride and CO trans to each other at axial sites.

2.3 Co(II)/dppe/CO/NaBH$_3$X (X=CN,H) reaction systems

2.3.1 [Co(CO)(η^2-dppe)$_2$]X (X=BH$_3$CN, 2.2a or BPh$_4$, 2.2b)

2.2a is isolated in moderate yields from reactions involving the addition of EtOH solutions of NaBH$_3$CN to solutions of CoBr$_2\cdot$6H$_2$O/dppe through which a stream of CO gas is being passed. The BPh$_4^-$ salt can be prepared from the reaction mixture by addition of NaBPh$_4$ and recrystallization of the resulting precipitate from CH$_2$Cl$_2$/EtOH gives dark orange crystals of **2.2b**. The cation has also been precipitated as the BPh$_4^-$ salt from Co(II)/dppe/CO/NaBH$_4$ reaction systems. Again this method of synthesis offers the advantage of being a a simple "one pot" reaction.

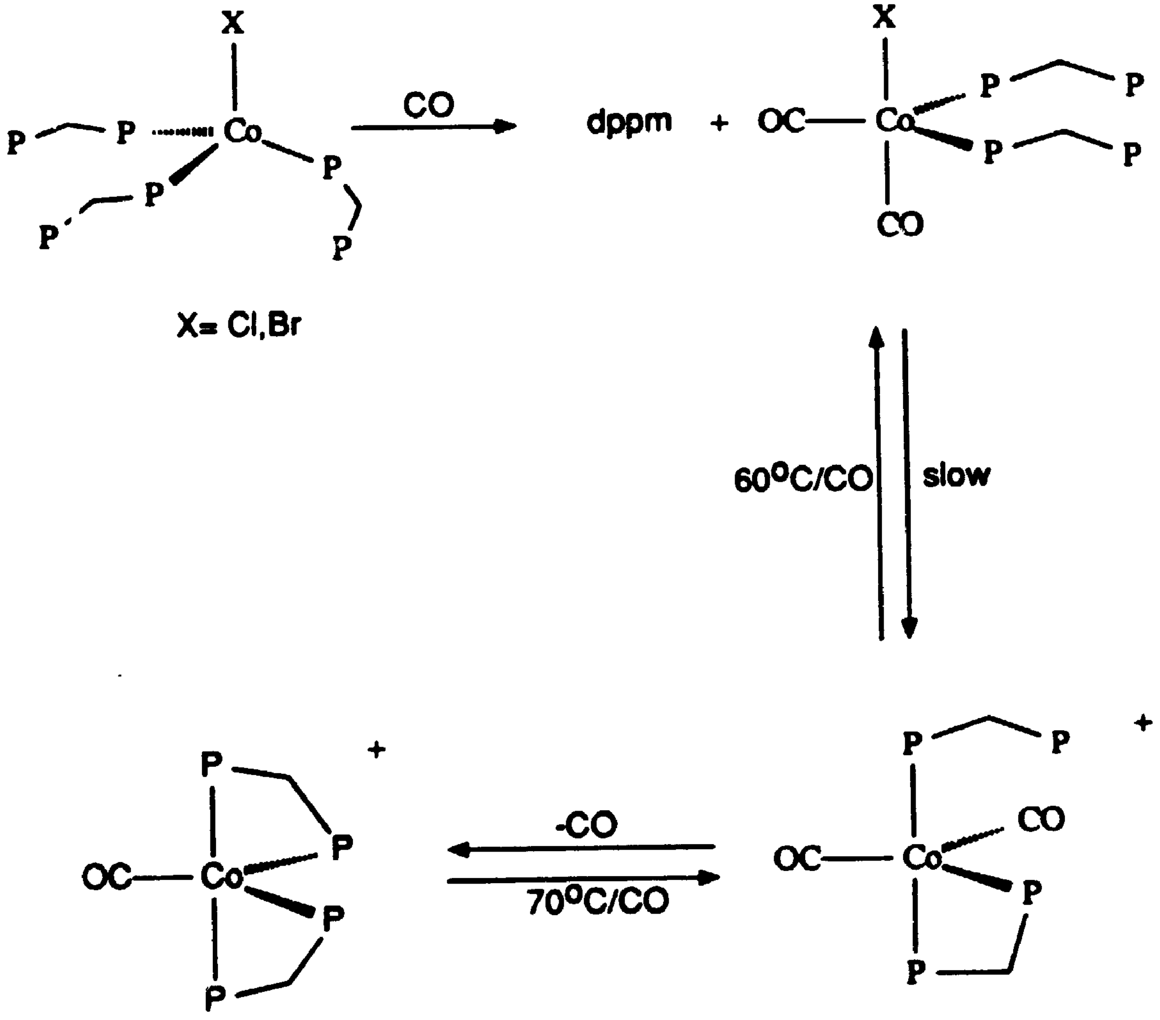
The cation has been characterized spectroscopically as well as analytically. The IR spectrum of **2.2a** and **2.2b** both exhibit a ν(CO) stretch at 1940 cm^{-1} consistent with a single terminal CO ligand. In addition **2.2b** exhibits various ν(BH) and ν(CN) stretches associated with the BH$_3$CN$^-$ counter ion as also seen in the analogous dppm complex. The ^{31}P nmr spectrum of the cation reveals a singlet at δ=69.7 indicating chemical equivalence of all four phosphorus atoms. The solid state structure of the cation is expected to be similar to that found in the dppm analogue with phosphorus atoms occupying both axial and equatorial sites in the TBP structure. The singlet in the ^{31}P NMR spectrum is therefore indicative of some fluxional process, the most likely being a Berry pseudo rotation or a turnstile rotation common to TBP structures as proposed for $[Co(CO)(\eta^2\text{-dppm})_2]^+$ (section 2.4.2).

2.4 Co(II)/dppm/NaBH$_3$X (X=H or CN) reaction systems

2.4.1 $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]BPh_4$ 2.3

Complex **2.3** was originally isolated from a $CoCl_2/Na_2[IrCl_6]$/dppm/CO/NaBH$_4$ reaction system, in attempts to prepare CoIr(μ-dppm) type complexes in a manner similar to those leading to $[CoRh(CO)_3(\mu\text{-dppm})_2]$. The reaction mixture was worked up in an analagous manner to those leading to $[CoRh(CO)_3(\mu\text{-dppm})_2]$ and NaBPh$_4$ added to ethanol washings produced an orange precipitate. This was recrystallized from CH_2Cl_2/EtOH to give a crystalline mixture containing mostly $[Co(CO)(dppm)_2]BPh_4$ and a small amount of **2.3** . Large yellow needles of **2.3** were handpicked for analysis and spectroscopic work. Subsequently quantities of **2.3** were observed as a minor constituent in samples of $[Co(CO)(dppm)_2]BPh_4$ prepared in other ways. The sequential ring opening of the η^2-dppm ligands in the $[Co(CO)(dppm)_2]^+$ cation via nucleophillic displacement of phosphorus donors by CO and halide has been established[15] (Scheme 2.1) and it is therefore not surprising that **2.3** is formed along with

Scheme 2.1: Reaction of [CoCl(η^1-dppm)$_3$] with CO



$[Co(CO)(dppm)_2]^+$.

2.4.1.1 Spectroscopic characterisation of 2.3

The IR spectrum of **2.3** contains ν(CO) stretches at 1990(s) and 1925(s) cm^{-1} consistent with two terminal carbonyls as proposed for the structure of **2.3**. The ^{31}P NMR spectrum of **2.3** at room temperature exhibits three sets of resonances at δ=-32.3(d), -7.5(br) and 46.2(m) integrating 1:2:1. At -90°C the resonances at δ=-32.3 and 46.2 remain essentially unchanged but the broad signal at δ=-7.5 resolves into two equal intensity multiplets at δ=13(tr) and -20(dd)(Figure 2.1). This limiting low temperature spectrum is consistent with the structure drawn in Figure 2.1.

The fluxionality in **2.3** involves Berry pseudo rotation or turnstile rotation, both common to TBP structures, resulting in the chemical equivalence of P_C and P_D atoms.

The ^1H nmr of **2.3** exhibits two multiplets at δ=2.40 and 4.16 for the methylene protons on the η^2-dppm and η^1-dppm ligands respectively.

2.4.2 $[Co(CO)(dppm)_2]X$ ($X=BH_3CN$ 2.4a, Cl 2.4b, Br 2.4c, $Co(CO)_4$ 2.4d or BPh_4 2.4e) complexes

The formation of the $[Co(CO)(dppm)_2]^+$ cation is evident in virtually all of the dppm reactions discussed in this chapter and in the syntheses of $[CoRh(CO)_3(dppm)_2]$. Some interesting properties of $[Co(CO)(dppm)_2]X$ complexes have been observed.

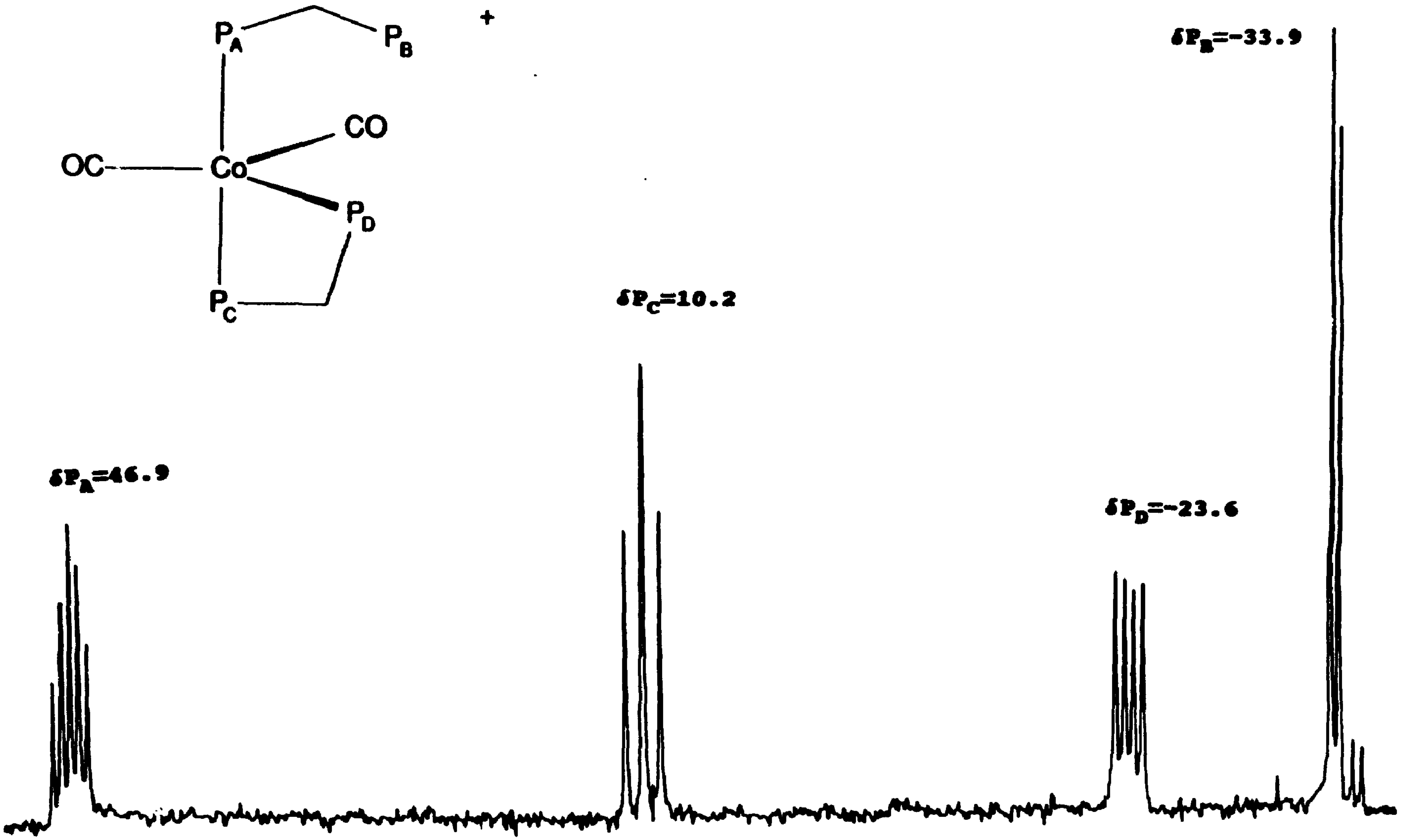


Figure 2.1: Limiting low temperature ^{31}P NMR spectrum of 2.3

The complex $[Co(CO)(dppm)_2]BH_3CN$ is produced in high yield from the reaction of $NaBH_3CN$ with $CoBr_2 \cdot 6H_2O$/dppm mixtures under a CO purge. The complex was characterized by IR, ^{31}P and ^{1}H NMR and elemental analysis. Evidence for the ionic vs coordinated nature of the BH_3CN^- comes from the fact that from bright red ethanol solutions of **2.4a** large quantities of an orange precipitate of **2.4e** form with the addition of $NaBPh_4$. The precipitate was subsequently characterized as $[Co(CO)(dppm)_2]BPh_4$. There is evidence however that an isomer of **2.4a** may exist and a coordinated BH_3CN^- may be involved. During the course of some preparations of **2.4a**, cooling of the reaction mixture in a freezer overnight resulted in the precipitation of large quantities of a green crystalline solid **2.4a**^{1}. The IR spectrum of **2.4a**^{1} is very similar to that of **2.4a** with the main differences being in the ν(BH) and ν(CN) regions of the spectrum. The complex is extremely sensitive to solvents such as EtOH and washing with EtOH immediately gives bright red solutions of **2.4a** quantitatively as indicated by ^{31}P NMR. Even exposure of **2.4a**^{1} to an atmosphere containing EtOH vapours was found to slowly convert a crystalline sample of **2.4a**^{1} to solid **2.4a**. The reaction appears to be reversible as washing red crystals of **2.4a** with C_6H_6 causes rapid decomposition of the material to give grey-green powders which subsequently dissolve in ethanol to give back **2.4a**. Evidence for this type of reaction is also apparent from $CoX_2 \cdot 6H_2O$/dppm/CO/$NaBH_4$ reaction systems leading to complexes $[Co_2(CO)_4(dppm)_2]$. Under the conditions used to work up these reactions any $[Co(CO)(dppm)_2][Co(CO)_4]$ present is converted to $[Co_2(CO)_4(dppm)_2]$ and what remains after this is extracted with C_6H_6 is a greyish green powder. The IR spectrum of the solid reveals a $\nu(CO)$ stretch at 1930 cm^{-1} which is consistent with that of the $[Co(CO)(dppm)_2]^+$ cation. The solid reacts with EtOH to give initially an orange solid which quickly dissolves to give bright red solutions from which $[Co(CO)(dppm)_2]BPh_4$ is precipitated with the addition of $NaBPh_4$. The presence of $[Co(CO)_4]^-$ as a counter ion in the $[Co(CO)(dppm)_2]^+$ containing grey-green powder can be ruled out for the reason given above and because solutions of $[Co(CO)(dppm)_2][Co(CO)_4]$ do not precipitate the cation with the addition of BPh_4^-. The anion is also unlikely to be some sort of complex anion such as $CoCl_4^{2-}$ due to the strongly reducing environment in which the complex is formed. A BH_4^- counter ion would reveal itself in the IR spectrum of the solid. Therefore the most reasonable ion would be the halide, either chloride, as in **2.4b**, or bromide, as in **2.4c**, associated with the Co(II) salt. Assuming this to be true, it appears that this reversible red-green reaction is observed for species with X=BH_3CN **2.4a**, Cl **2.4b**, and Br **2.4c**. **2.4e** and **2.4d** are stable to C_6H_6 washings. If some form of isomerism is being exhibited in this reaction then it may be linked to the ability of BH_3CN^-, $Cl^-$and Br^- to coordinate to a cobalt centre whereas BPh_4^- does not have this ability and is perfectly stable. One possible explanation is the formation of a neutral complex of the type [CoX(CO)(η^1-dppm)(η^2-dppm)] **2.5** promoted by nonpolar solvents such as C_6H_6 (equation 2.1).

$$[Co(CO)(\eta^2\text{-dppm})_2]X \;=\; [CoX(CO)(\eta^1\text{-dppm})(\eta^2\text{-dppm})] \qquad (2.1)$$

This type of behavior is exhibited in solution by [Co(CO)$_2$(η^1-dppm)(η^2-dppm)]$^+$, which in the presence of halide forms the neutral complex [CoX(CO)$_2$(η^1-dppm)$_2$]^{15} (Scheme 2.1). With [Co(CO)(dppm)$_2$]BPh$_4$ **2.4e**, the type of reaction illustrated above in equation 2.1 is precluded by the poor ligating properties of the BPh_4^- ion. This is consistent with the stability of **2.4e** to C_6H_6 washings.

[Co(CO)(dppm)$_2$]Co(CO)$_4$, **2.4d**, does in fact exhibit a similar reaction to that in equation 2.1 in the formation of [Co$_2$(μ-dppm)$_2$(CO)$_4$] species. However, the reaction is not reversible due to the loss of CO (equation 2.2).

$$[Co(CO)(dppm)_2]Co(CO)_4 \;=\; [Co_2(\mu\text{-dppm})_2(CO)_4] + CO \qquad (2.2)$$

This transformation can be accomplished by heating the solid in C_6H_6 or by simply heating the solid up to 75°C.

The reaction illustrated in eqn 2.1 could involve a nucleophilic substituion of a phosphorus donor by a two electron donating species, X^-. In **2.4d** the possibility of initial phosphine displacement in the cation to give a

$[(CO)_4Co\rightarrow Co(CO)(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$ intermediate may be quickly followed by the formation of a complex containing a μ-dppm ligand. A second η^2-dppm ring opening and subsequent coordination to the $Co(CO)_4^-$ fragment leads to $[Co_2(CO)_4(dppm)_2]$ species.

Assuming the interpretation of the chemistry of the complexes $[Co(CO)(dppm)_2]X$ is correct, the absence of similar behaviour for $[Co(CO)(dppe)_2]BH_3CN$ may be attributed to the larger bite of dppe and the stability of the resulting five membered $Co(\eta^2\text{-dppe})$ rings to the ring opening reaction postulated in equation 2.1.

2.4.3 Co(II)/dppm/CO/BH_4^- reaction systems

Essentially three types of products have been identified from these reaction systems, with control of the rate of addition of the borohydride being essential in determining the nature of the product formed. Rapid addition of $NaBH_4$ ($\leq$1min) provides complexes containing a μ-PPh_2 group resulting from P-C bond cleavage in dppm (section 6.2). Moderate addition times (between 5 and 10 min.) lead mainly to $[Co_2(CO)_4(dppm)_2]$ **2.6** directly. Slow addition of $NaBH_4$ provides good yields of $[Co(CO)(dppm)_2]Co(CO)_4$ **2.4d** which can subsequently be converted to $[Co_2(CO)_4(dppm)_2]$ by heating the solid by itself or as a C_6H_6 suspension to give solutions of **2.6**.

2.4.3.1 Structures of $[Co(CO)_2(dppm)]_2$ isomers

The isomers of [Co(CO)$_2$(dppm)]$_2$; namely [Co$_2$(μ-CO)$_2$(μ-dppm)$_2$(CO)$_2$] **2.6a** and [Co$_2$(μ-dppm)$_2$(CO)$_4$] **2.6b**, exist as a rapidly equilibrating mixture in solution and can be precipitated as a crystalline mixture from CH_2Cl_2 or C_6H_6 with EtOH. Large red and black crystals of **2.6a** and **2.6b** respectively were handpicked from these mixtures and used for subsequent chemical analysis, spectroscopic studies and a structural analysis by X-ray diffraction[16]. Both structures can be rationalized in terms of solution and solid state structures proposed for the related binary carbonyl [Co$_2$(CO)$_8$] .

2.4.3.1.1 Structure of 2.6a

An ORTEP representation of the molecule and selected bond angles and distances can be found in Figure 2.2 and Table 2.1 respectively. The molecule has approximately C_{2v} symmetry with a mirror plane containing the cobalt-cobalt axis and the terminal CO ligand on each cobalt. The other mirror plane is perpendicular to this and bisects the cobalt-cobalt axis and contains the bridging carbonyls. This type of structure is also found in the recently characterized meso-[Co$_2$(μ-CO)$_2$(CO)$_2$(eLTTP)][17] which contains the tetradentate ligand ($Et_2PCH_2CH_2$)(Ph)PCH_2P(Ph)($CH_2CH_2PEt_2$) and in the CO bridged isomer of [Co$_2$(CO)$_8$][18]. The Co-Co distance in **2.6a** is 2.444(2)Å which is significantly shorter than the distance of 2.513(4)Å found in [Co$_2$(μ-CO)$_2$(CO)$_2$(eLTTP)]. This is presumably due to the steric

Figure 2.2: Structure of 2.6a

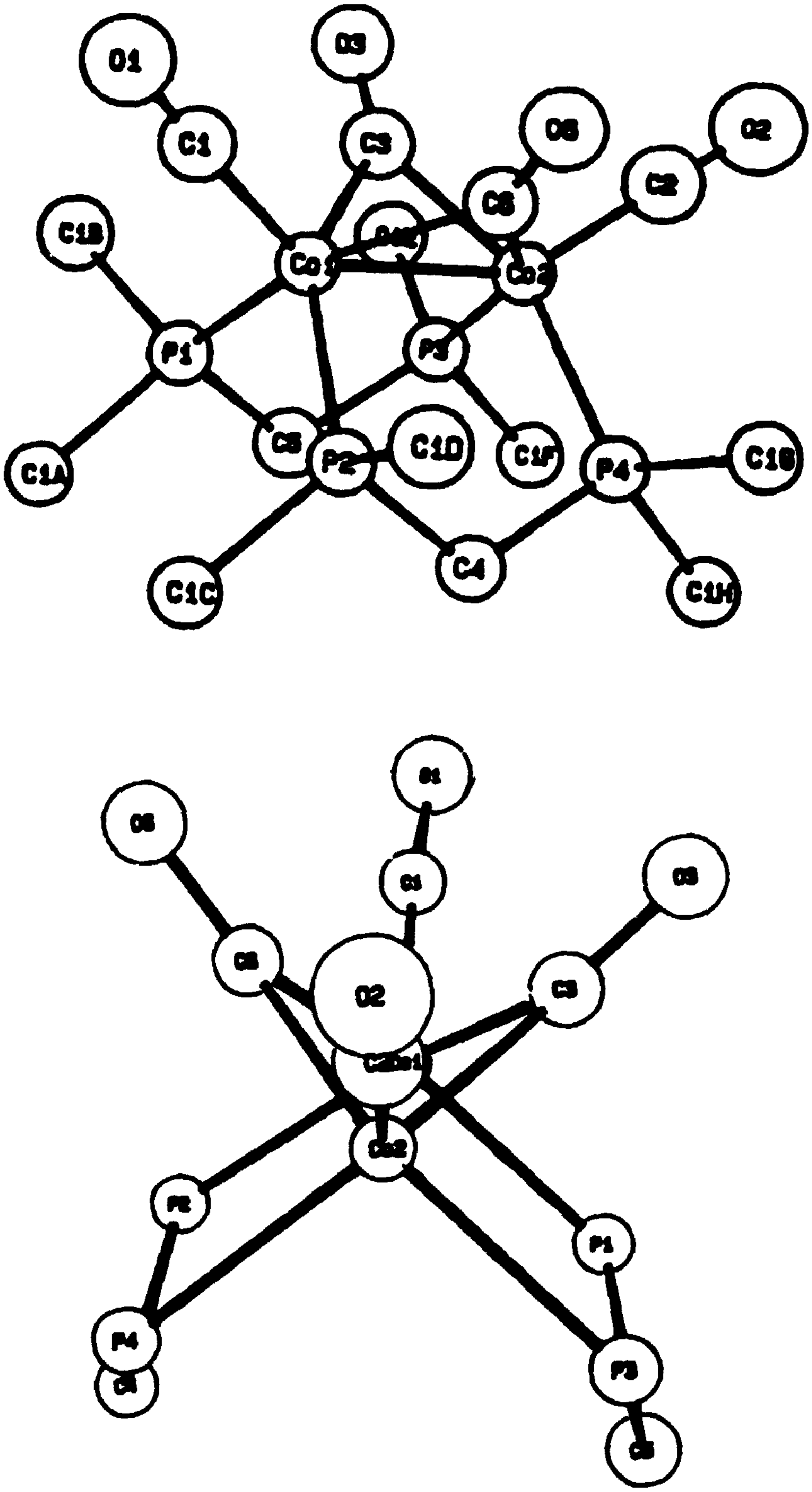


Table 2.1: Selected bond distances and angles in 2.6a

BOND DISTANCES

ATOMS	Å
Co1 - Co2	2.444(2)
Co1 - P1	2.268(3)
Co1 - P2	2.259(3)
Co1 - C1	1.724(9)
Co1 - C3	1.928(9)
Co1 - C6	1.948(10)
Co2 - P3	2.249(3)
Co2 - P4	2.258(3)
Co2 - C2	1.746(10)
Co2 - C3	1.932(9)
Co2 - C6	1.902(10)
C1 - 01	1.168(11)
C2 - 02	1.142(12)
C3 - 03	1.161(11)
C4 - 04	1.173(12)

ANGLES

P1 - Co1 - P2	98.4(1)
P3 - Co2 - P4	99.9(1)

requirements of the tetradentate ligand preventing closer approach of the metal atoms.

The structure of **2.6a** contains two essentially symmetrically bridging CO ligands as evident by the $\nu(\mu\text{-CO})$ stretches at 1767 and 1755 cm^{-1} in the IR spectrum of **2.6a**. The arrangement of the phosphines at each metal atom is cis as given by the P(3)Co(2)P(4) and P(1)Co(1)P(2) angles of 99.9(1) and 98.4(1)° respectively. The structure of **2.6a** can be related to the CO bridged solid state structure of $[Co_2(CO)_8]$ by substitution of the two terminal CO ligands coplanar with the $Co(\mu\text{-CO})_2$ group by two bridging phosphines. The cis arrangement of phosphines is fairly rare in $M_2(\mu\text{-dppm})_2$ type complexes but can be found in species such as $[Ni_2(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]$[19]. A-frame geometries as seen in $[Co_2(\mu\text{-I})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]^+$ [20] are more common.

2.4.3.1.2 Structure of 2.6b

An ORTEP representation of the molecular structure can be seen in Figure 2.3. The structure can be described in terms of the unbridged D_{3d} solution structure of $[Co_2(CO)_8]$[21]. A list of bond angles demonstrating the geometry about each cobalt atom is provided in Table 2.2. Each cobalt atom exhibits distorted TBP geometry with the phosphorus donors and a terminal carbonyl at equatorial sites. A cobalt atom and a terminal CO occupy axial sites. The staggering of the trigonal planes is short of the 60° expected in the D_{3d} structure of $[Co_2(CO)_8]$. Presumably this

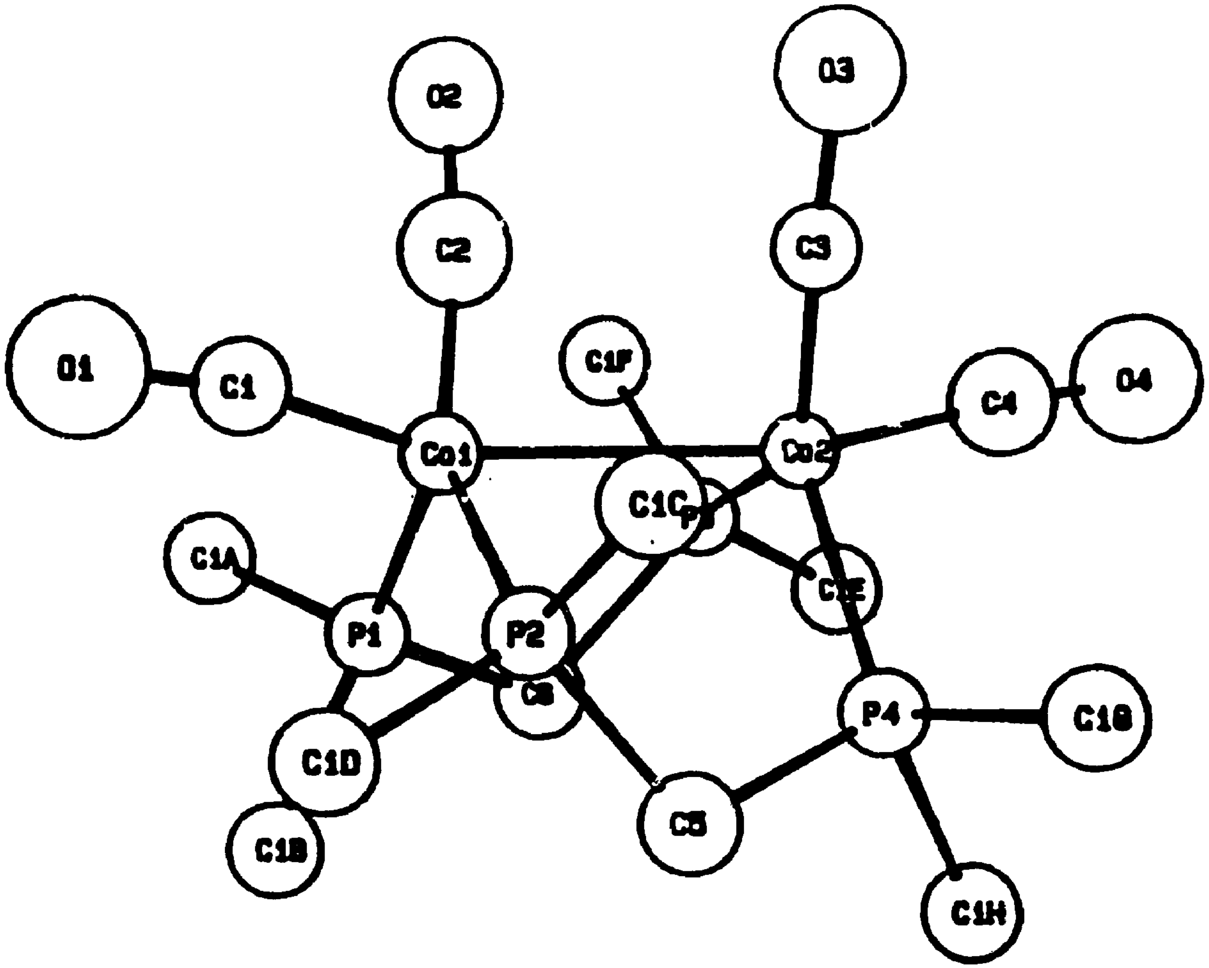


Figure 2.3: Structure of 2.6b

Table 2.2: Selected bond distances and angles in **2.6b**

BOND DISTANCES

ATOMS	Å
Co1 - Co2	2.809(6)
Co1 - P1	2.191(9)
Co1 - P2	2.196(10)
Co1 - C1	1.65(4)
Co1 - C2	1.585(4)
Co2 - P3	2.109(9)
Co2 - P4	2.216(9)
Co2 - C3	1.69(3)
Co2 - C4	1.65(4)

ANGLES

P1 - Co1 - P2	106.6(4)
P1 - Co1 - C2	113.6(1.4)
P2 - Co1 - C2	138.5(1.4)
P3 - Co2 - P4	107.1(4)
P3 - Co2 - C3	133.7(1.1)
P4 - Co2 - C3	118.9(1.1)
Co2 - Co1 - C1	159.2(1.2)
P1 - Co2 - C4	167.5(1.6)

is due to the strain produced in the molecule by the twisting of the five membered Co(μ-dppm)Co rings in **2.6b**. Again, as in **2.6a**, the phosphines are oriented cis to each other on each cobalt atom.

One unusual feature of **2.6b** is the extremely long Co-Co distance of 2.809(6)Å, almost 0.3 Å longer than that observed in **2.6a**. This is at the long end of the range expected for a cobalt-cobalt single bond. However, the Co-Co bond is a requirement for diamagnetism. A compilation of Co-Co single bond lengths in $[Co_2(CO)_8]$ and derivatives can be found in Table 2.3.

Quite a different structure from **2.6b** is observed in another non-CO bridged dinuclear complex $[Co_2\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2(CO)_4]$[22]. One cobalt atom has a nearly regular TBP stereochemistry with trans phosphines while the other cobalt atom has a more distorted TBP geometry with phosphorus donors at equatorial sites. The fusion of the two TBP fragments occurs at axial and equatorial sites forming the Co-Co axis as in the D_{2d} solution structure of $[Co_2(CO)_8]$. Again the Co-Co distance of 2.635(2)Å is significantly longer than in the CO bridged complexes just discussed but is significantly shorter than that found in **2.6b**.

In $[Co_2(CO)_4\{\mu\text{-}CH_3N[P(OCH_3)_2]_2\}_2]$[23], which contains only terminal carbonyls, the cobalt atoms exhibit distorted TBP and SP geometry. At the TBP cobalt atom a carbonyl and the other cobalt atom occupy axial positions and the two

Table 2.3: Cobalt-cobaltdistances in CO bridged and nonbridged derivatives of $[Co_2(CO)_8]$

$[Co_2(\mu\text{-}CO)_2(CO)_{6-2n}(\mu\text{-}LL)_n]$

Complex	**Co-Co distance(Å)**	**Ref.**
$[Co_2(CO)_8]$	2.52	18
$[Co_2(CO)_4(dppm)_2$	2.444(2)	this work
$[Co_2(CO)_4(eLTTP)]$	2.513(4)	17
$[Co_2(CO)_4(f_4fars)_2]$	2.482(4)	25
	$[Co_2(CO)_{8-2n}(\mu\text{-}LL)_n]$	
$[Co_2(CO)_4(dppm)_2]$	2.809(6)	this work
$[Co_2(CO)_4$ $\{CH_3N[P(OCH_3)_2]_2\}_2]$	2.698(1)	23
$[Co_2(CO)_4$ $\{(CH_2O)_2PN(Et)P(OCH_2)_2\}_2$	2.635(2)	22
$[Co_2(CO)_4$ $(\mu\text{-}N_2C_6H_4\text{-}4\text{-}CH_3)(dppm)]^+$	2.440(2)	24

phosphorus atoms and the other CO are at equatorial sites. The SP cobalt atom has a carbonyl in the apical position. The Co-Co distance of 2.698(1)Å, while shorter than in **2.6b**, is significantly longer than that found in **2.6a**.

2.4.3.2 Structure of 2.4d

Crystals of **2.4d** of suitable quality for X-ray diffraction[16] were obtained by passage of a stream of N_2 over a CH_2Cl_2/EtOH (1:1) solution of **2.4d**. An ORTEP representation of the cation, $[Co(CO)(\eta^2\text{-dppm})_2]^+$ and selected bond angles and distances can be found in Figure 2.4 and Tables 2.4 respectively. The structure of the cation in **2.4d** is very close to that found in $[Co(CO)(\eta^2\text{-dppm})_2]ClO_4$[26] prepared in a different manner. Bond lengths and angles in the two complexes agree within 0.02Å and 2.0° respectively. The cobalt atom in the cation displays distorted TBP geometry with phosphorus donors of each dppm at an equatorial and axial site respectively and a terminal CO at the remaining equatorial site.

The structure of the $[Co(CO)_4]^-$ anion, which exhibits tetrahedral geometry with an average C-Co-C angle of 109.5°, is in good agreement with the structure of the tetracarbonylate anion reported[27] previously.

2.4.3.2. Mechanism of formation of 2.6 and 2.4d

As mentioned in section 2.1 some interesting complexes have been identified from Co(II)/dppm/$NaBH_4$ reaction systems

Figure 2.4: Structure of the $[Co(CO)(\eta^2\text{-dppm})_2]^+$ cation

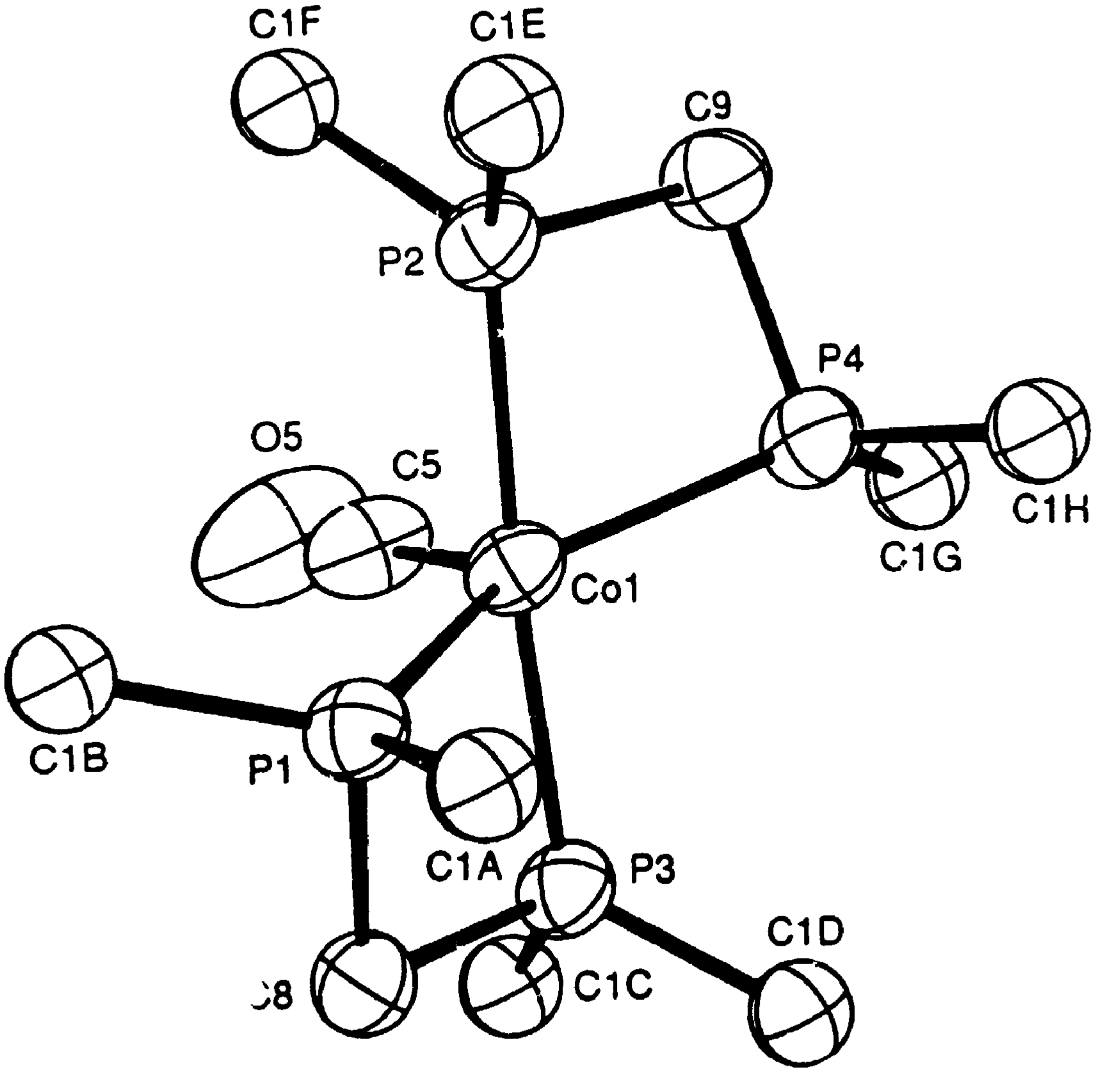


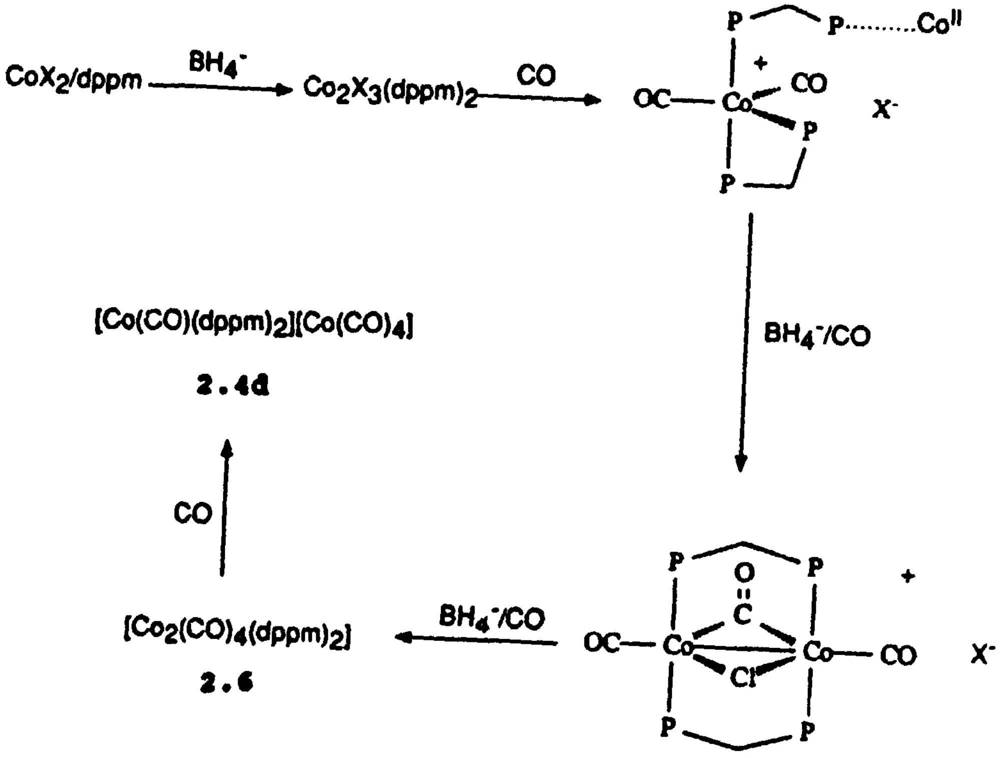
Table 2.4: Bond lengths (Å) and angles (°) in the coordination sphere of the cation $[\mathrm{Co(CO)}(\eta^2\text{-dppm})_2]^+$

(a) Bond Lengths	
Co1-P1	2.217 (3)
Co1-P2	2.208 (3)
Co1-P3	2.207 (3)
Co1-P4	2.227 (3)
Co1-C5	1.735 (12)
C5-O5	1.145 (14)
P1-C8	1.849 (10)
P3-C8	1.829 (10)
P2-C9	1.826 (10)
P4-C9	1.862 (10)
(b) Bond Angles	
axial to equatorial	
P2-Co1-C5	93.1 (3)
P2-Co1-P1	102.53 (3)
P2-Co1-P4	73.93 (11)
P3-Co1-C5	94.9 (3)
P3-Co1-P1	73.73 (11)
P3-Co1-P4	103.37 (11)
equatorial to equatorial	
P1-Co1-P4	133.73 (12)
P1-Co1-C5	113.8 (4)
P4-Co1-C5	112.5 (4)
axial to axial	
P2-Co1-P3	172.05 (11)

not involving CO. It was recognized[15] that Co(II) is unlikely to interact with CO and therefore reactions leading to reduced cobalt-phosphine-carbonyl complexes such as **2.6** and **2.4d** may proceed through intermediates such as those identified from Co(II)/dppm/$NaBH_4$ reactions not involving CO. Two species have been identified that act as substrates for the formation of cobalt-phosphine-carbonyl complexes. $[CoX(\eta^1\text{-dppm})_3]$ was shown to react cleanly with CO to give $[CoX(CO)_2(\eta^1\text{-dppm})_2]$ and an equivalent of dppm (Scheme 2.1). This reversibly loses halide and CO to give complexes $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]X$ and $[Co(CO)(\eta^2\text{-dppm})_2]X$ respectively. Thus the cationic portion of **4.5d** could be formed from $[CoX(\eta^1\text{-dppm})_3]$. However production of the anion $Co(CO)_4^-$ was not established to proceed under the $NaBH_4$ reducing conditions.

The mixed oxidation state dimer $[Co_2Cl_3(dppm)_2]$ is thought to have an A-frame type structure with bridging dppm ligands. It was shown to react with CO to produce $[(CO)_2(\eta^2\text{-dppm})Co(I)(\mu\text{-dppm})Co(II)]$[15] (Scheme 2.2). This was subsequently reduced with $NaBH_4$ under CO to give the $[Co_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]^+$ cation. This could then be further reduced by $NaBH_4$ in the presence of CO to give the binuclear complex **2.6**. In the presence of CO, complex **2.6** was shown to disproportionate to provide **2.5d**. This study has thus established the probable mechanism by which **2.6** and **2.5d** form and contradicts the original assumption that **2.5d** forms first in the sequence that produces **2.6**. In the formation of

Scheme 2.2: Formation of $[Co_2(CO)_4(\mu\text{-dppm})_2]$ from $[Co_2Cl_3(\mu\text{-dppm})_2]$



[CoRh(CO)$_3$(μ-dppm)$_2$] from Co(II)\Rh(III)\dppm\NaBH$_4$ reactions there is evidence for a [Rh(CO)(η^2-dppm)$_2$]Co(CO)$_4$ precursor (section 4.2).

Another species, tentatively identified as [Co$_2$H$_x$(μ-dppm)$_3$] has been isolated from Co(II)/dppm/NaBH$_4$ reactions. A X-ray structural determination of the compound has confirmed the [Co$_2$(μ-dppm)$_3$] core. Evidence for the hydrides comes from the presence of signals in the upfield region of the ^{1}H nmr spectrum of the complex. This complex was demonstrated by ^{31}P NMR to react with CO to produce [Co$_2$(CO)$_4$(dppm)$_2$] with loss of dppm.

2.4.4 Attempted synthesis of Co(μ-dppm)$_2$M heterobimetallics

2.4.4.1 Co(II)/MX$_n$/dppm/CO/BH$_4^-$ reactions

The success of Co(II)/dppm/CO/BH$_4^-$ reactions in producing Co(0) dppm bridged dimers inspired the attempted synthesis of heterobimetallic complexes containing Co(μ-dppm)$_2$M units by the reduction of mixtures of CoX$_2$ and MX$_n$ in the presence of CO and dppm. Thus such metal salts as NiCl$_2$, FeCl$_3$, ZnCl$_2$, CdCl$_2$, HgCl$_2$, CrCl$_3$, and PtCl$_2$(COD) were introduced. The ^{31}P nmr spectra of the reaction mixtures in all cases revealed a complex mixture of phosphorus containing species but no Co(μ-dppm)M type species were detected. The only successful reaction was that of equimolar amounts of CoCl$_2$ and RhCl$_3$ with NaBH$_4$ in the presence of dppm and CO which gave [CoRh(CO)$_3$(μ-dppm)$_2$] in acceptable yields[28].

2.4.4.2 Chemistry of the $[Co(CO)(dppm)_2]^+$ cation

The current interest in ligand activation by a heterobimetallic unit has prompted research into the synthesis of heterobimetallics stabilized by bridging phosphines. Great success has been achieved in making $MM^1(\mu$-dppm$)_2$ complexes (M=Rh or Ir) by opening of the $M(\eta^2$-dppm$)_2$ ring in $[M(CO)(dppm)_2]^+$ complexes[29]. As a logical extension, the reactivity of the analogous cobalt cation **2.4** towards numerous metal complexes was investigated. Various species including MCl_2 salts (M=Ni,Hg,Zn) $PtCl_2(COD)$, and $Cu(CH_3CN)_4^+$ were refluxed with $[Co(CO)(dppm)_2]BPh_4$, under a CO atmosphere, for extended periods of time. In all cases, ^{31}P nmr spectra of the reaction solutions reveal that the main phosphorus containing species present is the unreacted cation $[Co(CO)(dppm)_2]^+$.

$[M(CO)_6]$ complexes (M=Cr,Mo,W) and $[Fe_2(CO)_9]$ were also refluxed with **2.4e** with similar results. In the case of complexes $[M(CO)_6]$ the low reactivity may be due to the difficulty of dissociation of CO ligands from $[M(CO)_6]$. Thus the complex $[Mo(CO)_3(CH_3CN)_3]$ was prepared according to a literature method[30] in order to introduce labile leaving groups. This was refluxed with **2.4e** and did react, but the ^{31}P NMR spectrum of the reaction solution gave no evidence for formation of a complex containing the $Co(\mu$-dppm$)Mo$ unit.

The stability of the four membered chelate rings in $[Co(CO)(\eta^2$-dppm$)_2]^+$ is surprising given the lability of analogous rhodium and iridium complexes. The reason for the difference in reactivity may be due to the larger size of rhodium and iridium, which would create more ring strain in the chelate rings, and the tendency of rhodium and iridium to form 16 electron species, which would make the dissociation of a phosphorus donor from $[M(CO)(dppm)_2]^+$ more favourable.

The attempts at synthesizing cobalt-dppm bridged heterobimetallics from **2.4e** were made prior to recognition that both of the η^2-dppm rings in **2.5** can be sequentially opened with CO and halide to give ultimately $[CoX(CO)_2(\eta^1\text{-}dppm)_2]$[15]. Subsequently, heterobimetallic complexes have been prepared by the addition of metal complexes to solutions of the above species formed in situ. For example, addition of $[RhCl(CO)_2]_2$ to these solutions provides $[CoRh(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]^+$ [15] which has also been prepared by the reaction of $[CoRh(CO)_3(dppm)_2]$ with $HgCl_2$ or $CHCl_3$ (section 4.4).

The recognition that $[Co(CO)(dppm)_2][Co(CO)_4]$ reacts to form $[Co_2(CO)_4(dppm)_2]$, led to the conclusion that a strongly basic metal fragment is required to effect the nucleophillic displacement of a phosphorus donor from $[Co(CO)(dppm)_2]^+$, which is necessary for the ring opening reaction. Subsequently complexes $[CoM(CO)_5(\mu\text{-}dppm)_2]$ (M=Mn,Re) were prepared from $[Co(CO)(dppm)_2]^+$ and $[M(CO)_5]^-$ (section 5.2).

2.5 Experimental

All preparations are given using $CoBr_2 \cdot 6H_2O$ as reagent. Similar results were obtained using the chloride salt in all cases.

$[CoH(CO)(PPh_3)_3]$ 2.1

A solution of $NaBH_3CN$ (0.359g) in EtOH (10mL) deoxygenated by bubbling N_2 was added to a CO saturated solution of $CoBr_2 \cdot 6H_2O$ (0.62g) and PPh_3 (2.17g) in C_6H_6/EtOH (30mL,1:1) over a period of 10 minutes. The solution was allowed to stir under a stream of CO for an additional 30 min. and was filtered. The orange filtrate was concentrated to approximately one half its original volume with N_2 causing orange crystals of 2.1 to precipitate.

Yield : 45% Anal. calc. for $C_{55}H_{46}CoOP_3$: C,75.51: H,5.30

Found : C,75.78; H,5.42.

Spectroscopic data : NMR; $\delta^{31}P(CH_2Cl_2) = 55.6$,

IR(Nujol) : $\nu(CO) = 2020(w), 1909(s), 1865(w)\ cm^{-1}$.

$[Co(CO)(\eta^2\text{-dppe})_2]BH_3CN$ 2.2a

A solution of $NaBH_3CN$ (0.239g) in EtOH (10mL) deoxygenated by bubbling N_2 was added to a CO saturated solution of $CoBr_2 \cdot 6H_2O$ (0.418g) and dppe (1.00g) in C_6H_6/EtOH (20mL,1:1) over a period of 10 minutes. The solution was allowed to stir under a stream of CO for an additional hour and the solution was filtered. Yellow-orange crystals of 2.2a precipitated overnight from the filtrate kept at 0° C.

Yield : 30% Anal. calc. for $C_{54}H_{51}BCoNOP_4$: C,70.22; H,5.57; N,1.52 Found : C,70.10; H,5.63; N,1.65.

Spectroscopic data : NMR; $\delta^{31}P(CH_2Cl_2)$= 69.7, IR(Nujol) : ν(BH)= 2305(m), 2260(m); ν(CN)= 2200(w), 2155(w); ν(CO) = 1940(s)cm^{-1}.

[Co(CO)(η^2-dppe)$_2$]BPh$_4$ 2.2b

To the reaction filtrate containing **2.2a** from above was added excess $NaBPh_4$. The resulting orange precipitate was recrystallized from CH_2Cl_2/EtOH to give large orange crystals of **2.2b**.

Yield : 55% Anal. calc. for $C_{77}H_{68}BCoOP_4 \cdot CH_2Cl_2$: C,72.74; H,5.48 Found : C,72.43; H,5.43.

Spectroscopic data : NMR; $\delta^{31}P$(same as **2.2a**). IR(Nujol) : ν(CO)= 1940 cm^{-1}

[Co(CO)$_2$(η^1-dppm)(η^2-dppm)]BPh$_4$ 2.3

A solution of $NaBH_4$ (0.985g) in EtOH (10mL) deoxygenated by bubbling N_2 was added to a CO saturated solution of $CoBr_2 \cdot 6H_2O$ (0.426g) and dppm (1.00g) in C_6H_6/EtOH (20mL,1:1) over a period of 10 minutes. The solution was allowed to stir under a stream of CO for an additional 2 hours and the solvent was removed by vacuum. The residue was washed with EtOH (25mL) and the slurry was filtered. Excess $NaBPh_4$ was added to the orange filtrate producing a thick orange precipitate. The precipitate was filtered off and recrystallized from CH_2Cl_2/EtOH to give a crystalline mixture of **2.3** and **2.5d**. Yellow crystals of **2.3** were handpicked for analysis.

Yield : 10% (estimated from integration of ^{31}P NMR spectrum of a weighed mixture of **2.3** and **2.5d**) Anal. calc. for $C_{76}H_{64}BCoO_2P_4 \cdot 1/4CH_2Cl_2$: C,74.81; H,5.31 Found : C,75.01; H,5.33.

Spectroscopic data : NMR (CD_2Cl_2); δ^{31}P(-87°C, resonances assigned as in Figure 2.1) = 46.9[ddd, $J(P_AP_B)$= 50.7 Hz, $J(P_AP_C)$= 109 Hz, $J(P_AP_D)$= 58.0 Hz, P_A], -33.9[d, $J(P_AP_B)$= 50.7 Hz, P_B], 10.2[dd, $J(P_AP_C)$= 109 Hz, $J(P_CP_D)$= 113 Hz, P_C], -23.6[dd, $J(P_AP_D)$= 58.0, $J(P_CP_D)$=113 Hz, P_D]. IR(Nujol) : ν(CO) = 1990(s), 1925(s) cm^{-1}.

Green compound <u>2.4a</u>^{1}

A solution of $NaBH_3CN$ (0.250g) in EtOH (15 mL) deoxygenated by bubbling N_2 was added to a CO saturated solution of $CoBr_2 \cdot 6H_2O$ (0.42g) and dppm (1.00 g) in C_6H_6/EtOH (15 mL,2:1) over a period of 15 minutes. The solution was allowed to stir under a stream of CO for an additional two hours and was filtered. The red filtrate was stored at 0°C for 24 hours during which time green crystals of **2.4a**^{1} precipitated.

Yield : 25% Anal. calc. for $C_{52}H_{47}BCoNOP_4$: C,69.74; H,5.29; N,1.56 Found : C,69.18; H,5.42; N,1.45.

Spectroscopic data : NMR; δ^{31}P(same as **2.4a**). IR : ν(CO) = 1930 cm^{-1}.

$[Co(CO)(\eta^2\text{-dppm})_2]BH_3CN$ 2.4a

A solution of $NaBH_3CN$ (0.248g) in EtOH (10mL) deoxygenated by bubbling N_2 was added to a CO saturated solution of $CoBr_2 \cdot 6H_2O$ (0.430g) and dppm (1.02g) in C_6H_6/EtOH (20mL,1:1) over a period of 10 minutes. The solution was allowed to stir under a stream of CO for an additional hour and was filtered. The red filtrate was kept at 0°C for several days during which time red crystals of **2.4a** precipitated.
The same complex was prepared by dissolving complex **2.4a**[1] in EtOH and allowing hexane to diffuse into the red EtOH solutions over a period of several days to give crystals of **2.4a**.

Yield : 35% Anal. calc. for $C_{52}H_{47}BCoNOP_4$: C,69.74; H,5.29; N,1.54 Found : C,69.80; H.5.25; N,1.51.

Spectroscopic data : NMR; $\delta^{31}P(CH_2Cl_2/CD_3CN) = -5.1$. IR: $\nu(BH) = 2300(m), 2265(w)$; $\nu(CN) = 2200(w), 2160(w)$; $\nu(CO) = 1929\ cm^{-1}$.

$[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$ 2.4e

A large excess of $NaBPh_4$ was added to the reaction mixture, from above, containing **2.4a**. The resulting orange precipitate was filtered from solution and recrystallized from CH_2Cl_2/EtOH.

Yield : 65% Anal. calc. for $C_{75}H_{64}BCoO_2P_4$: C,75.64; H,5.42 Found : C,75.85; H,5.42.

Spectroscopic data : NMR; $\delta^{31}P$(same as **2.4a**). IR(Nujol) : $\nu(CO) = 1929\ cm^{-1}$.

$[Co(CO)(dppm)_2][Co(CO)_4]$ 2.4d

To a stirred, CO-saturated solution of 0.44g (1.35 mmol) of $CoBr_2 \cdot 6H_2O$ and 1.04g (2.70 mmol) of dppm in $C_6H_5CH_3$/EtOH (20 mL,1:1) was added a suspension of 0.116g (3.07 mmol) of $NaBH_4$ in EtOH (10 mL) dropwise over a period of 30 minutes. N_2 was passed through the EtOH suspension during the addition. A slow CO stream was passed through the stirring solution for an additional 3 hours followed by filtration. The bright red filtrate was concentrated to approximately half its original volume by a N_2 stream. The red crystals that had precipitated during this time were filtered off and washed with hexane.

Yield = 42% Anal. calc. for $C_{55}H_{44}Co_2O_5P_4$: C,64.34; H,4.32

Found : C,65.05; H,4.48.

Spectroscopic data : NMR; $\delta^{31}P$(same as 2.4a), $\delta^{1}H(d_6$-acetone)= 4.60[m, PCH_2P]. IR(Nujol) : ν(CO)= 2006(w), 1943(s), 1904(s), 1889(s), 1864(s) cm^{-1}.

$[Co_2(CO)_4(dppm)_2]$ 2.6

A suspension of $NaBH_4$ (0.183g) in EtOH (15mL) through which a slow stream of N_2 was passed, was added dropwise over a period of 30 minutes to a CO-saturated solution of $CoBr_2 \cdot 6H_2O$ (0.438g) and dppm (2.01g) in C_6H_6/EtOH (30mL,1:1). The mixture was allowed to stir for 2 hours under a slow stream of CO and the solvent was removed by vacuum. The residue was boiled with C_6H_6 (10mL) for 2 minutes to convert any of 2.5e present to the title complex and again the solvent was removed by vacuum. The solid was washed with EtOH (40 mL) and recrystallized from CH_2Cl_2/EtOH to give a crystalline mixture of **2.6a** and **2.6b** used for variable temperature, multinuclear NMR and variable temperature solution IR studies. Crystals of **2.6a** and **2.6b** were handpicked for elemental analysis and IR spectra.

Yield: 60%, **2.6a** Anal. calc. for $C_{54}H_{44}Co_2O_4P_4 \cdot 1/2CH_2Cl_2$: C,62.87; H,4.36 Found : C,62.70 ; H,4.35.

Spectroscopic data : NMR(CD_2Cl_2); $\delta^{31}P$(-70°C)= 44.8, $\delta^{13}C$(-70°C)= 206.0(terminal CO), 244.3(μ-CO), $\delta^{1}H$(-90°C)= 2.84, 3.71(PCH_aH_b). IR(Nujol) : ν(CO)= 1945(s), 1902(s), 1767(m), 1755(s) cm^{-1}.

2.6b Anal. calc. for $C_{54}H_{44}Co_2O_4P_4$: C,64.94; H,4.44 Found : C,65.82 ; H,4.75.

Spectroscopic data : NMR(CD_2Cl_2); $\delta^{31}P$(-70°C)= 37.4, $\delta^{13}C$(-70°C)= 213.95(CO), $\delta^{1}H$(-90°C)= 3.89(CH_2). IR(Nujol) : ν(CO)= 2000(m), 1951(s), 1941(s), 1929(s) cm^{-1}.

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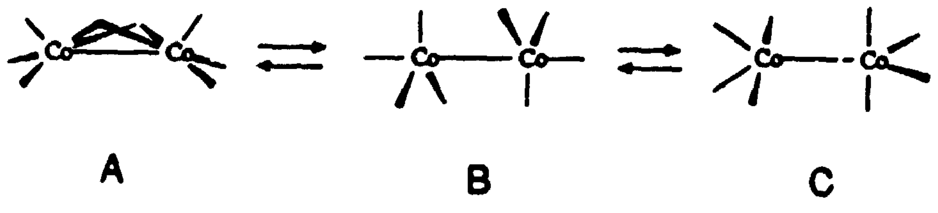
Chapter 3 : Solution Dynamics and Chemistry of $[Co_2(CO)_4(\mu$-dppm$)_2]$ Isomers

3.1 Introduction

$[Co_2(CO)_8]$ is a historically important species in organometallic chemistry as it is one of the first binary carbonyl complexes identified[1]. It is also of interest because it is a precursor for catalytically important species such as $[HCo(CO)_4]$ as illustrated below in Equation 3.1 [2].

$$[Co_2(CO)_8] + H_2 \rightarrow 2[HCo(CO)_4] \qquad (3.1)$$

In the solid state $[Co_2(CO)_8]$ has a C_{2v} stucture with a pair of bridging carbonyls[3]. In solution, in addition to the C_{2v} structure, IR evidence has suggested the presence of two non-bridged forms with D_{3d} and D_{2d} symmetry[4]. The interconversions of these isomers (Equation 3.2) has been the subject of a detailed investigation however the interconversions are too rapid even at -150° C for ^{13}C NMR to be of any use in determining the mechanism of fluxionality.



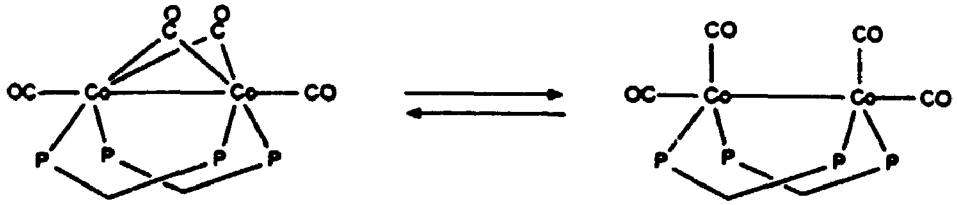
(3.2)

$[Co_2(CO)_8]$ has also served as a substrate for phosphine substitution and a variety of products have been made in this way (section 1.2.5.2). Generally with monodentate phosphines disproportionation occurs in polar solvents to give $[Co(CO)_{5-n}L_n]^+[Co(CO)_4]^-$ complexes while in nonpolar solvents $[Co_2(CO)_{8-n}L_n]$ complexes have been isolated. Substitution with bidentate phosphines has led to complexes of the type $[Co_2(CO)_4(\eta^2\text{-}PP)_2(\mu\text{-}PP)]^{2+}$, $[Co(CO)_3(PP)]^+[Co(CO)_4]^-$ or $[Co_2(CO)_{8-2n}(PP)_n]$ depending on the reaction conditions. Of the latter complexes, species with n=1 are known for dppm and related phosphines[5]. The ligand is found in a bridging mode in a doubly CO bridged structure resembling the solid state structure of $[Co_2(CO)_8]$. A second substitution to provide $[Co_2(\mu\text{-}PP)_2(CO)_4]$ complexes is generally observed only for ligands containing strong electron withdrawing substituents on the phosphorus donor such as $(RO)_2PN(R^1)P(OR)_2$ ($R=CH_2$,Me or Pr^i [6], $R=R^1=Me$[7]). Substitution in $[Co_2(\mu\text{-}CO)_2(CO)_2(norbornadiene)_2]$ by the tetradentate ligand $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$[8] provides the complex meso-$[Co_2(\mu\text{-}CO)_2(CO)_2(eLTTP)]$. With the bidentate ligand $CH_3N(PF_2)_2$ substitution of six carbonyls can be achieved to provide $[Co_2(\mu\text{-}PP)_3(CO)_2]$ complexes[9]. $[Co_2(CO)_4(PP)_2]$ type complexes are also known in which the phosphine adopts a chelating mode of coordination[10].

$[Co_2(CO)_8]$ and derivatives are very reactive to oxidative addition and in general metal-metal bond cleavage of $[Co_2(CO)_8]$ to give Co(II) fragments is observed. For example, reaction with X_2 (X=Cl,Br,I) agents results in the formation of Co(II) halides with loss of CO^{11}. Reaction of $[Co_2(CO)_8]$ with acetylenes leads to $[Co_2(CO)_6C_2RR^1]$ complexes in which the metal-metal bond is retained[12]. Incorporation of a bridging phosphine into $[Co_2(CO)_8]$ has allowed the study of the metal-metal bond in a Co(0) dimer. $[Co_2(CO)_6(\mu\text{-dppm})]$ has been reacted with numerous oxidizing agents with retention of the dinuclear unit. Two (μ-CH_2) units from diazomethane have been incorporated into the above species for example[13]. Reaction of I_2 and elemental sulphur in the presence of an equivalent of bridging phosphine produces $[Co_2(\mu\text{-X})(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-PP})(CO)_2]^{n+}$ (X=S,PP=dppm,n=0; X=I,PP=dppm or dmpm,n=1) complexes[14]. Similar complexes $[Co_2(\mu\text{-X})(\mu\text{-CO})(\mu\text{-PP})_2(CO)_2]^+$ (X=Cl,Br,I) are obtained from the reaction of $[Co_2(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]$ with CCl_4, Br_2 and Cl_2 respectively[15].

3.2 Dynamics and thermodynamics of equilibrium between bridged and non-bridged isomers of $[Co_2(CO)_4(\mu\text{-dppm})_2]$

Complexes $[Co_2(\mu\text{-CO})_2(\mu\text{-dppm})_2(CO)_2]$ **3.1a** and $[Co_2(\mu\text{-dppm})_2(CO)_4]$ **3.1b** are both readily soluble in most organic solvents and thus characterization by NMR and solution FTIR techniques was possible. These techniques were employed to study the dynamics and thermodynamics of the equilibrium between the carbonyl bridged isomer **3.1a** and the nonbridged isomer **3.1b** (Equation 3.3) and the analogous dmpm complexes[16].



(3.3)

3.2.1 Variable temperature ^1H, ^{13}C and ^{31}P NMR investigation

The ^{31}P NMR spectrum of either mixtures of 3.1a and 3.1b or of pure 3.1a or 3.1b exhibit singlets in organic solvents indicating an equilibrium between the two limiting structures which is rapid on the NMR time scale. Similarly, the ^{13}C and ^1H NMR spectrum of mixtures reveal singlets in the carbonyl and PCH_2P regions of the spectrum respectively. Thus a variable temperature multinuclear NMR study was pursued in order to establish the mechanism of fluxionality.

The decoalesence of the room temperature ^{31}P singlet is shown in Figure 3.1. Two resonances appear for each of 3.1a and 3.1b at lower temperatures. The decoalescence of the carbonyl region of the ^{13}C NMR spectrum of 3.1 can be seen in Figure 3.2. A singlet at δ=221.6 resolves into three resonances at -92°C. The sharp resonance at δ=247 is assigned to the bridging carbonyls on the limiting structure

Figure 3.1: Variable temperature ^{31}P NMR spectra of $[Co_2(CO)_4(\mu\text{-}dppm)_2]$

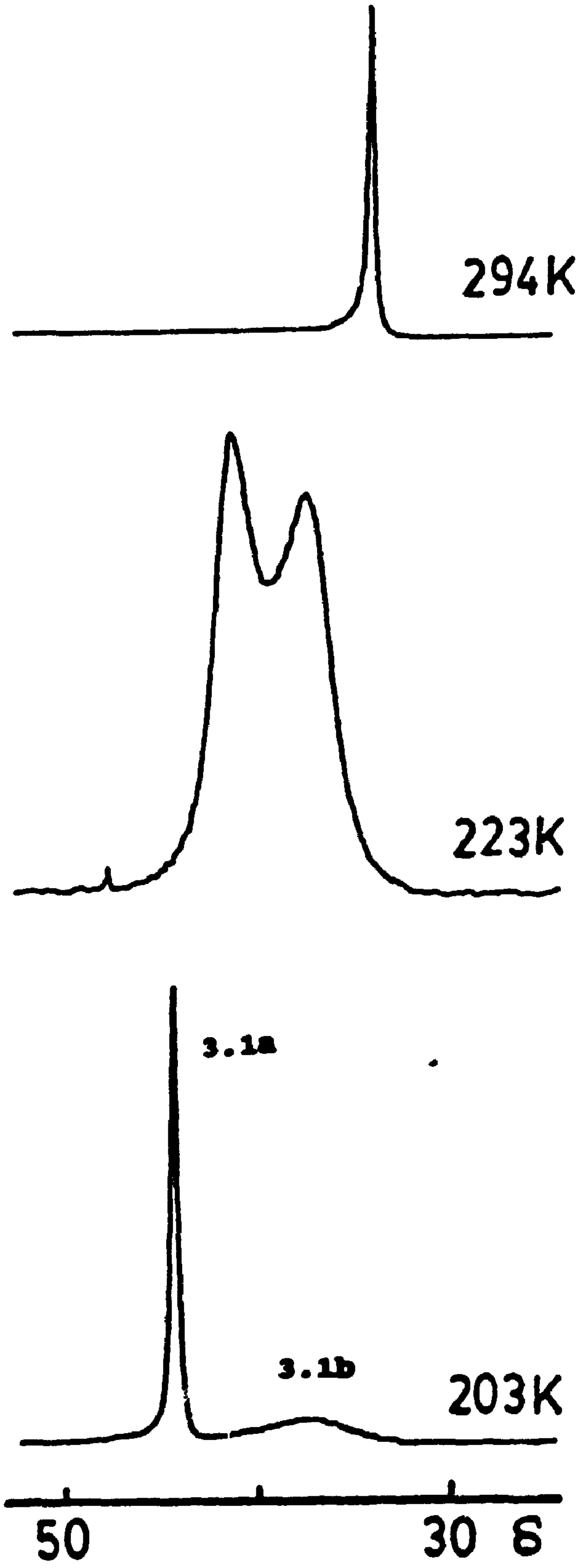
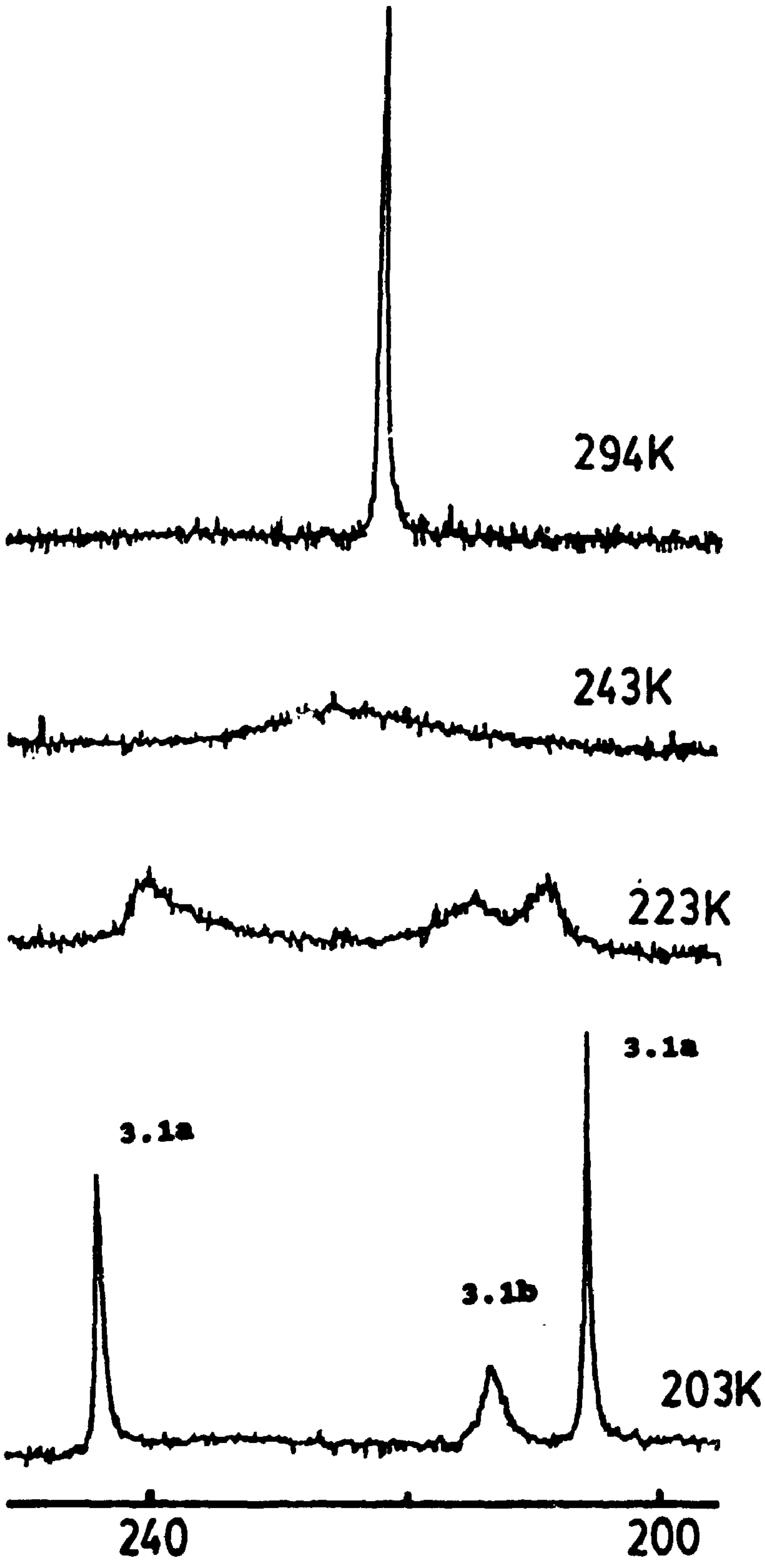
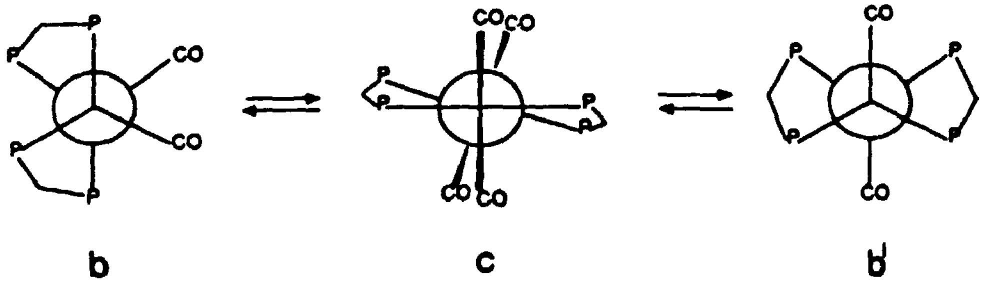


Figure 3.2: Variable temperature ^{13}C NMR spectra of $[Co_2(CO)_4(\mu\text{-dppm})_2]$



3.1a. This assignment is based on the tendency of bridging carbonyls to be shifted downfield relative to terminal carbonyls and the similarity to shifts observed for μ-CO groups in related molecules such as $[Co_4(CO)_8(\mu\text{-dppm})_2]$ and $[Co_2(CO)_6(\mu\text{-dppm})]^{17}$. The other sharp signal at δ=205 integrates to the former 1:1 and thus is assigned to the terminal carbonyls on **3.1a**. The broad resonance at δ=214 is assigned to the carbonyl groups of **3.1b**. The solid state structure indicates chemical inequivalence of the carbonyls occupying axial and equatorial sites on the TBP coordinated cobalt atoms and thus more than one resonance is expected. The broadness of the signal at 214 ppm is thus associated with a second type of fluxionality in the non-bridged isomer which makes all the carbonyls in **3.1b** equivalent on the NMR time scale. This is also consistent with the variable temperature ^1H NMR results as will be discussed. The equilibrium between **3.1a** and **3.1b** (equation 3.3) most likely involves the windshield wiper type motion exchanging terminal carbonyls on one cobalt atom to the other cobalt atom via a CO bridged intermediate like that in **3.1a**.

The ^1H NMR spectrum of **3.1** exhibits a singlet in the dppm CH_2P_2 methylene region of the spectrum. At lower temperatures two broad resonances assigned to the methylene protons of **3.1a** and a single broad resonance assigned to **3.1b** are observed. The solid state structure of **3.1b** indicates chemical inequivalence of the methylene protons on each dppm and thus a $CH_aH_bP_2$ type spectrum is expected as seen for 3.1a at the same temperature. This confirms that a second form of fluxionality with a much lower activation energy must occur within 3.1b. Equation 3.4 illustrates a possible mechanism for this fluxionality making all carbonyls and CH_2P_2 protons equivalent. The structures are shown as Newman projections along the Co-Co axis.



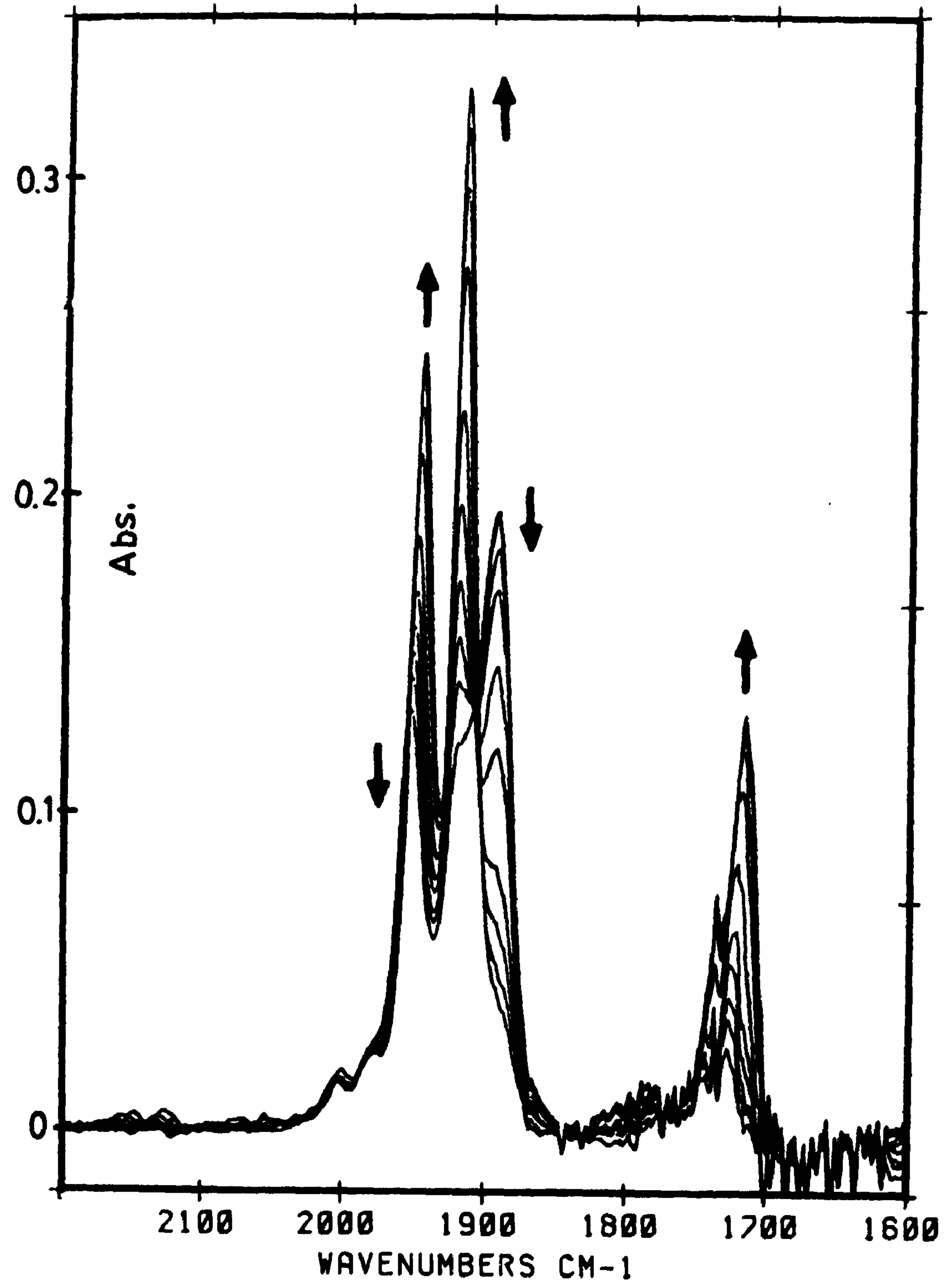
(3.4)

The reversible b⇌c reaction is most reasonable as c has an analogous structure to the D_{2d} isomer (c isomer in eqn 3.1) of $[Co_2(CO)_8]$. The formation of of a third isomer b^1 through c is possible but not necessary to explain the NMR data. A variable temperature, multinuclear NMR investigation of $[Co_2(CO)_4(\mu\text{-dmpm})_2]$ isomers[16] has produced results consistent with that found for 3.1.

3.2.2 Variable temperature IR study

The thermodynamics of the 3.1a⇌3.1b equilibrium were determined by variable temperature solution FTIR spectroscopy (Figure 3.3). The room temperature spectrum exhibits strong terminal ν(CO) stretches with increasing amounts of ν(μ-CO) signals at with lowering temperature

Figure 3.3: Variable temperature solution FTIR spectra of $[Co_2(CO)_4(\mu\text{-dppm})_2]$



demonstrating that the unbridged form is favoured at higher temperatures. Equilibrium constants, K, were determined from these spectra over the temperature range 190-301 K and a plot of *lnK* vs 1/T resulted in a good linear fit giving an estimate of ΔH and ΔS according to the equation :

$$\ln K = -\Delta H/RT + \Delta S/R$$

The thermodynamic data for **3.1**, anolagous dmpm isomers, and $[Co_2(CO)_8]$ are presented in Table 3.1. The enthalpy term strongly favours the bridged form while the entropy term strongly favours the unbridged form in each case. However this trend is least evident with $[Co_2(CO)_8]$.

3.3 Chemistry of $[Co_2(CO)_4(\mu\text{-dppm})_2]$ 3.1

Compound **3.1** is very reactive towards oxidation and complexes resulting from reactions with reagents such as $HgCl_2$, $CHCl_3$, $CHBr_3$, I_2, MeI, S_8, HBF_4, PPh_2H and H_2 in refluxing C_6H_6 have been characterized as seen in Scheme 3.1. In addition **3.1** reacts with PPh_2Cl and C_2H_2.

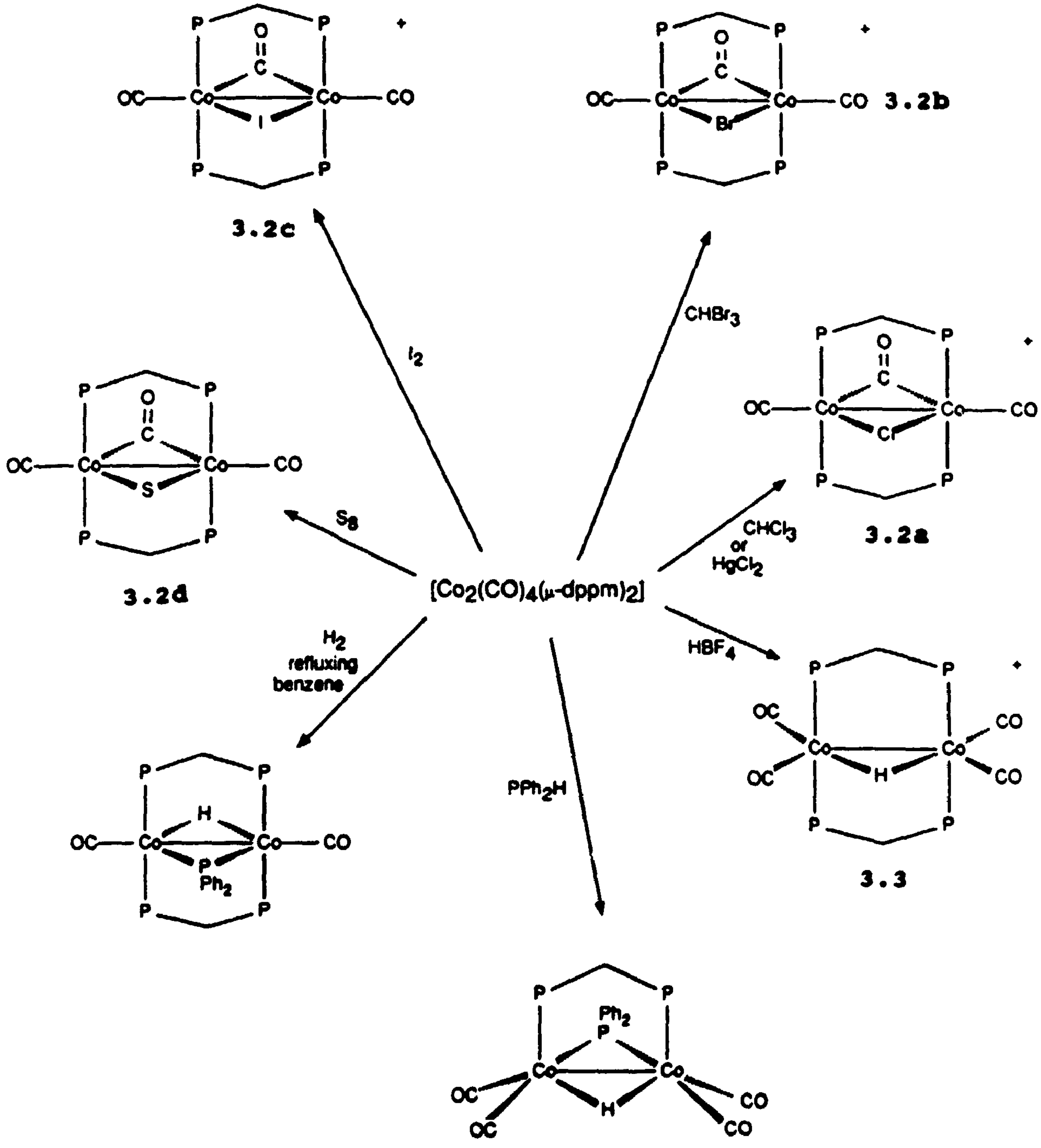
3.3.1 $[Co_2(\mu\text{-X})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]^{n+}$ complexes

A number of complexes of formula $[Co_2(\mu\text{-X})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]^{n+}$ [X=Cl(**3.2a**),Br(**3.2b**),I(**3.2c**),n=1; X=S(**3.2d**),n=0] have been prepared by oxidation of **3.1** with the appropriate reagent. Complexes **3.2a-c** each exhibit two terminal ν(CO) stretches and a ν(μ-CO) stretch their IR

Table 3.1 : Thermodynamic and Kinetic Data for the Carbonyl-Bridged Nonbridged Isomerism

complex	ΔH/kJ mol^{-1}	ΔS/J K^{-1}mol^{-1}	ratio b:nb		ΔG^{*}/kJ mol^{-1}
			298K	190K	
$[Co_2(CO)_8]$	+5.6	+21	44:56	74:26	27
$[Co_2(CO)_4(\mu\text{-dppm})_2]$	+22.1(1.5)	+102(8)	3:97	85:15	41.5(1.0)
$[Co_2(CO)_4(\mu\text{-dmpm})_2]$	+26.3(2.1)	+107(13)	9:91	98:2	47(1)

Scheme 3.1: Addition chemistry of **3.1**



spectra, consistent with the above formulation. All the complexes are readily soluble in chlorinated solvents and characterization by ^{31}P and ^{1}H NMR was possible. They all exhibit a singlet in their ^{31}P NMR spectra consistent with a mirror plane bisecting the dppm ligands through the methylene carbon, as suggested in the above formulation, making all four phosphorus atoms chemically equivalent. The small range of shifts observed for these complexes is significantly downfield of those observed for **3.1**. This downfield shift is indicative of deshielding of the ^{31}P nucleus concurrent with the increase in the oxidation state of the metal which results in reduced electron density on the phosphorus atom either through reduced M→P π backbonding or increased polarization of the phosphorus lone pair by the more electronegative M(1) centre.

The ^{1}H NMR spectra of the complexes exhibit an AB pattern for the $CH_aH_bP_2$ methylene protons of dppm. The asymmetry is introduced by the formation of the $Co_2(\mu\text{-}X)(\mu\text{-}CO)$ double bridge which makes the methylene protons inequivalent.

The structure of **3.3c**, prepared by the addition of I_2 to a solution of $[Co_2(CO)_6(\mu\text{-dppm})]$ and an equivalent of dppm, and the structure of the analogous $(OMe)_2PN(Et)P(OMe)_2$ complex have been determined crystallographically[14,15]. In contrast to complexes **3.1a** and **3.1b**, the phosphines in **3.2c** are oriented trans to each other. The similarity in the spectroscopic properties of **3.2a**-**3.2d** suggests that they have similar structures.

Similar structures are seen in numerous Rh(I) and Ir(I) complexes of the type $[M_2(\mu\text{-X})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]^+$ [18]. In many cases the (μ-CO) group results from the reversible addition of an equivalent of CO to $[M_2(\mu\text{-X})(\mu\text{-dppm})_2(CO)_2]^+$ with concurrent M-M bond formation. This behaviour is not observed in the analogous homodinuclear cobalt complexes discussed in this chapter reflecting the reluctance of cobalt to form 16 electron complexes as required in the $[M_2(\mu\text{-X})(\mu\text{-dppm})_2(CO)_2]^+$ formulation.

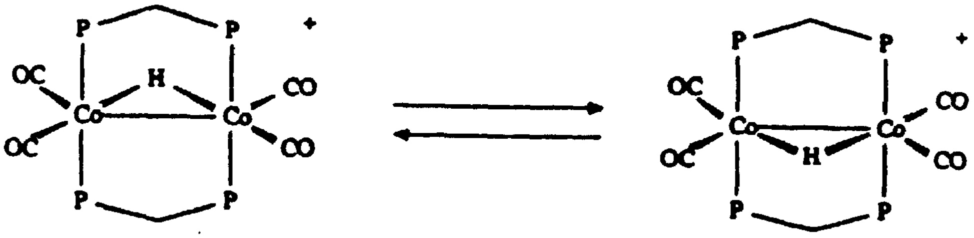
The complex $[Co_2(\mu\text{-S})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]$ **3.2d**, had been previously prepared from the reaction of $[Co_2(CO)_6(\mu\text{-dppm})]$ with S_8 in the presence of an equivalent of dppm[14]. Analogous structures are also found in $[CoRh(\mu\text{-S})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]$ (section 4.4.1.2) and $[Ir_2(\mu\text{-S})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]$[19]. Complexes containing 16 electron metal centres $[M_2(\mu\text{-S})(\mu\text{-dppm})_2(CO)_2]$ (M=Rh or Ir) are also known[19].

3.3.2 $[Co_2(\mu\text{-H})(\mu\text{-dppm})_2(CO)_4]X$ (X=BF_4,3.3a;X=BPh_4,3.3b)

Reaction of **3.1** with HBF_4(aq) results in the formation of **3.3a** in high yield. Addition of BPh_4^- and EtOH to CH_2Cl_2 solutions of **3.3a** results in precipitation of **3.3b** in high yield. The IR spectrum of **3.3** exhibits four ν(CO) stretches in the range 2000 to 1923 cm^{-1} consistent with four terminal carbonyls as in the formula given above. ^1H NMR evidence for the presence of the hydride will be discussed shortly.

The compound is readily soluble in CH_2Cl_2 and thus characterization by NMR was possible. The ^{31}P NMR spectrum of **3.3** exhibits a singlet at δ=49.6 which agrees with the other symmetrical Co(I) dppm bridged structures of **3.2a-d**. The ^{1}H NMR spectrum of **3.3** gives a quintet at δ=-10.8 which can be attributed to the strongly shielded environment experienced by a metal hydride. The multiplicity of the signal is indicative of $^{2}J(PH)$ coupling of a hydride to four equivalent phosphorus atoms indicating a (μ-H) group. The magnitude of the coupling of 13 Hz agrees with $^{2}J(PH)$ values in other hydrido-cobalt-phosphine complexes such as $[CoHX(\eta^2\text{-dppm})_2]^+$ [20].

A singlet is observed in the region expected for the CH_2P_2 protons on dppm whereas an AB pattern would be expected for the CH_aH_b protons in the suspected solid state structure of **3.3**. The structure of the related $[Co_2(\mu\text{-H})(\mu\text{-PP})(CO)_4]^+$ $[PP=(RO)_2PN(Et)P(OR)_2]$ complex, prepared from the reaction of $Co_2(\mu\text{-PP})_2(CO)_4$ with HBF_4, has been determined crystallographically[21]. The structure contains four terminal CO ligands, a bridging hydride, and phosphines oriented trans on each cobalt atom. Presumably this type of structure is found in **3.3** in which case the chemical inequivalence of the CH_2P_2 protons is evident. A ^{13}CO enriched sample of **3.3a** was made by the reaction of HBF_4 with a ^{13}CO enriched sample of **3.1**. The presence of the bridging hydride introduces asymmetry with respect to the terminal carbonyls, however a singlet is observed in the carbonyl region of the ^{13}C nmr spectrum of 3.3a at room temperature. The singlet at 199.1 ppm persists at lower temperatures with significant broadening at -90°C indicating the beginnings of decoalescence. Thus, the ^{13}C and ^{1}H NMR evidence point toward a low energy fluxional process making the dppm methylene protons and carbonyl ligands equivalent on the NMR time scale. The most likely mechanism is inversion of the $Co_2(\mu\text{-}H)$ group through the Co-Co axis (Equation 3.5).



(3.5)

This type of mechanism is also proposed for the fluxionality observed in $[CoRh(\mu\text{-}H)(\mu\text{-}dppm)_2(CO)_3]^+$(section 4.4.1.3.1).

The type of structure postulated for 3.3 and seen in the $(RO)_2PN(Et)P(OR)_2$ analogue is quite different from those seen in related homodinuclear complexes $[M_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]^+$ and $[M_2(\mu\text{-}H)(\mu\text{-}dppm)_2(CO)_2]^+$ (M=Rh[22] or Ir[23]) which are 16 electron complexes.

3.3.2.1 Reaction of 3.3 with acetylene

Complexes 3.3a and 3.3b react readily with acetylene at room temperature to give a complex 3.4 which is as of yet unidentified. The IR spectrum of 3.4 reveals both terminal and bridging carbonyl stretches. The ^{31}P NMR spectrum of 3.4 exhibits a singlet at 45.3 ppm which persists down to -80°C. No signals are observed in the upfield region of the ^{1}H NMR spectrum of 3.4 suggesting that a hydride ligand is not present. Also, the BPh_4^- protons are conspicuously absent in the ^{1}H NMR of 3.4 produced from the reaction of 3.3b with C_2H_2 and thus the complex is not ionic. One possible explanation for these ^{1}H NMR data is that the reaction of 3.3 with C_2H_2 proceeds with the elimination of a proton. Loss of the metal-hydride by insertion of acetylene into the metal-hydride to give a vinyl ligand, for example, would still give a cationic complex. The ^{1}H NMR of 3.4 also exhibits multiplets at 3.20 and 2.83 ppm with a combined intensity 10% that of the dppm phenyl protons as expected for chemically distinct methylene protons on dppm. Another multiplet appears at 3.84 ppm with intensity approximately 5% that of the dppm phenyl protons consistent with two acetylenic protons.

3.3.3 Reaction of 3.1 with MeI

3.1 is unreactive towards an excess of MeI at room temperature in CH_2Cl_2. Under U.V. irradiation, however, the addition of MeI to solutions of 3.1 results in rapid lightening of the dark red brown solution. A ^{31}P NMR spectrum of the reaction mixture exhibits three sets of resonances at δ=54.2(s,br), 50.6(s), and 39.0(s,br). The singlet at 50.6 ppm is attributed to the $[Co_2(\mu\text{-}I)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]^+$ cation which can be isolated from the reaction mixture with the addition of $NaBPh_4$. The similar shape and intensity of the remaining two resonances is suggestive of an asymmetric dppm bridged dimer possibly resulting from the addition of MeI across the Co-Co bond.

3.3.4 Reaction of 3.1 with PPh_2X (X= H,Cl)

Addition of a slight excess of PPh_2H to dark red-brown CH_2Cl_2 solutions of 3.1 is followed by a change in the colour of the solution to dark green over a period of hours. A ^{31}P NMR spectrum of the reaction mixture indicates the presence of three species. The excess of PPh_2H gives a singlet resonance at δ=-44.6. The remaining signals are attributed to a 1:1 mixture of free dppm (δ=-27.6) and $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)(CO)_4]$ [δ=55.8(d,$^2J\{PP\}$=94.6 Hz), 216(tr,$^2J\{PP\}$= 94.6Hz)]^{24}. The characterization of this complex, prepared previously^{24} and by another method in this work, is discussed in section 6.2.

The oxidative addition of PPh_2H to a dinuclear centre with formation of a $\mu\text{-}PPh_2$ group requires that dissociation of two, 2-electron donating ligands, as the bridging PPh_2^- ligand acts as a four electron donor. It is apparent that a dppm ligand, which fits this requirement, is lost rather than two carbonyls in the formation of the known $[Co_2(\mu\text{-}$

H)(μ-PPh_2)(μ-dppm)$(CO)_4$] species. This result is surprising given the known stability of M_2(μ-dppm) five membered rings. This behaviour is also noted for the reaction of 3.1 with acetylene (section 3.3.5).

The reason for the displacement of dppm rather than CO may be steric in nature. Thus, addition of PPh_2H to 3.1 is sterically hindered and this hindrance would be reduced more by loss of a bulky dppm ligand than by the loss of two CO ligands. It should be noted that [Co_2(H)(PPh_2)$(dppm)_2(CO)_2$] is a known stable complex (section 6.2) and so the selective loss of a dppm ligand in the present reaction may be attributable to kinetic control. The M_2(μ-PPh_2)$(\mu\text{-dppm})_2$ structure is also seen in the [Ni_2(μ-PPh_2)$(\mu\text{-dppm})_2(CO)_2]^+$ cation (section 6.2).

The reaction of PPh_2H with [CoRh$(CO)_3(\mu\text{-dppm})_2$] proceeds quite differently than that with 3.1 and [CoRh(μ-H)(μ-PPh_2)$(\mu\text{-dppm})_2(CO)_2$] is produced (section 4.4.1.4). The most obvious difference between the two substrates is the presence of a 16 electron rhodium centre in [CoRh$(CO)_3(\mu\text{-dppm})_2$] while in 3.1 both metal atoms have 18 electron counts. In [CoRh$(CO)_3(\mu\text{-dppm})_2$], oxidative addition of PPh_2H can be preceded by coordination of the phosphine as a two electron donor to the rhodium centre without loss of a ligand. This in some way may result in the eventual loss of a CO rather than a dppm ligand.

3.1 also reacts with H_2 in refluxing C_6H_6 to give [Co_2(μ-H)(μ-PPh_2)$(\mu\text{-dppm})_2(CO)_2$] in moderate yields. The synthesis and characterization of this and other μ-PPh_2 complexes is discussed in Chapter 6.

The addition of PPh_2Cl to solutions of 3.1 was pursued in nopes of isolating a complex of type $Co_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(\mu\text{-}dppm)_n$ which is related to the species discussed above by replacement of a μ-H by a μ-Cl group. The occurrence of a reaction was indicated by a change in the colour of the solution from dark red-brown to green. A ^{31}P NMR spectrum of the reaction solution shows a very complicated series of peaks and separation of the various components of the mixture was not attempted.

3.3.5 Reaction of <u>3.1</u> with acetylene

Passage of C_2H_2 through a CH_2Cl_2 solution of 3.1 for 30 minutes gives a mixture as indicated by ^{31}P NMR. An intense, sharp doublet at δ=-31.9[$^2J(PP)$=45.8 Hz] and three broad resonances in the region of 43-34 ppm dominate the spectrum of the reaction mixture. This type of spectrum is reminiscent of those seen for complexes $[(CO)_2(\eta^1\text{-}dppm)Co(\mu\text{-}dppm)X]$ (X=$Mn(CO)_4$,$Re(CO)_4$ or BH_2) (Table 5.4) where the shift and $^2J(PP)$ for the free end of the monodentate dppm fall in the ranges of -28.5 to -30.6 ppm and 20.5 to 63 Hz respectively. The δPCo values fall in the range of 30.6 to 53.8 ppm. Thus it appears that the reaction of C_2H_2 with 3.1 proceeds by displacement of a phosphorus of dppm to give a η^1-dppm ligand. Repeated attempts at purification and crystallization of this interesting complex by fractional crystallization have failed.

3.4 Experimental

$[Co_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]BPh_4$ 3.2a

3.1 (0.40g) was dissolved in degassed CH_2Cl_2 (25 mL) and $HgCl_2$ (0.11g) was added. After 5 minutes the solvent was removed by vacuum and the solid was washed with EtOH (20 mL). An excess of $NaBPh_4$ was added to the red EtOh washings and the resulting orange precipitate was filtered, washed with EtOH and recrystallized from CH_2Cl_2/EtOH.

Yield: 89%

The same complex was prepared by simply dissolving **3.1** in $CHCl_3$ and working up in the manner above. High yields of **3.2a** are obtained. However, a mixture of compounds is precipitated from CH_2Cl_2/EtOH.

Anal. calc. for $C_{77}H_{64}BClCo_2O_3P_4$: C, 69.80; H, 4.87 Found : C, 69.83; H, 5.05

Spectroscopic data: NMR; $\delta^{31}P(CD_2Cl_2)$= 47.5[s, PCo], $\delta^{13}C(CD_2Cl_2)$= 233.7[s, μ-CO], 197.8[q, $^2J(PC)$= 14 Hz, 2(CO)Co], $\delta^{1}H(d_6\text{-acetone})$= 3.73[m, CH_aHP_2], 3.64[m, CHH_bP_2].

IR(Nujol): ν(CO)= 1965.7(m), 1946.4(s), 1832.6(m).

$[Co_2(\mu\text{-}Br)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]BPh_4$ 3.2b

3.1 (0.24g) was dissolved in $CHBr_3$ (5 mL). The solvent was removed under vacuum and the residue was washed with EtOH (20 mL). An excess of $NaBPh_4$ was added to the EtOH washings and the resulting orange precipitate was filtered and recrystallized from CH_2Cl_2/EtOH.

Yield: 66%

Anal. calc. for $C_{77}H_{64}BBrCo_2O_3P_4$: C, 67.50; H, 4.71 Found : C, 67.52; H, 4.82.

Spectroscopic data: NMR; $\delta^{31}P(CH_2Cl_2/CD_3CN)$= 46.6[s, PCo], $\delta^{1}H(d_6$-acetone)= 4.26[m, $CH_aH_bP_2$].

IR(Nujol) : ν(CO)= 1963.8(m), 1948.3(s), 1817.2(m).

[$Co_2(\mu$-I)(μ-CO)(μ-dppm)$_2$(CO)$_2$]BPh_4 <u>3.2c</u>

3.1 (0.40g) and I_2 (0.10g) were dissolved in CH_2Cl_2 (20 mL) and allowed to stir for 5 minutes. The solvent was removed by vacuum and the residue was washed with EtOH (30 mL). An excess $NaBPh_4$ was added to the red EtOH washings after filtration and the orange solid precipitated was subsequently recrystallized from CH_2Cl_2/EtOH.

Yield: 92%

Anal. calc. for $C_{77}H_{64}BCo_2IO_3P_4$: C,65.28; H,4.55, Found : C,65.20; H,4.63.

Spectroscopic data : NMR; $\delta^{31}P(CH_2Cl_2)$= 50.6 [s, PCo], $\delta^{1}H(d_6$-acetone)= 4.87[m, CH_aHP_2], 4.53[m, CHH_bP_2].

IR(nujol) : ν(CO)= 1967.6(m), 1952.2(s), 1817.2(m).

[$Co_2(\mu$-S)(μ-CO)(μ-dppm)$_2$(CO)$_2$] <u>3.2d</u>

3.1 (0.320) and S_8 (0.0288g) were dissolved in CH_2Cl_2 (15mL) and EtOH was allowed to diffuse into the resulting dark brown solution over a period of several days to precipitate dark brown crystals of 3.2d.

Yield : 48% Anal. calc. for $C_{53}H_{44}Co_2O_3P_4S\cdot CH_2Cl_2$: C,59.63;

H,4.26 Found : C,59.74; H,4.30.

Spectroscopic data : NMR; $\delta^{31}P(CD_3CN/CH_2Cl_2)$=41.9[s, PCo]; $\delta^{1}H(d_6$-acetone)= 4.21[m, PCH_aHP], 2.50[m, $PCHH_bP$].

IR(Nujol) : ν(CO)= 1950(s), 1931(vs), 1779(m) cm^{-1}.

FAB-MS : m/z = 1002, 918, 890, Calc. for $C_{53}H_{44}Co_2O_3P_4S$[P] : 1002, P-2CO-S 914, P-4CO 890.

$[Co_2(\mu\text{-}H)(\mu\text{-}dppm)_2(CO)_4]X$ ($X=BF_4$ <u>3.3a</u>, BPh_4 <u>3.3b</u>)

$X=BF_4$

3.1 (0.35g) was dissolved in degassed CH_2Cl_2 (20 mL) and concentrated aqueous HBF_4 (1.5 mL) was added and the solution was stirred for 10 minutes. The CH_2Cl_2 was removed by vacuum and the solid was washed with EtOH (15 mL) to remove the water and was then recrystallized from CH_2Cl_2/EtOH.

Yield: 85%

Spectroscopic data : NMR; $\delta^{31}P(d_6$-acetone)= 49.6[s, PCo], $\delta^{13}C(CD_2Cl_2)$= 199.1[s, (CO)Co], $\delta^{1}H(CD_3CN)$= 4.81[s, CH_2P_2], -10.8[q, ^2J(PH)= 13 Hz, CoH].

IR(Nujol) : ν(CO)= 2000.4(m), 1973.4(s), 1938.7(s), 1923.1(m) cm^{-1}.

$X=BPh_4$

Excess $NaBPh_4$ was added to a CH_2Cl_2 (15 mL) solution of 3.3a (0.23g) and EtOH was allowed to slowly diffuse into the red CH_2Cl_2 solution to give crystalline 3.3b.

Yield : 68% Anal. calc. for $C_{78}H_{65}BCo_2O_4P_4$: C,71.03; H,4.97 Found : C,70.85; H,4.83.

Spectroscopic data : same as for **3.3a**.

Complex 3.4

C_2H_2 was bubbled through a CH_2Cl_2 solution (30mL) of **3.3b** (0.24g) for 30 minutes. The solvent was removed by vacuum and the residue was washed with hexane. Recrystallization of the solid from either EtOH/hexane or CH_2Cl_2/hexane resulted in the formation of a red oil.

Spectroscopic data : NMR(CD_2Cl_2); δ^1H= 2.83, 3.20[m, PCH_aH_bP], 3.84[m, C_2H_2]; $\delta^{31}P$(-80°C)= 45.8[s, PCo].

IR(Nujol) : ν(CO)= 1970(m), 1950(s), 1939(s), 1900(w), 1825(m).

3.5 References

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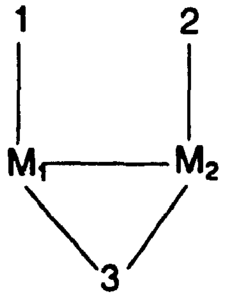
Chapter 4 : Synthesis, Characterization and Chemistry of $[CoRh(\mu\text{-}dppm)_2(CO)_3]$

4.1 Introduction

The interest in heterobimetallic complexes is in part due to the unique chemistry sometimes offered over homobinuclear analogues. This can be attributed to the three different coordination sites on the heterodinuclear core available for a ligand as shown below[1].



Ligand activation can occur preferentially at one of the three sites. In a catalytic system, this can be a desirable property given the diversity of activation steps occurring in a typical catalytic cycle. In fact, catalytic activity of multimetal systems often differs and is enhanced relative to the corresponding homometallic systems and this synergism is attributed to the in situ formation of mixed metal species[1].

Synergistic effects of cobalt-rhodium mixtures have been observed in the homogeneous catalytic hydroformylation and hydrogenation reactions[1]. It has been speculated that the synergism of $[Co_2(CO)_8]/[Rh_4(CO)_{12}]$ mixtures in the hydroformylation of diketenes is due to the formation of cobalt-rhodium carbonyl complexes. It was subsequently shown that $[Co_2(CO)_8]$ and $[Rh_4(CO)_{12}]$ are in equilibrium with $[CoRh(CO)_7]$. This complex reversibly adds an equivalent of CO to form $[(CO)_4Co\text{-}Rh(CO)_4]$, slowly disproportionates under a CO atmosphere to $[Co_2(CO)_8]$ and $[Rh_4(CO)_{12}]$, and forms $[Co_2Rh_2(CO)_{12}]$ reversibly with loss of CO.

The kinetics of molecular hydrogen activation by $[CoRh(CO)_7]$ were studied over a range of temperatures, H_2 and CO pressures[2]. The products initially formed in the H_2 activation were identified as $[HCo(CO)_4]$ and $[Rh_4(CO)_{12}]$.

$[RhCo(CO)_7]$ has also been prepared[3] by the reaction of $[RhCl(CO)_2]_2$ and $Na[Co(CO)_4]$ under a CO atmosphere at -78°C or by the treatment of $[Co_2Rh_2(CO)_{12}]$ with a 25 bar atmosphere of CO at 0°C.

Recently, $[Co_2Rh_2(CO)_{12}]$ was found to catalyze the reaction of hydrosilanes with 1-hexyne[4]. Species identified as $[(PhMe_2Si)_2Rh(CO)_nCo(CO)_4]$ (n=2 or 3) and $[RhCo(n\text{-}BuC{\equiv}CH)(CO)_5]$ were found to be important catalyst species for the "silylformylation" reaction.

The implication of $[CoRh(CO)_7]$ and related species in the enhanced catalytic activity of Co/Rh mixtures has provided incentive for further studies of these systems. Substituted derivatives of $[CoRh(CO)_7]$ have not been prepared directly but rather by exploiting the disproportionation of $[Co_2Rh_2(CO)_{12}]$ and substituted derivatives[1]. In the presence of four equivalents of PEt_3,

$[Co_2Rh_2(CO)_{12}]$ fragments to provide two equivalents of $[(CO)_4Co\text{-}Rh(CO)(PEt_3)_2]$, 4.1. The compound is also prepared by the reaction of trans-$[RhCl(CO)(PEt_3)_2]$ with $Na[Co(CO)_4]$.

The X-ray structure of 4.1[5] reveals distorted square-planar and tetrahedral geometries about the rhodium and cobalt atoms respectively (Figure 4.1), suggestive of M(I) and M(-I) oxidation states as suspected in the parent carbonyl $[CoRh(CO)_7]$[3]. A list of selected bond angles and distances in 4.1 can be found in Table 4.1.

The metal-metal bond in 4.1 has been interpreted in terms of a dative bond between a $[Co(CO)_4]^-$ centre and the $[Rh(CO)(PEt_3)_2]^+$ fragment. The Co-Rh distance of 2.6769(1)Å is consistent with a single bond between the two atoms while it is significantly longer than the cobalt-rhodium bonds found in $[Co_2Rh_2(\eta\text{-}C_5Me_5)_2(CO)_7]$ {2.618(3), 2.606(4), 2.591(3), 2.574(4)Å}[6] supporting the polar nature of the metal-metal bond in $[CoRh(CO)_5(PEt_3)_2]$. The structure of $[CoRh(CO)_2(PPh_3)(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_{11})]$, formed by the reaction of $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_{11})]$ and $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)]PF_6$, has been determined crystallographically and it contains an even longer Co-Rh bonded distance of 2.746(3)Å[7]. In this case however, the +1 oxidation state of the cobalt precludes a dative bond of the type proposed for $[CoRh(CO)_7]$ and derivatives. The structure of 4.1 also exhibits two weakly semibridging carbonyl ligands from the $[Co(CO)_4]^-$ unit to the $[Rh(CO)(PEt_3)_2]^+$ fragment as shown by the Co-C-O angles of 170.0(7)° and

Figure 4.1: ORTEP representation of 4.1

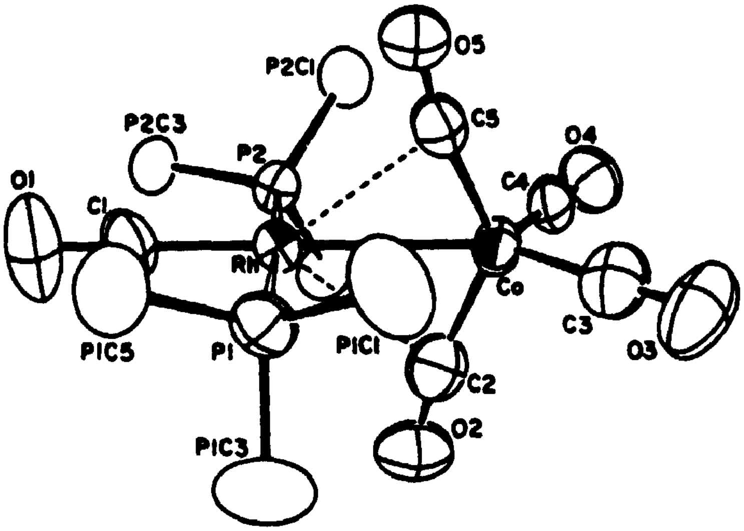


Table 4.1: Selected bond distances and angles in 4.1

Bond	Distance (Å)	Angle	Degrees(°)
Rh-Co	2.676(1)	P(1)-Rh-P(2)	175.18(5)
Rh-P(1)	2.346(2)	Co-Rh-C(1)	178.4(2)
Rh-P(2)	2.344(2)	C(1)-Rh-P(1)	87.13(3)
Rh-C(1)	1.811(7)	C(1)-Rh-P(2)	88.50(3)
Rh-C(2)	2.555(8)	Co-Rh-P(1)	87.1(2)
Rh-C(5)	2.466(6)	Co-Rh-P(2)	88.5(2)
Co-C(2)	1.774(7)	Co-C(2)-O(2)	169.4(6)
Co-C(3)	1.770(7)	Co-C(5)-O(5)	170.0(7)
Co-C(4)	1.758(7)	C(2)-Co-C(3)	103.0(3)
Co-C(5)	1.769(7)	C(2)-Co-C(4)	105.5(4)
		C(2)-Co-C(5)	129.1(3)
		C(3)-Co-C(4)	107.0(3)
		C(3)-Co-C(5)	102.2(3)
		C(4)-Co-C(5)	108.3(3)

169.4(6)°. The long Rh-C distances of 2.555(8) and 2.466(6)Å, while significantly longer than those found in other rhodium-carbonyl complexes, are indicative of weak metal-carbon interactions. The monosubstituted derivative of $[CoRh(CO)_7]$, $[CoRh(CO)_6(PEt_3)]$ has also been isolated.

The chemistry of 4.1, which is dominated by the facile heterolytic cleavage of the cobalt-rhodium bond, has been investigated by Roberts et al[5]. The thermodynamics, kinetic and equilibrium parameters for the reaction shown in Equation 4.1 :

$$4.1 + CH_3CN \rightarrow [(PEt_3)_2(CO)(CH_3CN)Rh]^+ + [Co(CO)_4]^- \qquad (4.1)$$

have been reported. Displacement of the $[Co(CO)_4]^-$ unit from the rhodium atom by halide occurs with [PPN]Cl $\{PPN=(PPh_3)_2N^+\}$, HCl and CH_3I to provide $[RhCl(CO)(PEt_3)_2]$ and $[PPN][Co(CO)_4]$, $[RhCl(CO)(PEt_3)_2]$ and $[HCo(CO)_4]$, and, $[RhI(CO)(PEt_3)_2]$ and $[CH_3Co(CO)_4]$ respectively.

The complex fails to react with the alkynes $PhC\equiv CX$ (X=H,Ph). However, $CH_3O_2CC\equiv CCO_2CH_3$ (DMAD) gives a complex which analyzes as a 1:1 adduct of the parent with DMAD. Based on the disproportionation chemistry already discussed, the product is believed to be $[Rh(CO)(PEt_3)_2(DMAD)][Co(CO)_4]$ formed by the displacement of $[Co(CO)_4]^-$ by the acetylene. Retention of the cobalt-rhodium bond is observed in $[CoRh(CO)_6(\mu\text{-}\eta^2\text{-}RC_2R)]$ (R=Ph or C_6F_5) which is formed from the reaction of $[Co_2Rh_2(CO)_{10}(\mu_4\text{-}\eta^2\text{-}RC_2R)]$ with CO and another equivalent of acetylene[8]. The metal-metal unit is also maintained in the reaction of 4.1 with acetyl chloride to give $[(CO)_4Co\text{-}RhCl\{C(O)Me\}(PEt_3)_2]$.

The polar nature of the Co-Rh bond in 4.1 is evident from the reactivity of 4.1, the long Co-Rh bond and the distorted tetrahedral geometry at the cobalt atom. Thus the complex is thought to contain formally Co(-I) and Rh(+I) centres. The apparent problem of investigating the chemistry of 4.1 is that the very nature of the cobalt-rhodium bond renders it unsuitable for study as disproportionation, or displacement of $[Co(CO)_4]^-$, occurs so readily. It is recognized that metal-metal bonding in heterobimetallics often tends towards polar or dative bonding[9]. M. Cowie and coworkers have produced a series of heterobimetallics $[RhM(\mu\text{-dppm})_2(CO)_n]$ (M=Co,n=3;M=Mn or Re;n=4)[10] which are formulated as Rh(I)-M(-I) complexes with a dative bond from the M(-I) centre to the Rh(I) centre. Presumably these complexes would be susceptible to the same type of nucleophilic displacement of a M(-I) unit as observed in $[CoRh(CO)_5(PEt_3)_2]$ except the incorporation of bridging phosphine ligands prevents such fragmentation. The complexes $[RhM(\mu\text{-dppm})_2(CO)_n]$ have been synthesized from the reaction of $[RhCl(\eta^2\text{-dppm})_2]$ with the appropriate M(-I) carbonylates and the structures of all but that with M=Co, and including M=Ir,n=3[11] synthesized by a different method, have been determined by Cowie and support the M(-I)→Rh(I) formulation. The chemistry of $[RhRe(\mu\text{-dppm})_2(CO)_4]$ with various reagents, for example, has been reported to proceed with retention of the bimetallic unit[12,13].

4.2 Synthesis of [CoRh(μ-dppm)$_2$(CO)$_3$] 4.2

It is desirable to introduce a bridging ligand onto the [CoRh(CO)$_7$] parent in order to study the chemistry of the dimer while maintaining the nuclearity of the cluster. Dppm is ideally suited for this purpose due to its well known binucleating ability and the capacity of phosphines to stabilize low oxidation state metal complexes[14]. Traditionally, the method of producing phosphine substituted binary carbonyls involves mixing together the phosphine and metal carbonyl, sometimes in the presence of a catalyst, and inducing the substitution thermally or photochemically. The main reason for avoiding this type of preparation is the high toxicity and low thermal stabililty of [CoRh(CO)$_7$]. Acceptable yields (40%) of [CoRh(CO)$_3$(μ-dppm)$_2$] are produced in a one step synthesis involving the reduction of Co(II)/Rh(III) halide mixtures with $NaBH_4$ in the presence of dppm and CO[15]. With the production of dppm bridged Co(0) dimers, [$Co_2(CO)_4$(μ-dppm)$_2$], from reduction of Co(II) salts by $NaBH_4$, it was hoped that the introduction of a second metal salt would provide a general one step synthesis of heterobimetallics (section 2.4.4.1). Thus far this method has been sucessful only for the introduction of $RhCl_3\cdot(H_2O)_n$.

As with the other syntheses using $NaBH_4$, a number of factors, most notably the rate of the BH_4^- addition and the form and purity of the borohydride used, affect the reproducibility of the reaction. With the Co(II)/Rh(III) system, the highest yields of $[CoRh(CO)_3(\mu\text{-dppm})_2]$ are obtained by the rapid addition of BH_4^-. Increasing amounts of $[Rh_2(CO)_3(\mu\text{-dppm})_2]$[16],**4.3**, are formed as the time of addition increases, so that pure or nearly pure **4.2** is obtained with an addition time of less than one minute while >50% of the $[Rh_2(CO)_3(\mu\text{-dppm})_2]$ species is observed for addition times of 5 minutes or longer. **4.2** and **4.3** cocrystallize and are therefore very difficult to separate.

Subsequent to the characterization of the $[Co_2(CO)_4(\mu\text{-dppm})_2]$ dimers, a modification of the reaction conditions led to the isolation of $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$ and this has been shown to lose CO and form the Co(0) dimers. A similar complex, $[Rh(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, is suspected in the production of $[CoRh(CO)_3(\mu\text{-dppm})_2]$. While it has not been isolated, the ^{31}P NMR spectra of reaction mixtures, from which high yields of **4.2** can be obtained, show the complex $[Rh(CO)(dppm)_2]^+$ $(\delta=-22.6[d,\ ^2J(PP)=97.5\ Hz])$[17] to be the major phosphorus containing species present in the initial stages of the reaction. This is indicative of the cobalt being present as a non phosphine containing species such as the $[Co(CO)_4]^-$ ion. Also the yields of the dimer increase significantly when the total metal:phosphine ratio is changed from 1:1 to 1:2, which should promote the formation of a bis-chelate dppm complex. This phenomenon is also observed in the Co(II) reductions leading to the Co(0) dimers [Co_2(μ-dppm)$_2$(CO)$_4$]. The complex [Rh(CO)(dppm)$_2$][Co(CO)$_4$] was found to be produced from the reaction of 4.2 with ^{13}CO according to equation 4.2.

$$4.2 + 2CO \rightarrow [Rh(CO)(dppm)_2][Co(CO)_4] \qquad (4.2)$$

The ring strain associated with Rh(I)(η^2-dppm) complexes has been exploited to make numerous μ-dppm heterobimetallics[10,11,18], but [Co(CO)(η^2-dppm)$_2$]$^+$ has proved to be much less reactive. M. Cowie[10] has concurrently produced [CoRh(CO)$_3$(dppm)$_2$] from a multistep reaction involving a ring opening reaction of the chelating phosphines in [RhCl(η^2-dppm)$_2$].

4.3 Characterization of complex 4.2

4.3.1 X-ray Crystal Structure of 4.2

The complex crystallizes from CH_2Cl_2 to give dark red-brown crystals of suitable quality for a X-ray diffraction study[15]. The compound is isostructural with [Rh_2(μ-dppm)$_2$(CO)$_3$][19], 4.3 and cocrystallizes with 4.3 when both compounds are present in solution. The numbering system in the ORTEP representation of [CoRh(CO)$_3$(μ-dppm)$_2$] (Figure 4.2) is the same as that used for 4.3 so that direct comparisons are possible. A list of selected bond distances and angles in 4.2 can be found in Table 4.2.

The molecule contains coordination numbers of four and

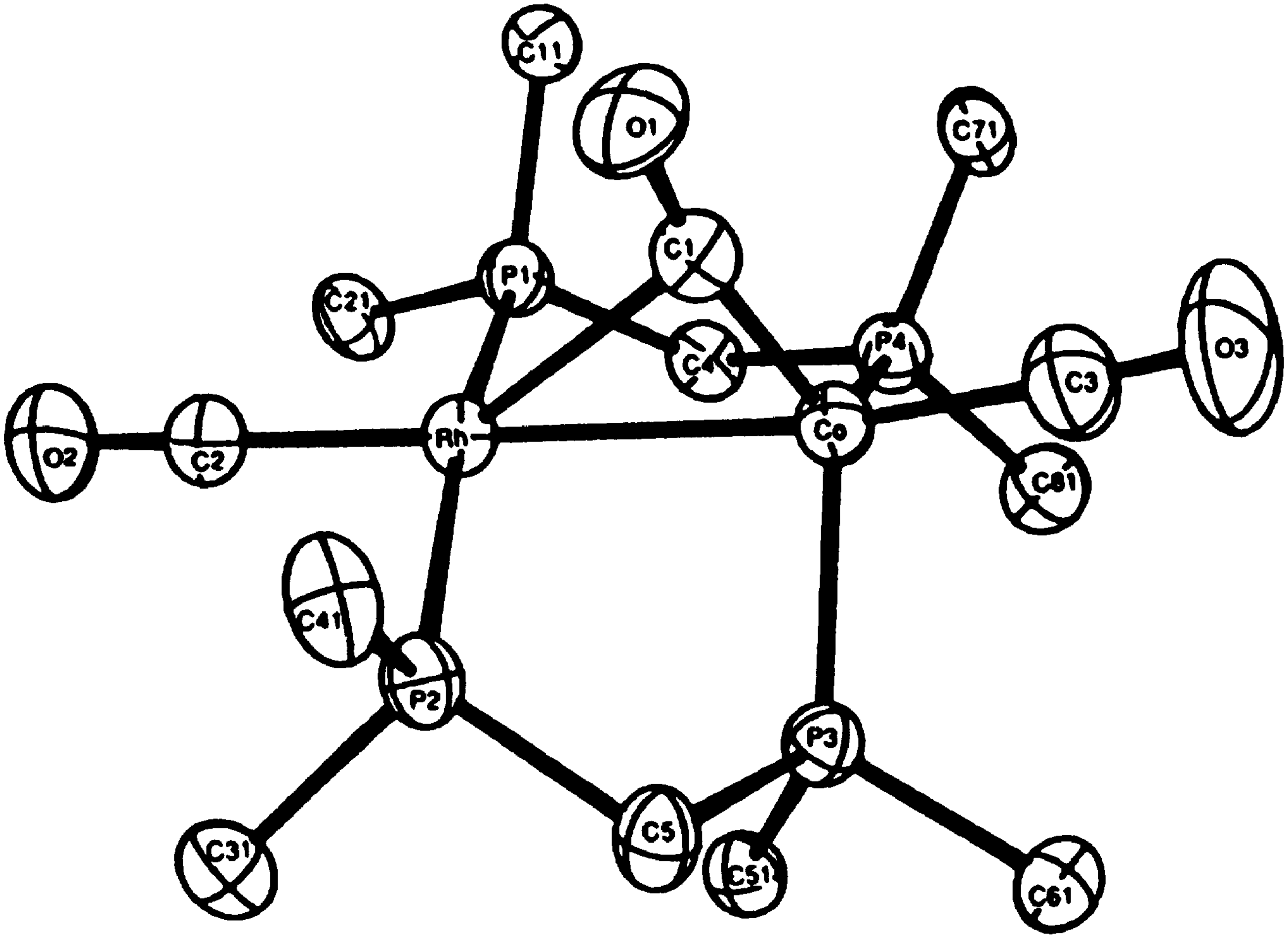


Figure 4.2: ORTEP representation of 4.2

Table 4.2: Selected bond distances and angles in 4.2 and deviations of the cobalt atom from TBP and tetrahedral geometry.

Bond	Distance(Å)	Bond	Distance(Å)
Rh-Co	2.6852(7)	Co-P(3)	2.1731(11)
Rh-P(1)	2.3061(11)	Co-P(4)	2.1832(12)
Rh-P(2)	2.3090(11)	Co-C(1)	1.735(4)
Rh-C(1)	2.420(4)	Co-C(3)	1.748(5)
Rh-C(2)	1.846(4)		
C(1)-O(1)	1.171(5)		
C(2)-O(2)	1.138(5)		
C(3)-O(3)	1.149(6)		

Angle	Degrees(°)	Angle	Degrees(°)
Co-Rh-C(2)	178.95(13)	Rh-C(2)-O(2)	177.8(4)
Co-Rh-P(1)	88.45(3)	Co-C(3)-O(3)	177.2(5)
P(1)-Rh-P(2)	167.8(3)	Co-C(1)-O(1)	166.8(4)
Co-Rh-C(1)	88.80(10)		
P(2)-Rh-C(2)	91.63(14)		
P(2)-C(1)	89.62(10)		

angle found(°)	expected for T_d(°)	distortion (°)	expected for TBP(°)	distortion (°)	favours
P(3)-Co-P(4)=108.88(4)	109	0	120	11	tet
P(3)-Co-C(1)=125.05(13)	109	16	125	5	tbp
P(4)-Co-C(1)=118.06(14)	109	9	120	2	tbp
P(3)-Co-C(3)=99.52(17)	109	9	90	10	-
P(4)-Co-C(3)=100.41(16)	109	9	90	10	- }1/2 way
C(1)-Co-C(3)=98.55(21)	109	10	90	9	-
mean distortion		9		8	
Rh-Co-P(3)=86.31(3)		-	90	4	
Rh-Co-P(4)=96.98(3)		-	90	7	
Rh-Co-C(1)=62.06(13)		-	90	28	
Rh-Co-C(3)=158.67(16)		-	180	21	

five for the rhodium and cobalt atoms respectively. This difference reflects the tendency for rhodium to adopt a four coordinate 16-electron configuration while cobalt forms 18-electron species almost exclusively when in a low oxidation state. The coordination geometry at the rhodium atom is square planar with the cobalt fragment at one coordination site trans to the C(2)O(2) ligand and phosphorus atoms occupying trans sites. There is also a weak interaction with C(1) of the corresponding carbonyl as shown by the Rh-C(1) distance of 2.420(4)Å. The semibridging nature of this ligand, as opposed to terminal, is reflected by the bending of the Co-C(1)-O(1) angle from the ideal of 180° in a terminal carbonyl to 166.8(4) and by a ν(CO) at 1815 cm^{-1} in the IR spectrum of **4.2**.

The geometry of the cobalt atom can be described as a distorted TBP with the two phosphorus atoms and the semibridging C(1) atom occupying equatorial sites and the rhodium fragment and the C(3)O(3) ligand at axial sites.

The main structural differences between the complexes $[MRh(\mu\text{-dppm})_2(CO)_3]$ (M=Co,**4.2**;M=Rh,**4.3**) arise from the smaller size of the cobalt atom. For example, this leads to opening up of the P(3)-M-P(4) angle from 104.39(3)° in **4.3** to 108.88(4)° in **4.2**. The smaller cobalt atom results in a shorter M-Rh distance {2.6852(7)Å in **4.2** vs 2.739(1)Å in **4.3**} which in turn gives a shorter Rh-C(1) distance {2.420(4)Å} in **4.2** than in **4.3** {2.533(3)Å}. Also a more acute Rh-M-C(1) angle is subtended in **4.2** {62.06(13)°} than in **4.3** {63.5(1)°}.

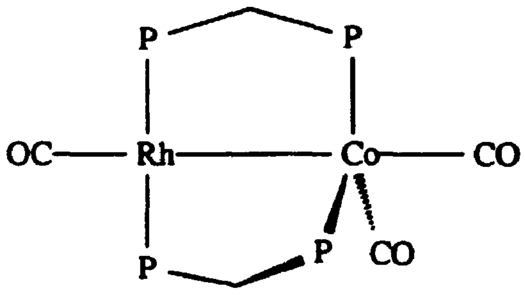
The structure of **4.2** has the unusual feature of a twisting of the $M(\mu\text{-}P\text{-}CH_2\text{-}P)_2M^1$ 8 membered ring due to the trans and cis arrangements of the phosphines on rhodium and cobalt respectively. In most dimers of the type $M_2(\mu\text{-dppm})_2$ the phosphines are trans giving A-frame type complexes or they are mutually cis as in $[Ni_2(CO)_3(\mu\text{-dppm})_2]^{20}$ and $[Co_2(\mu\text{-}CO)_2(CO)_2(dppm)_2]$ (section 2.4.3.1.1) which are described as having a cradle type structure. Examples of the cis-trans arrangement include of course the isostructural $[Rh_2(CO)_3(\mu\text{-dppm})_2]^{19}$ and other complexes $[MM^1(CO)_3(\mu\text{-dppm})_2]$ $(M{=}Rh, M^1{=}Ir; M{=}M^1{=}Ir)^{10,11}$ and also $[CoMn(\mu\text{-dppm})_2(CO)_5]$ (section 5.3.1).

The Co-Rh distance of 2.6852(7)Å in **4.2** is indicative of a weak Co-Rh interaction. Single cobalt-rhodium bonds are found in Co_2Rh_2 type clusters such as $[Co_2Rh_2(CO)_{10}(\mu_4\text{-}\eta^2\text{-}RC_2R)]$ $(R{=}C_6F_5)$, made from the reaction of $[Co_2Rh_2(CO)_{12}]$ with acetylenes[8]. It is a butterfly type cluster with the $\mu_4\text{-}\eta^2\text{-}RC{\equiv}CR$ ligand bridging the cobalt wingtips. The cobalt-rhodium single bonded distances in this cluster are 2.513(2), 2.515(2), 2.541(3) and 2.539(3) Å. Comparable cobalt-rhodium distances to that in **4.2** are seen, however, in $[CoRh(CO)_5(PEt_3)_2]^5$ **4.1**{2.6769(1)Å} and $[CoRh(CO)_2(PPh_3)(\eta^4\text{-}C_4Me_4)(\eta^5C_2B_9H_{11})]^7$ {2.746(3)Å}. In **4.1** the long Co-Rh distance has been attributed to a dative Co(-1)→Rh(1) bond and this is supported by the tendency of this and related molecules to dissociate into $[Co(CO)_4]^-$ and

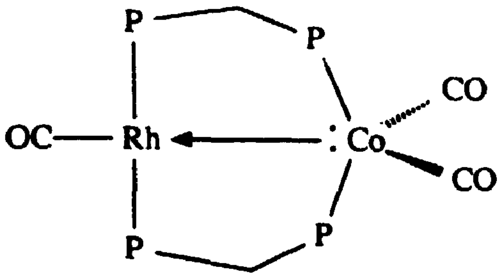
Rh(I) fragments in the presence of Lewis bases. Thus the structure of the molecule is interpreted in terms of square planar Rh(I) with the tetrahedral $[Co(CO)_4]^-$ anion acting as a two electron donor to one site on rhodium. If the presence of the long cobalt-rhodium bond in **4.2** can be rationalized by a dative interaction, as speculated by M.Cowie[10], then the coordination geometry at the cobalt can be interpreted as being a distorted tetrahedron and not TBP. Selected bond angles subtended at the cobalt atom in **4.2** are listed in Table 4.2. The mean deviations of these angles from those expected for ideal TBP and tetrahedral geometries, based on six angles, are shown to be very similar (9° and 8° respectively). Major distortions from TBP geometry are seen in the RhCoC(1)=62° and RhCoC(3)=159° angles. The reason for this distortion is apparently the semibridging nature of the C(1) carbonyl ligand which closes these angles from the 90° and 180° expected for TBP geometry.

The true nature of the Co-Rh bond in **4.2** probably lies somewhere between the two limits of dative and covalent bonding shown in Figure 4.3. In both cases there are two electrons in the bond. In **A** the electrons are equally shared and both metal atoms have formal oxidation states of zero. In **B** both electrons are donated by the $[Co(CO)_2P_2]^-$ unit. In both **A** and **B** the rhodium should have square planar geometry. The cobalt geometry should be TBP in **A** whereas in **B** it should be closer to tetrahedral as expected for a $Co(CO)_4^-$ fragment. The Co(-I)→Rh(+I) interaction is more reasonable

Figure 4.3: Structural limits and metal-metal bonding in 4.2



A



B

in a complex like 4.1 which has only carbonyl ligands on the cobalt. Carbon monoxide is good at stabilizing low oxidation states by reducing electron density on the metal through π backbonding. Phosphines are generally considered to be poor π acceptors and thus the phosphine coordinated cobalt center in 4.2 is not likely to be a derivative of $[Co(CO)_4]^-$.

4.3.2 Spectroscopic characterisation of 4.2

4.3.2.1 ^{31}P NMR

Complex 4.2 is readily soluble in most organic solvents and thus it was possible for characterization by NMR. The ^{31}P NMR spectrum of 4.2 at room temperature in CH_2Cl_2 consists of two resonances at δ=29.1(br) and 17.9(dt) assigned to the phosphorus atoms on the cobalt and rhodium respectively (Figure 4.4). These assignments are based on the observed doublet splitting of the resonance at δ=17.9 by 129.4 Hz which is consistent with other $^1J(RhP)$ values in the literature[13]. Also these shifts compare favourably with other homodinuclear dppm bridged metal(0) complexes such as $[Co_2(CO)_4(\mu\text{-dppm})_2]$[21] ($\delta$=32.3) and $[Rh_2(CO)_3(\mu\text{-dppm})_2]$[19] ($\delta$=20.4).

At lower temperatures the broad signal at δ=29.1 begins to sharpen into a triplet. ^{59}Co has a nuclear spin of 7/2 and the broadness of the room temperature signal is probably due to a quadrupolar ^{59}Co-^{31}P coupling mechanism[22]. The sharpening of the signal at lower temperatures is consistent with the thermal decoupling model as discussed in section

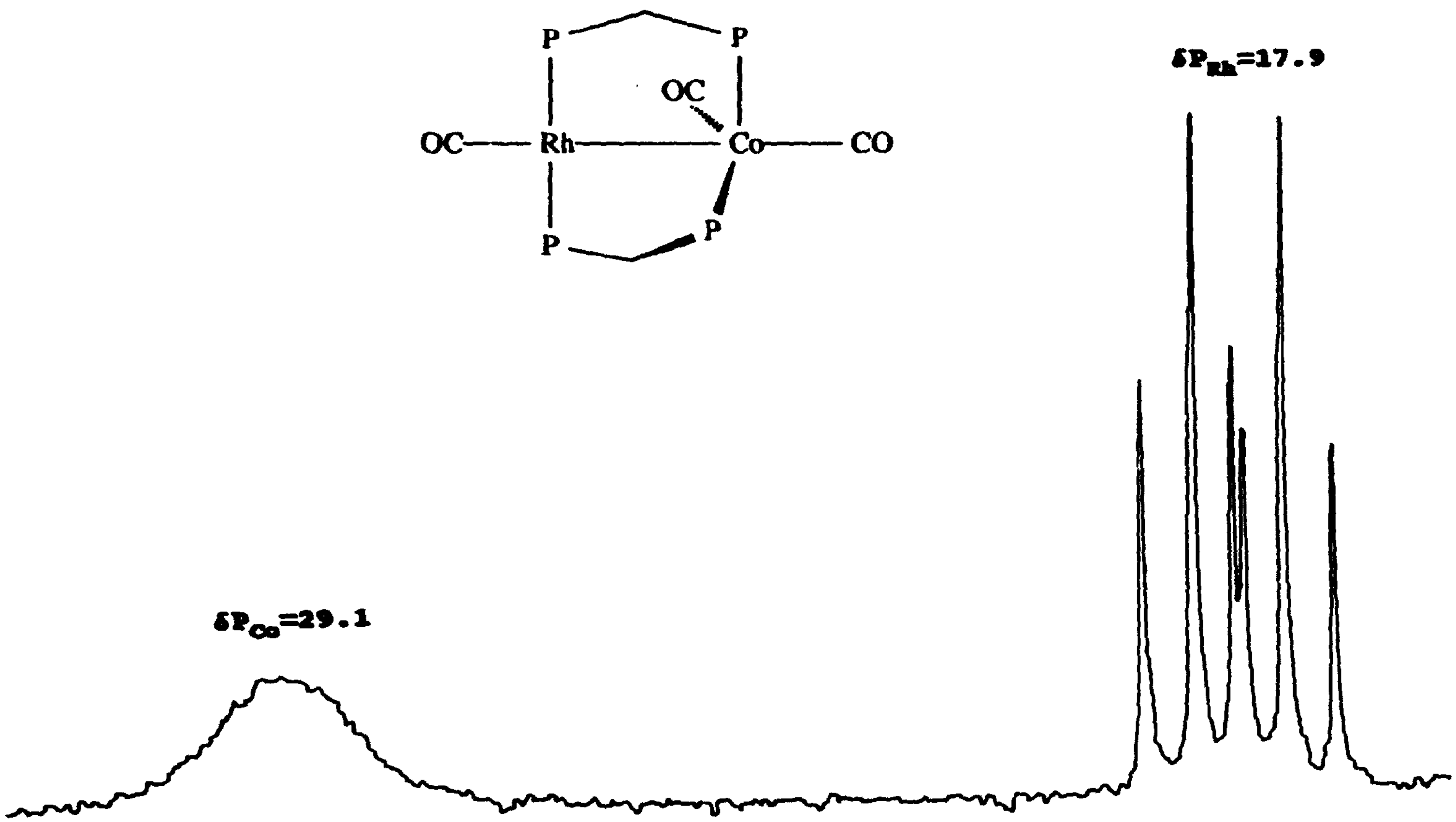


Figure 4.4: ^{31}P NMR spectrum of 4.2

1.1.3.1.

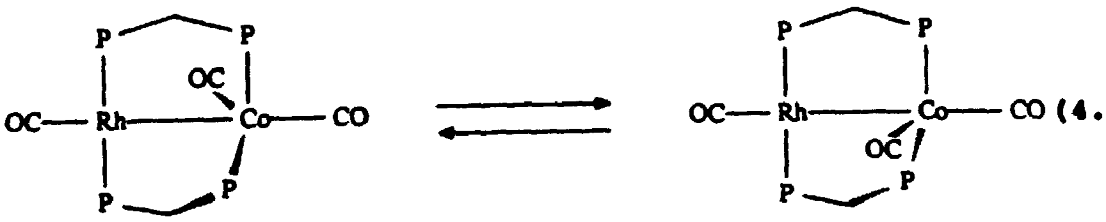
The appearance of the triplets in the ^{31}P nmr spectrum of 4.2 is consistent with a A_2M_2X spin system whereas an AA^1MM^1X spectrum is anticipated due to the magnetic inequivalence of the phosphorus atoms on cobalt and rhodium respectively.

4.3.2.2 ^{13}C NMR of 4.2

^{13}CO enrichment of 4.2 was obtained by stirring of a CH_2Cl_2 solution of 4.2 under a ^{13}CO atmosphere for 24 hours. The solvent was removed by vacuum and the resulting solid was recrystallized from CH_2Cl_2/EtOH. Based on a comparison of ν(CO) stretches in the IR spectra of normal and enriched samples of 4.2, the degree of enrichment is estimated to be approximately 50%. The room temperature ^{13}C NMR spectrum exhibits two sets of resonances in the carbonyl region at δ=214.3[br,s] and 180.7[dt]. These resonances are assigned to the carbonyls on cobalt and rhodium respectively based on the doublet splitting of the resonance at 180.7 ppm, consistent with other $^1J(RhC)$ values found in the literature[12] and the tendency of cobalt carbonyls to have downfield shifts relative to rhodium carbonyls[23]. Also the appearance of a broad singlet for the resonance at 214.3 ppm is consistent with quadrupolar ^{59}Co-^{13}C coupling obliterating the relatively small ^{31}P-^{13}C coupling.

The appearance of a singlet for the C1 and C2 ligands on cobalt indicates that chemical equivalence of the two carbonyls has been attained in solution. Distinction of the C3 ligand on rhodium from the cobalt-carbonyls at room temperature, however, suggests that the fluxional process must be a localized exchange on the cobalt atom and does not involve a merry go round mechanism as seen in [$Co_2(CO)_4$(μ-dppm)$_2$]^{24}, [$Mn_2(CO)_6$(μ-dppm)$_2$]^{25} and other similar molecules.

At lower temperatures the singlet resonance at 214.3 ppm resolves into two singlets (δ=214.7 and 214.4) as expected for the asymmetric solid state structure of 4.2 (Figure 4.5). The type of fluxional process consistent with the NMR data is illustrated below in Equation 4.3. This type of wagging involving the $CoP_2(CO)_2$ fragment is also found in [$Mn_2(CO)_5$(dppm)$_2$]^{25} and [$CoMn(CO)_5$(dppm)$_2$] (section 5.3.2.1)



(4.3)

The initial interpretation of the ^{13}C NMR spectrum of 4.2 was complicated by the appearance of additional signals at δ=214.5 [octet, ^1J(CoC)=246 Hz] in the room temperature spectrum and 199.5[dq, ^1J(RhC)=72.4 Hz, ^2J(PC)=12 Hz] in the low temperature spectrum. These were eventually identified

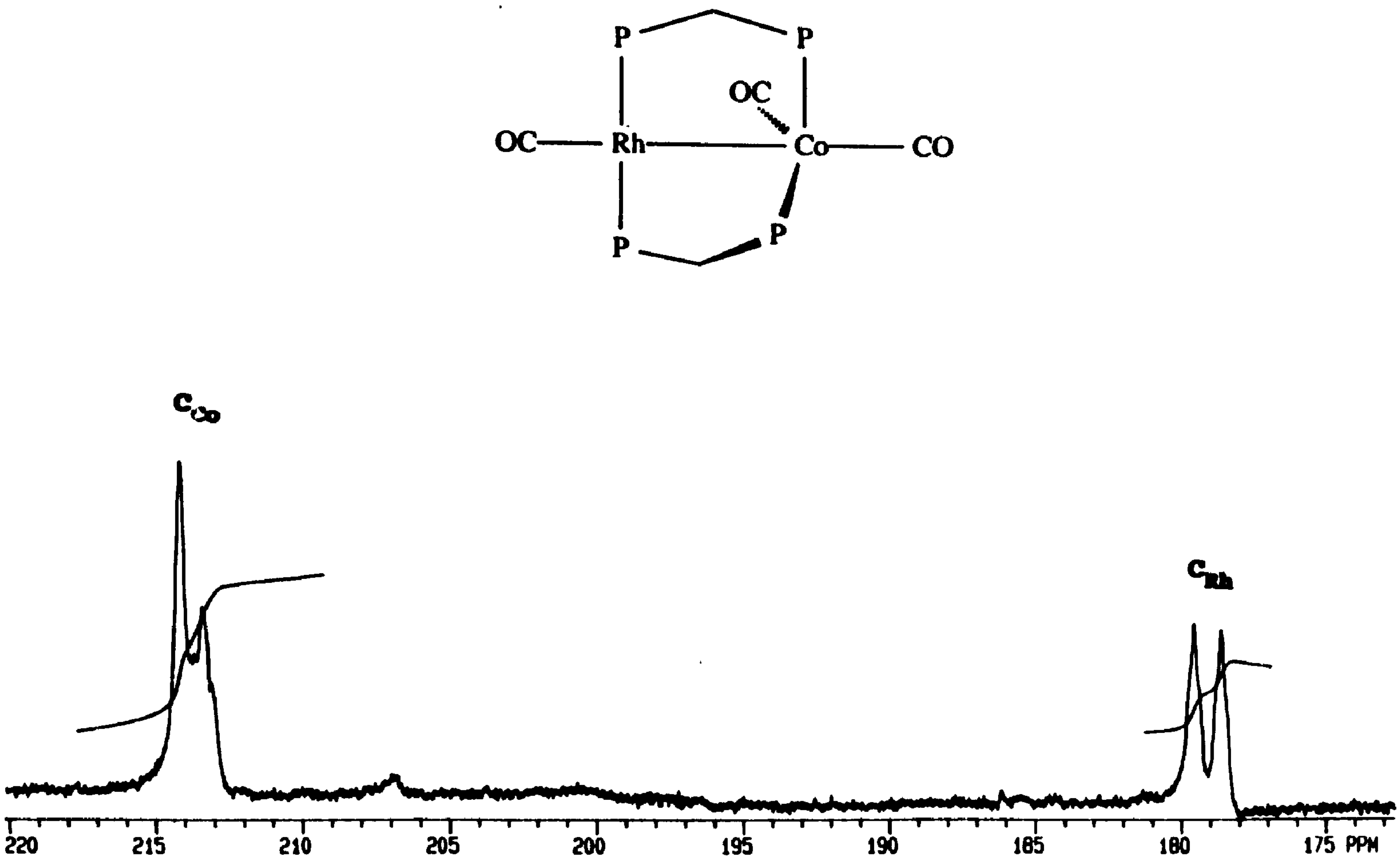


Figure 4.5: Limiting low temperature ^{13}C NMR spectrum of 4.2

as being due to $[Co(CO)_4]^-$ [26] and $[Rh(CO)(dppm)_2]^+$ species respectively. These ions are present due to the disproportionation of **4.2** in the presence of CO according to equation 4.2. The disproportionation illustrated in equation 4.2 is reminiscent of chemistry of $[(CO)_4Co(-I)\rightarrow Rh(I)(CO)(PEt_3)_2]$ and derivatives[5].

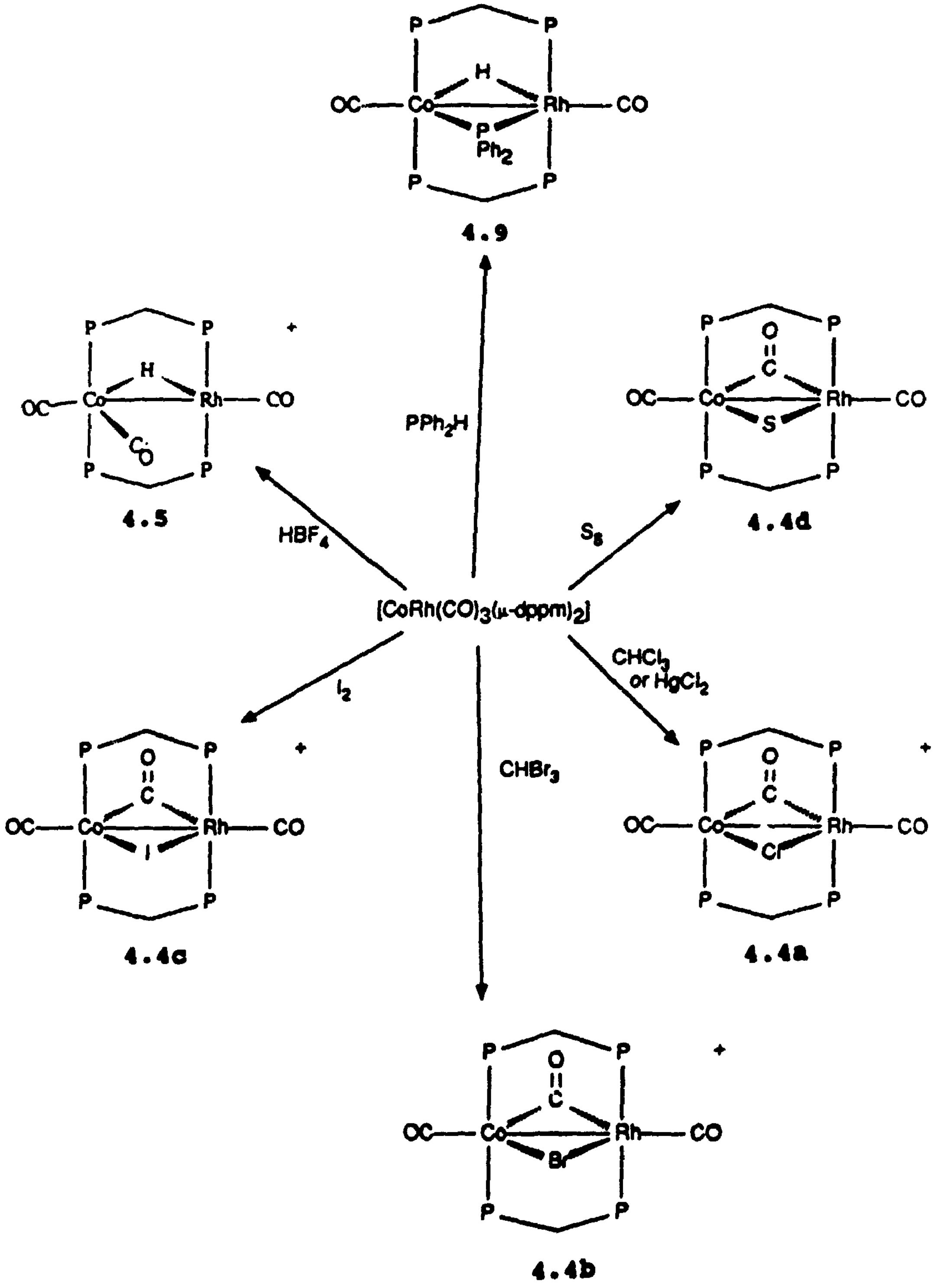
4.3.2.3 ^{1}H NMR of 4.2

The ^{1}H NMR of **4.2** exhibits a singlet at $\delta=4.24$ attributable to the CH_2P_2 methylene protons on dppm. The solid state structure of **4.2** indicates chemical inequivalence of the methylene protons and thus the observed singlet is explained by the fluxional process deduced by variable temperature ^{13}C NMR. At -90° C the 4.24 ppm resonance broadens significantly indicating the beginnings of decoalescence of the $CH_aH_bP_2$ protons.

4.4 Chemistry of 4.2

Complex **4.2** is a good substrate for oxidative addition and such reactions usually occur with retention of the metal-metal bond (Scheme 4.1). This observation exemplifies the advantages of incorporating bridging dppm ligands into di- and polynuclear systems such as $[CoRh(CO)_7]$ which are prone to fragmentation. **4.2** reacts with $HgCl_2$, $CHBr_3$, and I_2 followed by precipitation with $NaBPh_4$ to give complexes $[CoRh(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]BPh_4$ (X=Cl, **4.4a**; X=Br, **4.4b**; X=I, **4.4c**). Complex **4.4a**, with a Cl^- counter ion was

Scheme 4.1: Addition chemistry of **4.2**



produced quantitatively by dissolving **4.2** in $CHCl_3$ and another complex **4.4a**[1] was also isolated from this reaction. **4.2** reacted with S_8 to give $[CoRh(\mu\text{-}S)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$ **4.4d** and with PPh_2H to give $[CoRh(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)_2(CO)_2]$ **4.6** which has been characterized by X-ray diffraction. Complex **4.5** is produced via the protonation of **4.2** with HBF_4. An exception to retention of the cobalt-rhodium bond is seen with the reaction of **4.2** with $CHBr_3$. Two complexes identified as **4.4b** and a rhodium-(η^2-dppm) complex {δ=-32.1[d, $^1J(RhP)$=74.3 Hz]} are observed by ^{31}P NMR. This is consistent with a disproportionantion of **4.2** to give Rh(I) and Co(I) fragments · the presence of an oxidizing agent. This behaviour is observed with the related complex $[CoRh(PEt_3)_2(CO)_5]$ which forms $[Rh(CO)(PEt_3)_2X]$ and $[Co(CO)_4Y]$ complexes when reacted with reagents XY[5].

Complex **4.2** is unreactive to a number of unsaturated organic molecules under the mild conditions tested (e.g. acetylene, ethylene), in contrast to the homodinuclear cobalt (section 3.3.5) and rhodium systems[27]. **4.2** also fails to activate H_2, in contrast to the related complex $[CoRh(CO)_7]$[2].

4.4.1 Characterisation of addition products

4.4.1.1 $[CoRh(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]Y$ (X=Cl 4.4a;X=Br 4.4b;X=I 4.4c) complexes

Products **4.4a**, **4.4b**, and **4.4c** have all been identified by their IR, ^1H and ^{31}P NMR spectra in addition to carbon and hydrogen elemental analysis. All spectroscopic data are consistent with the structure $[CoRh(\mu-X)(\mu-CO)(\mu-dppm)_2(CO)_2]^+$ for the cation. The ^{31}P NMR of the compounds have the "A_2M_2" type pattern containing pseudo triplets characteristic of the $CoRh(\mu-dppm)_2$ unit. The ^{31}P NMR spectrum of **4.4a** can be seen in Figure 4.6. The ^1H NMR spectra exhibit two resonances in the region associated with the dppm methylene $(CH_aH_bP_2)$ protons consistent with an AB pattern expected for the structure above. The appearance of the AB pattern also indicates the structures are rigid on the NMR timescale with respect to carbonyl/halide exchange at room temperature. The IR spectra of the complexes exhibit three $\nu(CO)$ stretches; one bridging and two terminal, as expected for the $(CO)Co(\mu-CO)Rh(CO)$ frame.

The $[M_2(\mu-X)(\mu-CO)(\mu-dppm)_2(CO)_2]^+$ type of structure is also well characterized in homodinuclear cobalt (section 3.3.1), rhodium and iridium (μ-dppm) complexes and the phosphines are generally oriented at each metal in a trans fashion giving A-frame type structures. For example, the structure of the cation $[Co_2(\mu-I)(\mu-CO)(\mu-dppm)(\mu-dmpm)(CO)_2]^+$ [28] has been determined by X-ray diffraction and the P-Co-P angles are 168.9(1)° and 168.5(1)°. The analogous chloride bridged rhodium dimer has also been structurally characterized[29]. $[M_2(\mu-X)(\mu-CO)(dppm)_2(CO)_2]^+$ complexes (M=Rh,X=O_2CR[30],CN[31],H[32]; M=Ir,X=Cl[33],H[34]) are also known.

One significant difference observed between the homodinuclear cobalt and cobalt-rhodium, and the

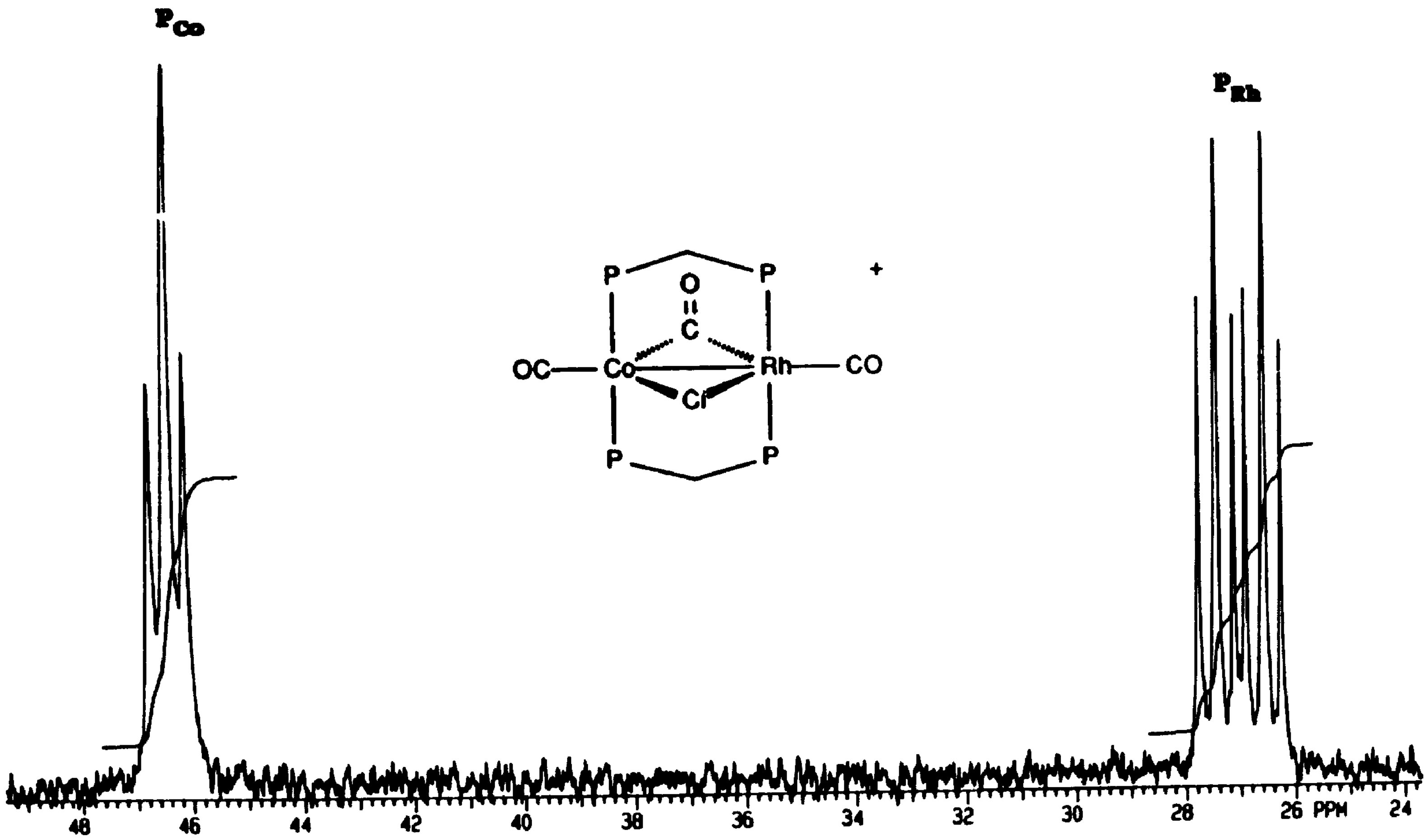


Figure 4.6: ^{31}P NMR spectrum of **4.4a**

homodinuclear rhodium and iridium systems of this type is the tendency of the cobalt containing systems to retain the μ-CO ligand while, with rhodium and iridium complexes, in many cases the addition of CO to $[M_2(\mu\text{-}X)(CO)_2(dppm)_2]^+$ to give $[M_2(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]^+$ is reversible[33]. This difference reflects the tendency of cobalt to achieve an 18 electron count which requires the presence of a metal-metal bond and a μ-CO group in $[Co_2(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]^+$ if a symmetrical structure is retained. In complexes $[M_2(\mu\text{-}X)(CO)_2(\mu\text{-}dppm)_2]^+$ there is no metal-metal bond and each metal has a 16 electron count.

Complex **4.4a** was initially produced from the reaction of **4.2** with $HgCl_2$, however, in the alternative synthesis of **4.4a**, **4.2** is simply dissolved in $CHCl_3$ to afford the $[CoRh(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]^+$ cation in solution. The quantitative conversion of **4.2** to **4.4a** was confirmed by ^{31}P NMR spectra of samples of **4.2** dissolved in $CHCl_3$. The **4.4a** cation can be precipitated with the addition of $NaBPh_4$. If, however, EtOH is allowed to slowly diffuse into the original $CHCl_3$ solution of the **4.4a** cation, large dark green crystals of **4.4a^1** are precipitated. The compound has not been characterized spectroscopically due to its low solubility in most organic solvents and the tendency to dissociate into the $[CoRhCl(CO)_3(dppm)_2]^+$ cation in solution. For example when washed with EtOH a pale orange solution is produced from which **4.4a** precipitates upon the addition of $NaBPh_4$. CH_2Cl_2 solutions of **4.4a^1** are initially light green but in the time required to run the ^{31}P NMR decomposition apparently occurs and the spectrum of the 4.4a cation is observed.

The IR of 4.4a[1] indicates two terminal and one bridging ν(CO) stretches consistent with the $(CO)ClCo(\mu\text{-}CO)RhCl(CO)$ formulation.

4.4.1.2 $[CoRh(\mu\text{-}S)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$ 4.4d

Complex 4.2 reacts with elemental sulphur to give a highly crystalline complex characterized as $[CoRh(\mu\text{-}S)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$, 4.4d. The IR spectrum of 4.4d exhibits ν(CO) stretches at 1971(s), 1958(s) and 1796(m) cm^{-1} consistent with the presence of two terminal and a bridging carbonyl.

The complex is readily soluble in most organic solvents and thus NMR characterization was also possible. The ^{31}P NMR of 4.4d consists of the characteristic triplet and doublet of triplets seen for other complexes containing the $[CoRh(\mu\text{-}dppm)_2]$ unit. The chemical shifts for the phosphorus atoms on the cobalt and rhodium atoms of δ=36.0 and 23.1 respectively.

The ^{13}C NMR spectrum of a sample of 4.4d enriched with ^{13}CO was recorded (Figure 4.7). The carbonyl region of the spectrum exhibits three resonances at δ=222.6(s), 211.0(t) and 197.7(dt). The signal at 197.7 ppm can be assigned to the terminal carbonyl on rhodium due to the observed $^{1}J(RhC)$= 73 Hz[12]. Also, the chemical shift is comparable to

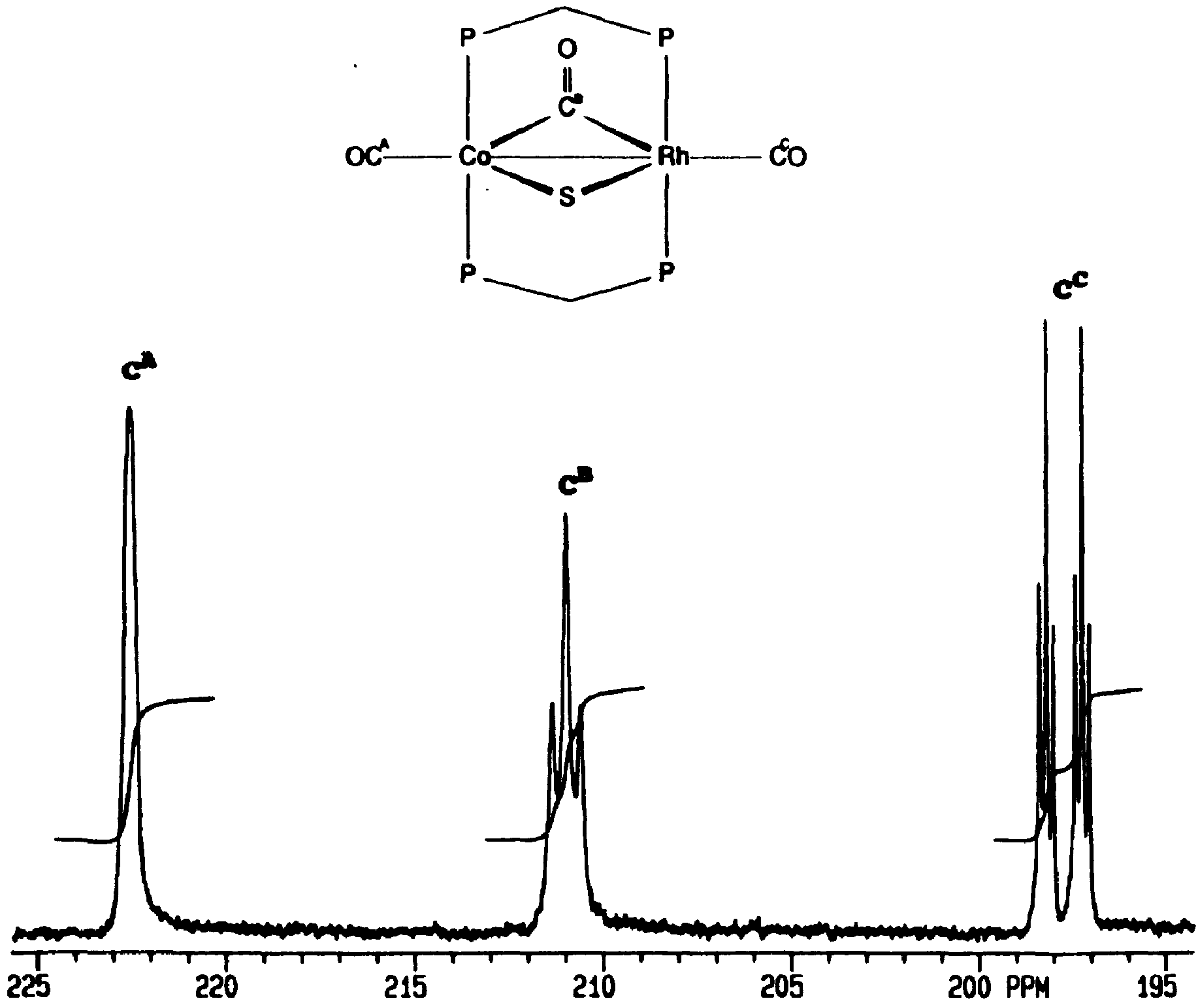


Figure 4.7: ^{13}C NMR spectrum of 4.4d

shifts of similar rhodium carbonyl complexes in the literature[12]. Assignments of the other two signals have to be made more tentatively. The lack of any structure to the δ=222.6 resonance suggests it is associated with the cobalt atom. This phenonenon is seen in other cobalt-carbonyl-phosphine complexes and is attributed to loss of P-C couplings due to quadrupolar broadening. The shift is also comparable to those of terminal carbonyls on cobalt in related complexes[35]. The signal at 210.0 ppm is thus assigned to the bridging carbonyl whose presence is confirmed by the ν(CO) stretch at 1796 cm^{-1} in the IR spectrum of **4.4d**. The appearance of a triplet suggests that the carbonyl couples to only two of the four phosphorus atoms. The possibility of weakly semibridging CO, as in **4.2**, resulting in this coupling is ruled out by the low ν(CO) value of 1796 cm^{-1}. A more reasonable explanation is that the coupling of the ^{13}C to the ^{31}P atoms on cobalt is obscured by the quadrupolar mechanism. Another question arises however, and that is why, if a $^{1}J(RhC)$ coupling is observed for the δ=197.7 signal, no $^{1}J(RhC)$ coupling is observed for the bridging carbonyl. The ^{13}C NMR spectra of the transient complexes $[(CO)(SR)Rh(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)_2Re(CO)_2]$ have been recorded and a similar phenomenon is reported[12], that is that the terminal carbonyl on rhodium shows a $^{1}J(RhC)$ splitting of 71 hz, but that all other carbonyls, including the proposed μ-CO, exhibit a singlet. No IR data were available on these labile intermediates and thus the presence of a μ-CO group was considered tentative.

The chemical shift of the tentatively assigned bridging carbonyl probably results from the combination of two trends. Bridging carbonyls tend to be shifted downfield relative to terminal carbonyls, which contradicts the assignment of the δ=222.6 and 211.0 peaks as due to the terminal and bridging carbonyls respectively. Another trend, however, is that 2nd row transition metals exhibit upfield carbonyl shifts relative to the lighter metals[23]. Thus the "heavy" Rh substituent on the bridging carbonyl may cause the chemical shift for the μ-CO ligand to lie somewhere between the expected value for a terminal carbonyl on cobalt and rhodium.

Even with the ambiguity in the assignment of the resonances in the ^{13}C NMR spectrum of 4.4d there is considerable evidence for the $[(CO)Co(\mu\text{-}S)(\mu\text{-}CO)(\mu\text{-}dppm)_2Rh(CO)]$ formulation. The homodinuclear cobalt analogue $[Co_2(\mu\text{-}S)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]$ and related rhodium and iridium dimers $[M_2(\mu\text{-}S)(\mu\text{-}dppm)_2(CO)_2]$[36,37] are well characterized. The lack of a bridging carbonyl and a metal-metal bond in the latter complexes again emphasizes the differences in the electronic requirements of cobalt and the heavier elements in the triad.

The iridium and rhodium derivatives have been shown to have A-frame type structures with trans phosphines and the related $[CoM(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2(CO)_2]$ (M=Co or Rh) are likely to have a similar structure with the addition of a metal-

metal bond and a bridging carbonyl. This type of structure is also expected for the series of halide bridged cations $[CoRh(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_2]^+$ (X=Cl,Br,I) as discusssed in section 4.4.1.1.

4.4.1.3 Characterisation of $[CoRh(\mu\text{-}H)(\mu\text{-}dppm)_2(CO)_3]X$ 4.5 ($X=BF_4$, 4.5a; $X=BPh_4$, 4.5b)

4.4.1.3.1 Structure of 4.5a

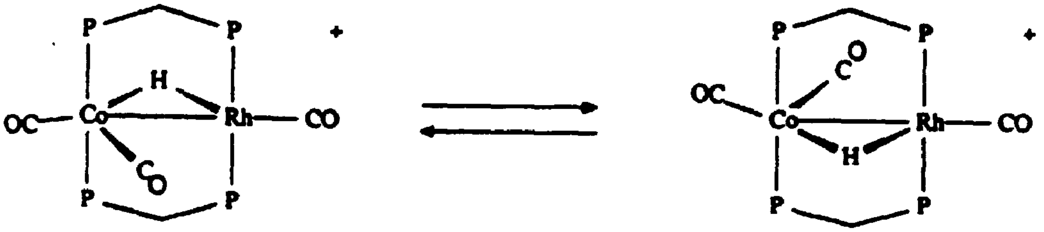
Crystals of suitable quality for an X-ray diffraction study[38] were obtained by recrystallization of 4.5a from CH_2Cl_2/hexane. The structure of 4.5a contains features in common with 4.2. For example, angles subtended at the cobalt and rhodium atoms by the phosphorus donors are 131.98(6)° and 162.71(6)° respectively. The cis and trans orientation of the phosphines at the cobalt and rhodium atoms is also found in 4.2. Both 4.5a and 4.2 contain a semibridging carbonyl more strongly bonded to the cobalt atom. The distance from the rhodium atom to the carbon atom of the semibridging ligand is 2.279(6)Å in 4.5a and 2.420(4)Å in 4.2 indicating that the ligand is closer to a symmetrical bridge in 4.5a. One unusual feature in 4.5a is the Co-Rh distance of 2.6480(8)Å when compared to 2.6852(7)Å in 4.2. Protonation of a metal-metal bond with formation of a (μ-H) group is usually accompanied by an increase in the metal-metal bond distance associated with a three centre,two electron bond. For example, the metal-metal distance in $[RhRe(CO)_4(\mu\text{-}dppm)_2]$ increases from 2.7919(6)Å to 3.0036(7)Å upon protonation[10,13]. The cobalt-cobalt distance in $[Co_2(CO)_4\{\mu-(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]^{39}$ is 2.635(2)Å while in the protonated complex $[Co_2(\mu-H)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^{40}$ the metal-metal distance is 2.736(1)Å.

4.4.1.3.2 IR spectrum of 4.5

The IR spectrum of 4.5 contains ν(CO) stretches at 1981, 1946 and 1933 cm^{-1}. The lowest stretch at 1933 cm^{-1} is suggestive of a terminal carbonyl, however, the solid state structure of 4.5a clearly demonstrates a semibridging carbonyl more strongly attached to the cobalt atom. A ν(CO) stretch for complex 4.2 at 1815 cm^{-1} is also attributed to a semibridging carbonyl more strongly attached to the cobalt atom. The discrepancy between the two values can probably be attributed to the presence of the proton in 4.5a which could reduce the backbonding to the carbonyl ligand resulting in a higher ν(CO) stretch.

4.4.1.3.3 ^{31}P and ^1H NMR spectra of 4.5

The ^{31}P NMR spectrum of 4.5 exhibits the characteristic triplet and doublet of triplets seen in the other $CoRh(\mu-dppm)_2$ type complexes. The chemical shifts of the phosphorus atoms on cobalt and rhodium are shifted downfield 13.3 and 2.7 ppm respectively from 4.2. This downfield shift is consistent with the deshielding of the phosphorus atoms resulting from the increase in the oxidation state of the metal atoms from M(0) to M(I). The ^1H NMR of 4.5 reveals a broad resonance at $\delta=-13.4$ indicating the presence of a metal hydride. A singlet resonance at $\delta=3.80$ appears for the dppm methylene protons (CH_2P_2). The hydride bridged structure suspected for 4.5 has no mirror plane containing the Co-Rh axis and thus an AB type pattern is expected for the $CH_aH_bP_2$ protons. Two possible types of fluxionality could account for this discrepancy. A rapid delocalized carbonyl/hydride exchange would make the protons chemically equivalent. However, the structure was shown to be rigid with respect to delocalized CO exchange at room temperature by ^{13}C NMR. Alternatively, inversion of the hydride through the metal-metal bond axis, as shown in Equation 4.4, would accomplish the same thing.



(4.4)

Similar hydride inversions have been observed in related complexes such as $[Pt_2(H)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ [41].A variable temperature ^1H nmr investigation of 4.5 failed to provide any insight into the mechanism of fluxionality as the room temperature singlet seen for the CH_2P_2 protons on dppm is merely broadened at -90°C.

4.4.1.3.4 ^{13}C NMR spectra of 4.5

The ^{13}CO enriched sample of 4.5 was prepared by the reaction of a ^{13}CO enriched sample of 4.2 with HBF_4 in an analogous manner to the preparation of an unenriched sample. The ^{13}C nmr of 4.5 exhibits two resonances, with integrated intensities of 2:1, in the carbonyl region of the spectrum. They are assigned to the carbonyl ligands on cobalt(δ=206.9,s) and rhodium(δ=182.0,dt)respectively. The assignments were made on the basis of the $^1J(RhC)$ splitting of the δ=182 resonance and the tendency of cobalt carbonyls to be deshielded relative to rhodium carbonyls[23]. Also the lack of $^1J(P-C)$ splitting at the δ=208 resonance is consistent with broadening of the signal due to $^{59}Co-^{13}C$ quadrupolar coupling.

The solid state structure of 4.5a indicates chemically distinct carbonyls on the cobalt atom and yet the singlet at δ=206.9 persists down to -82°C, indicating there is a fluxional process operating. The mechanism postulated for the observed chemical equivalence of the $CH_aH_bP_2$ protons in the ^1H NMR of 4.5, which involves inversion of the hydride through the Co-Rh axis (equation 4.4), would also make the carbonyl ligands on cobalt equivalent on the NMR time scale. The appearance of two sets of resonances in the ^{13}C NMR spectrum even at room temperature rules out the possibility of a carbonyl exchange between metal centres.

4.4.1.3.5 Differences in $[MM^1(H)(CO)_n(dppm)_2]^+$ complexes

A series of complexes $[MM^1(H)(CO)_n(dppm)_2]^+$ ($M=M^1=Co, n=4$; $M=Co, M^1=Rh, n=3$; $M=M^1=Rh, n=2$ or 3; $M=M^1=Ir, n=2, 3$ or 4; $M=Rh, M^1=Ir, n=3$) are also known. In $[Co_2(\mu\text{-}H)(\mu\text{-}dppm)_2(CO)_4]^+$ (section 3.3.2) and $[Ir_2(\mu\text{-}H)(CO)_4(\mu\text{-}dppm)_2\}$[42] all carbonyls are assigned as terminal and each metal has an 18 electron count. The complexes $[M_2(\mu\text{-}H)(CO)_3(dppm)_2]^+$ (M=Rh[19] or Ir[42]) are assigned a structure similar to that found in **4.5** only with a symmetrical (μ-CO) group. The bridging CO is reversibly removed to give the complexes $[M_2(\mu\text{-}H)(CO)_2(dppm)_2]^+$. The mixed metal complex $[RhIr(H)(CO)_3(dppm)_2]^+$ [11] is thought to contain only terminal carbonyls based on the lowest ν(CO) stretch (1899 cm^{-1}) in its IR spectrum. Based on the assignment of the $\nu(CO)=1933$ cm^{-1} to the semibridging carbonyl in the structurally characterized complex **4.5a**, the structure of $[RhIr(\mu\text{-}H)(CO)_3(\mu\text{-}dppm)_2]^+$ should probably be reevaluated.

A common structural feature of most of the complexes discussed above, in addition to the μ-H group, is presumably the trans orientation of the phosphines about each metal to give A-frame structures as opposed to the cis-trans arrangement of the phosphine in **4.2** and in the complexes $[M_2(CO)_3(dppm)_2]$ (M=Rh[19] or Ir[10]). The structure of the cation $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ [43] containing trans phosphines, has been determined and presumably $[Co_2(\mu\text{-}H)(CO)_4(dppm)_2]^+$ has the same structure. However, **4.5a**, the first structurally characterized complex of the type $[M_2(\mu\text{-}H)(CO)_3(\mu\text{-}dppm)_2]^+$, demonstrates cis and trans phosphines at the cobalt and rhodium atoms respectively.

4.4.1.3.6 Reactions of <u>4.5</u> with O_2

Dark brown solutions of **4.5** dissolved in either CH_2Cl_2 or acetone react over a period of hours with pure or atmospheric oxygen to give bright yellow solutions. ^{31}P NMR spectra of these solutions consistently reveal a single product **4.6** with resonances at δ=37.7 {t,$^2J(PP)$=17.2 Hz} and 18.4 {dt,$^2J(PP)$=17.2 Hz, $^1J(RhP)$=128.2 Hz)}. The observed pattern in the ^{31}P NMR spectrum of this new yellow complex is characteristic of the $CoRh(\mu\text{-}dppm)_2$ frame as seen in the numerous other complexes discussed in this chapter. Solutions of $[Ir_2I_2(CO)(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ in CH_2Cl_2 were also recently found to react with pure or atmospheric oxygen to give a structurally characterized complex in high yield[44]. $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(\mu\text{-}dppm)_2]$ provides the first example of a peroxy-bridged complex having a accompanying metal-metal bond to give a cyclic dimetallo-peroxide grouping. Evidence for the presence of a dioxygen ligand in **4.6** is provided from a ^{31}P NMR spectrum of a pure sample of the yellow complex which had decomposed overnight in a sealed NMR tube. When the spectrum was rerun, resonances attributable to the peroxy complex $[Rh(O_2)(\eta\text{-dppm})_2]^+$ {δ=-14.4[m,^1J(RhP)=112.4 Hz], -30.8[m, ^1J(RhP)=82 Hz]}[17] were observed along with the starting material. If the structure of 4.6 is similar to that of $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(\mu\text{-dppm})_2]$ only containing a cobalt and a rhodium center then it is conceivable that decomposition could proceed via extrusion of the $[Rh(O_2)(dppm)_2]^+$ cation. The IR spectrum was obtained on a ^{13}CO enriched sample of the complex obtained by accidental exposure of a ^{13}CO enriched sample of 4.5 to atmospheric O_2. The spectrum consisted of stretches, presumably due to the various isotopomers, in the region 1981-1923 cm^{-1} and thus 4.6 contains only terminal carbonyls as in the structure of $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(\mu\text{-dppm})_2]$. For complete characterization more spectroscopic and analytical evidence is required and a structural determination by X-ray crystallographic methods is desirable. Attempts at growing crystals have proven fruitless due to the decomposition problem discussed above. However on one occasion several large orange yellow crystals had precipitated from reaction solutions containing the yellow species. From these a single crystal was selected and data were collected on the crystal[45]. Two regions of high electron density presumably representing metal centres, were located in bonding proximity as expected for a $CoRh(\mu\text{-dppm})_2$ type structure. A third centre of electron density was located at a nonbonding distance from the bonded metal atoms. It is possible that the complex is ionic and the isolated metal atom is present as an ion such as $[CoCl_4]^{2-}$

which could form in a solvent like CH_2Cl_2. Resolution of the structure past this state has not proceeded.

4.4.1.3.7 Complex containing the $CoRh_2(\mu\text{-dppm})_3$ core 4.7

A very interesting complex 4.7 thought to contain a $CoRh_2(\mu\text{-dppm})_3$ core has been detected under two sets of reaction conditions. CH_2Cl_2 solutions of 4.5 resulting from the addition of aqueous HBF_4 to solutions of 4.2 exposed to atmosphere for several days (as opposed to hours in the formation of 4.6) result in mixtures containing 4.7. The reason for the difference between conditions leading to 4.7 and 4.6 may be due to the presence of water in reactions leading to 4.7 whereas recrystallized samples of 4.5 are used in the preparation of 4.6. Samples of 4.2 that have been exposed to atmosphere for several weeks develop a surface layer of grey material indicating surface decomposition presumably through oxidation. On two occasions samples of 4.2 in this state were reacted, in CH_2Cl_2 that had not been deoxygenated, with HBF_4(aqueous) to give bright yellow solutions. The ^{31}P NMR spectrum of a solution reveals that 4.7 is essentially the only phosphorus containing species present.

The ^{31}P NMR spectrum of 4.7 (Figure 4.8) consists of three sets of resonances integrating as 1:1:1 at δ=16.9 (ddtr), 28.0 (ddd) and 63.6 (dd). The spectrum can be interpreted in terms of an $A_2B_2C_2X$ system where A and B are the phosphorus atoms on rhodium, C are the phosphorus atoms

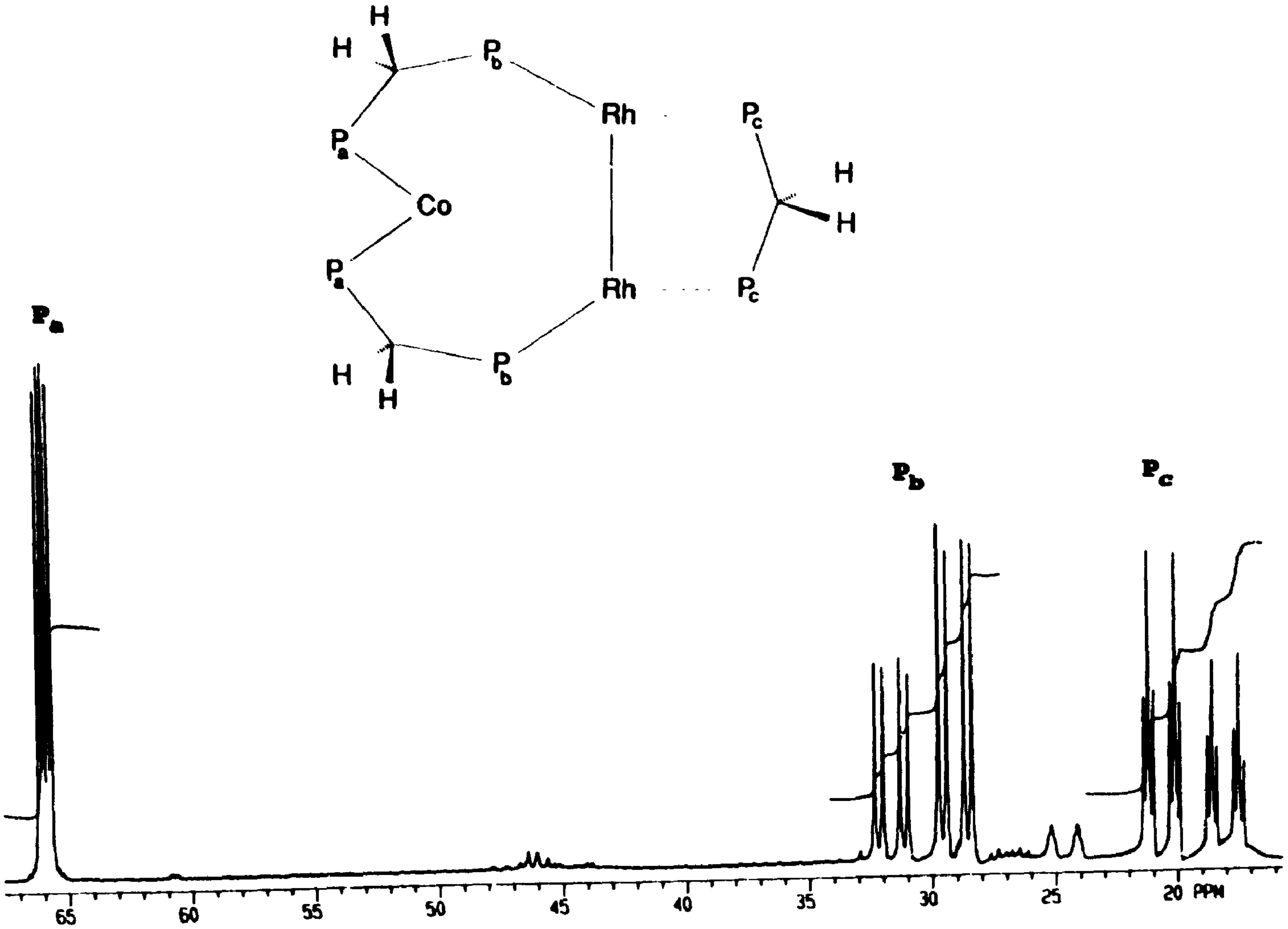


Figure 4.8: ^{31}P NMR spectrum of 4.7

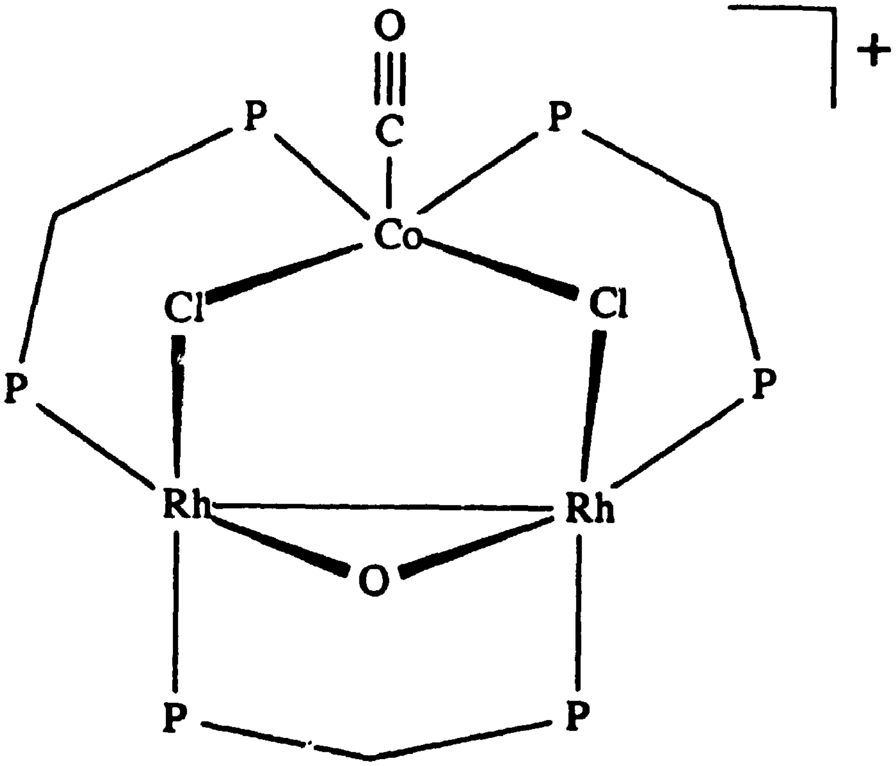
on the cobalt and X is the NMR active rhodium nucleus as shown in Figure 4.8. The resonances at 28.0 and 16.9 ppm are attributed to the phosphorus atoms on the rhodium atoms and $^1J(RhP)$ values of 124.4 and 132.6 Hz are observed. The large 316.5 Hz splitting common to both multiplets suggests a trans $^2J(PP)$ coupling. The chemical shifts for the designated P_b and P_c resonances are also consistent with μ-dppm phosphorus on rhodium as seen in numerous $Rh_2(\mu\text{-dppm})_2$ type complexes[30]. The other splitting in the P_b and P_c multiplets can be attributed to coupling between the P_b and P_c nuclei with the P_a nuclei coordinated to cobalt. The chemical shift of 63.6 ppm is more consistent with a μ-dppm phosphorus atom on a cobalt than a rhodium centre. If the structural interpretation of the spectrum is correct then the complex is very interesting in two respects. Trinuclear complexes of the cobalt triad are not very diverse and include molecules like $[Co_3(CO)_9CR]$[46] and $[Rh_3(\mu\text{-}PPh_2)_3(PPh_3)_2(CO)_3]$ [47].The trinuclear $CoRh_2$ frameworks is also found in the paramagnetic cluster $[(Cp^*Rh)_2(CpCo)(\mu_3\text{-}CO)_2]$[48]. The arrangement of the phosphines as suggested by the ^{31}P NMR spectrum, is also very interesting. In other $M_3(\mu\text{-dppm})_3$ systems such as $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (M=Pd[49],Pt[50]), the phosphines are arranged cis to each other on each metal and the six phosporus donors and three metal atoms form a roughly planar arrangement. In 4.7 the ^{31}P NMR suggests that one dppm spans a Rh-Rh unit while one of each of the remaining dppm ligands occupies a site trans to the phosphorus donors in the $Rh_2(\mu$-dppm) fragment. The other end of each remaining dppm is coordinated to the cobalt and considerable twisting of the CoRh(μ-dppm) ligands would therefore be required to accomodate trans phosphines on the rhodium if cobalt-rhodium bonds are present. The strain associated with this twisting may be the reason for the cluster to fragment as will be discussed.

The ^1H NMR spectrum of 4.7 exhibits some very interesting features. For the structure drawn in Figure 4.8 two sets of resonances are expected integrating 2:1 for the methylene protons on the CoRh(μ-dppm) and $Rh_2(\mu$-dppm) ligands respectively. Two resonances at 4.03 and 4.60 ppm are observed and although the weaker resonance is overlapped by another signal due to some unknown species, it appears to be approximately one half the intensity of the stronger signal. The ^{31}P NMR spectrum run on the same sample reveals minor phosphorus containing impurities which presumably account for some of the weaker intensity signals that are not attributable to 4.7. The resonances at 4.03 and 4.60 ppm appear as singlets which is consistent with a planar arrangement of phosphorus atoms around the metal triangle.

The ^1H NMR spectrum of 4.7 also exhibits a broad resonance at -12.0 ppm indicating the presence of a metal hydride. More evidence for the nuclearity of the cluster comes from fast atom bombardment (FAB) mass spectroscopic results. A peak at 1417 amu is found corresponding to the $CoRh_2(\mu$-dppm$)_3$ frame. Another cluster of peaks the largest of which is at 1532 is also observed.The presence of CO and a hydride are indicated by the ν(CO) stretch at 1983 cm^{-1} and signal at δ= -12.0 in the IR and ^1H NMR spectra of 4.7 respectively. A possibility to explain the 1532 centered cluster of peaks could be a $CoRh_2(\mu\text{-dppm})_3(CO)^{35}Cl_2(O)(H)$ cluster. The chloride and oxygen could have been generated by the CH_2Cl_2 used as solvent and atmospheric oxygen respectively. In addition to the mass spectroscopic evidence for a $[CoRh_2H(O)(CO)Cl_2(dppm)_3]$ parent ion, carbon and hydrogen analysis are consistent with a $[CoRh_2H(O)(CO)Cl_2(dppm)_3][BF_4]_2$ formulation.

Based on the various spectroscopic evidence, a possible structure for 4.7 can be proposed (Figure 4.9). In the structure drawn in Figure 4.10 the chlorides bridge the cobalt-rhodium edges and there are no cobalt-rhodium bonds. The cobalt(I) centre has an 18 electron count and the two rhodium(II) centers have 16 electron counts and the overall charge on the cluster is +1. It is unlikely that the metal, phosphorus, chloride and oxygen atoms are coplanar in the solid state of the' molecule, however, a fluxional inversion of the chloride and through the μ-dppm ligands could create a time averaged mirror plane containing the $CoRh_2$ triangle consistent with the ^1H NMR spectrum of 4.7. The lack of cobalt-rhodium bonds may also explain the ease of decompositon of 4.7 into cobalt and rhodium complexes as will be discussed. Protonation of the cluster would provide a 2+ cation consistent with the chemical analysis of 4.7.

Figure 4.9: Possible structure of 4.7



The ν(CO) value of 1983 cm^{-1} is consistent with a terminal carbonyl as drawn in Figure 4.10.

Attempts at growing single crystals suitable for X-ray structural analysis were made from various solvent systems and decomposition to a variety of crystalline products results in each case. In the case of recrystalization from acetone, two products are consistently produced. One is a pink crystalline material which exhibits no signal in its ^{31}P NMR spectrum, either due to the absence of phosphorus in the complex or due to paramagnetism of the complex. The pink colour is reminiscent of hydrated Co(II)-halide complexes which could account for both possibilities. The second complex **4.8** is a yellow diamagnetic species whose ^{31}P NMR spectrum (Figure 4.10) exhibits two sets of resonances at δ=-30.6{dt,$^2J(PP)$=30.5 Hz, $^1J(RhP)$=96.3Hz} and -46.1 {dt,$^2J(PP)$=30.5 Hz, $^1J(RhP)$=75.0Hz}. This spectrum is very similar to that of the known $[Rh(O_2)(\eta^2\text{-dppm})_2]^+$ cation[17] and the complex is tentatively formulated as cis-$[RhCl_2(\eta^2\text{-dppm})_2]BF_4$ as indicated in Figure 4.11. Further evidence for this formulation is provide by FAB-MS which gives peaks at 941, 906 and 871, consistent with the parent ion $[RhCl_2(dppm)_2]^+$ and sequential loss of both chlorides.

4.4.1.4 Structure of $[CoRh(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-dppm})_2(CO)_2]$ 4.9

The complex crystallizes from CH_2Cl_2/EtOH as dark grey-green crystals of suitable quality for X-ray diffraction studies[15]. An ORTEP representation of the structure is shown

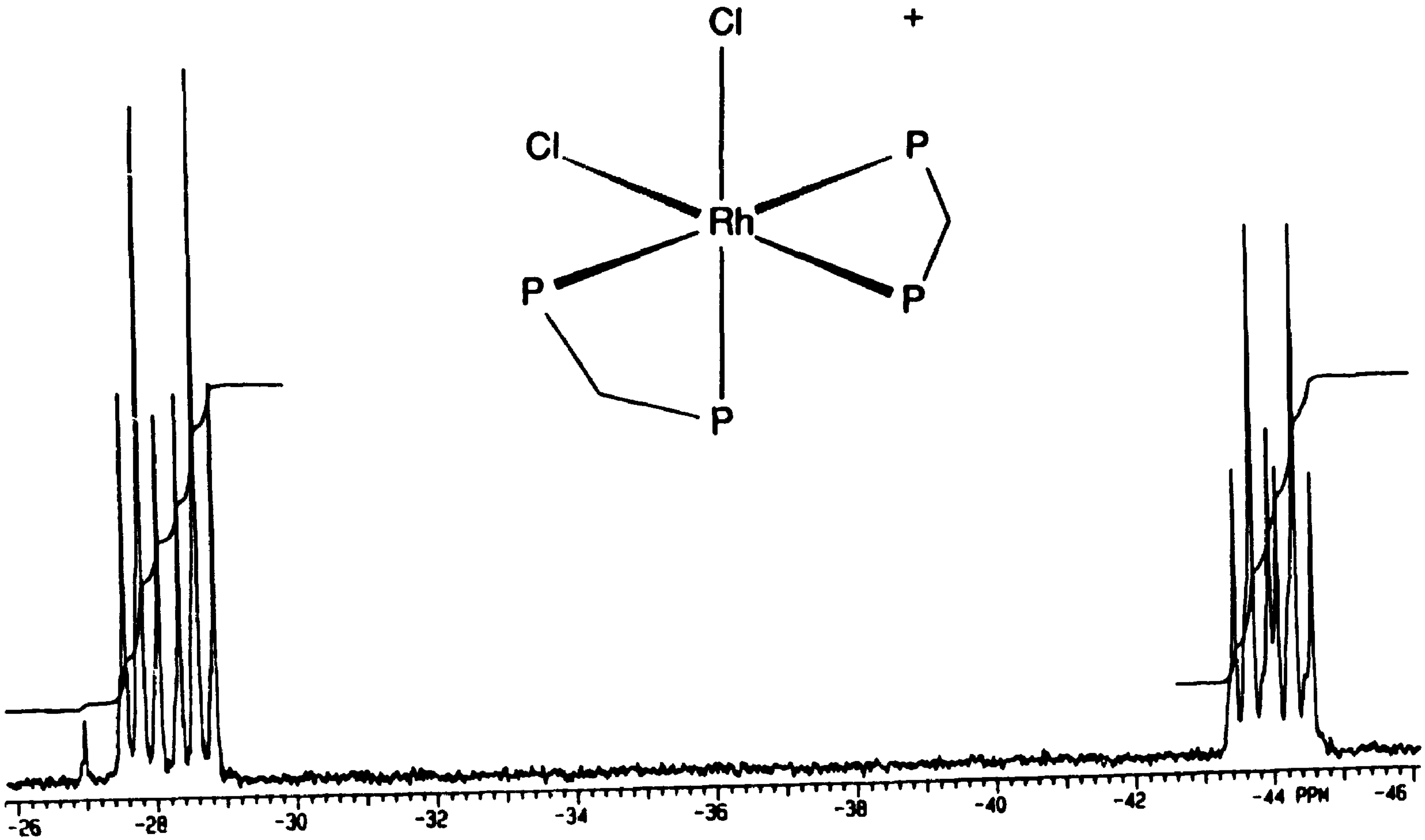


Figure 4.10: ^{31}P NMR spectrum of 4.8

Figure 4.11: ORTEP representation of 4.9

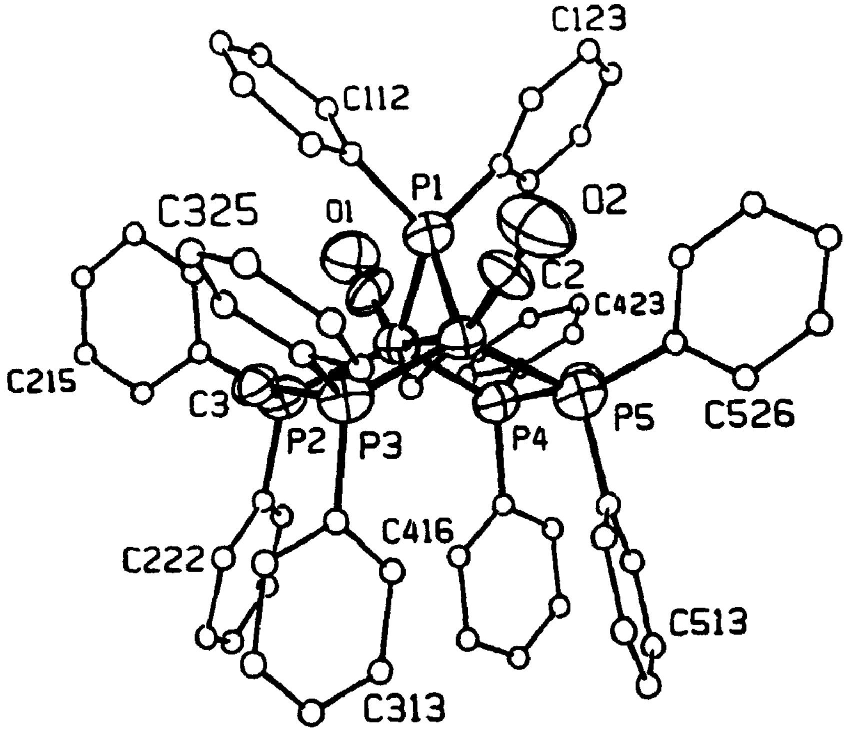


Table 4.3: Selected bond distances and angles in 4.9

Bond	**Distance(Å)**	**Bond**	**Distance(Å)**
M(1)-M(2)	2.795(3)	M(2)-P(1)	2.238(7)
M(1)-P(2)	2.247(7)	M(2)-P(3)	2.242(8)
M(1)-P(4)	2.252(7)	M(2)-P(5)	2.262(8)
M(1)-C(1)	1.747(22)	M(2)-C(2)	1.739(25)
M(1)-H	1.80	M(2)-H	1.48
M(1)-P(1)	2.217(7)		
O(1)-C(1)	1.14(3)		
O(2)-C(2)	1.18(3,		

Angle	**Degrees(°)**	**Angle**	**Degrees(°)**
M(2)-M(1)-P(1)	51.5(2)	M(1)-M(2)-P(1)	50.8(2)
M(2)-M(1)-P(2)	94.7(2)	M(1)-M(2)-P(3)	93.0(2)
M(2)-M(1)-P(4)	94.3(2)	M(1)-M(2)-P(5)	93.8(2)
M(2)-M(1)-C(1)	145.5(8)	M(1)-M(2)-C(2)	150.4(9)
P(1)-M(1)-P(2)	112.7(3)	P(1)-M(2)-P(3)	112.6(3)
P(1)-M(1)-P(4)	112.8(3)	P(1)-M(2)-P(5)	110.0(3)
P(1)-M(1)-C(1)	94.1(8)	P(2)-M(2)-C(2)	99.6(9)
P(2)-M(1)-P(4)	128.0(3)	P(3)-M(2)-P(5)	129.7(3)
P(2)-M(1)-C(1)	100.4(9)	P(3)-M(2)-C(2)	101.5(8)
P(4)-M(1)-C(1)	100.2(8)	P(5)-M(2)-C(2)	96.4(9)
C(1)-M(1)-H	166	C(2)-M(2)-H	167

in Figure 4.11. Selected bond angles and distances in **4.9** are given in Table 4.3. The structure is disordered in that there is a 0.5 occupancy by cobalt and rhodium in each metal position. Thus bond distances other than the Co-Rh distance, and bond angles involving the metal centres are average values. This disorder therefore only allows analysis of gross structural features. The Co-Rh distance of 2.795(3) Å is significantly longer than that found in **4.2** {2.6852(7)Å}. This difference can be attributed to the presence of a CoRh(μ-H) 3c-2e bond in **4.9**. ^{1}H NMR provides evidence for the presence of a hydride and, despite the disorder in the structure, a peak appeared in the difference Fourier map at a position expected for the hydride and thus is included in the ORTEP representation of the structure of **4.9**.

The structure of **4.9** differs significantly from those suggested for the series of complexes [CoRh(μ-X)(μ-CO)(dppm)$_2$(CO)$_2$]$^{n+}$ (X=Cl,Br or I, n=1; X=S,n=0) discussed in section 4.4.1.1. In these complexes each metal is thought to have a TBP geometry, ignoring the metal-metal interaction, with the phosphine donors of the dppm ligands in the axial sites and with the two TBP's fused through the bridging ligands at shared equatorial sites. In **4.9** the coordination geometry about each metal is again distorted TBP but the average angle subtended by the phosphine donors of the dppm ligands at each metal is 128.0°, much closer to the 120° angle found between equatorial ligands than axial in a TBP structure. A similar structural feature is also observed at the cobalt atom in 4.2. Thus the two metal centered TBP's are fused through bridging hydride and PPh_2 ligands which occupy shared metal axial and equatorial sites respectively. The phosphine donors of the dppm ligands occupy equatorial sites and the remaining axial site is taken by a terminal carbonyl on each metal.

The distortion of the structure from that observed for other $M_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-dppm})_2$ type dimers probably results from the very different steric requirements of the μ-H and μ-PPh_2 which force the dppm ligands towards the hydride bridged side of the dimer. It would be interesting to prepare a less sterically hindered complex $[M_2(\mu\text{-}H)(\mu\text{-}PMe_2)(\mu\text{-dmpm})_2(CO)_2]$ to see if steric factors alone control the geometry of this complex.

The structure of the related complex $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-dppm})(CO)_4]$ has been determined and it contains a very similar arrangement of ligands around the metal atoms[51]. The main difference arises from the relief of the steric constraints found in 4.9 by substitution of a μ-dppm by a terminal carbonyl on each metal atom. The homodinuclear cobalt analogue of 4.9 and the similar nickel derivative $[Ni_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2(CO)_2]^+$ [52] have also been characterized (section 6.2).

4.4.1.4.1 Spectroscopic characterisation of 4.9

The complex is readily soluble in many organic solvents and thus characterization by NMR techniques was possible.

The ^{1}H NMR spectrum of 4.9 exhibits a broad resonance at δ=-15.49 which is strong evidence for the presence of a metal hydride. In addition multiplets at δ=2.91 and 1.78 consistent with the chemical inequivalence of the dppm $CH_aH_bP_2$ methylene protons as observed in the solid state structure of 4.9, are obsreved.

The ^{31}P NMR spectrum of 4.9 consists of 3 sets of resonances at δ=26.0, 43.9 and 211 assigned to the dppm phosphorus atoms on rhodium and cobalt and the bridging phosphide respectively. The spectrum is interesting in two respects. It provides the first example of observed second order coupling in the series of complexes containing the [CoRh(μ-dppm)$_2$] unit which have been synthesized. The PRh signal consists of at least 16 lines and is characteristic of an AA^1XX^1MN (A,X,N=^{31}P; M=Rh) type spectrum. The PCo resonance consists of considerably fewer and broader lines, presumably due to the ^{59}Co quadrupolar broadening effect. The other interesting feature is that at lower temperatures the PCo signal sharpens considerably while the RhP multiplet becomes much broader. The sharpening of the PCo signal is expected from thermal ^{59}Co-^{31}P decoupling. Low temperature broadening of a signal is usually interpreted in terms of freezing out of fluxionality but it is difficult to envisage a fluxional process involving the sterically hindered and anchored phosphines on rhodium.

The appearance of second order splitting in 4.9 raises the following question; is the appearance of the second order splitting in **4.9** the result of the suspected difference in phosphine orientation from other M(1) dimers or is it the result of introduction of a third type of phosphorus atom or some other factor?

4.5 Miscellaneous reactions

In addition to the reactions of **4.2** and related complexes discussed in the previous sections, numerous other reagents were tried. For example, as indicated by ^{31}P NMR, CH_2Cl_2 solutions of **4.2** failed to react when H_2, $HC\equiv CH$, $MeC\equiv CH$, or $H_2C=CH_2$ are bubbled through the solution for several minutes. **4.2** also fails to react with an excess of $PhC\equiv CPh$ under refluxing conditions. Dimethyl acetylenedicarboxylate (DMAD) does react with CH_2Cl_2 solutions of **4.2** however. A ^{31}P NMR spectrum of a reaction mixture, in addition to other resonances, reveals two signals at 50 ppm and 28 ppm the general appearance of which is familiar to the $CoRh(\mu\text{-dppm})_2$ core. Attempts at obtaining a pure crystalline compound by fractional crystallization were not successful. DMAD complexes of homodinuclear rhodium[53] and iridium[54] μ-dppm derivatives are well known. For example, the structure of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMAD})(dppm)_2]$[53] has been determined crystallographically and the C-C axis in the acetylene is parallel to the metal-metal axis. The complexes $[Rh_2(CO)_2(\mu\text{-dppm})_2(PhC\equiv CPh)]$[55] and $[Co_2(CO)_2(\mu\text{-dppm})_2(\mu\text{-RC}\equiv CR)]$[56] (R=Me,Ph,$CO_2Me$) contain the acetylene orthogonal to the metal-metal axis. **4.2** also reacts with the substituted ethylene, $C_2H_2F_2$, however the ^{31}P NMR spectrum reveals cluster degradation.

An interesting feature of [CoRh(CO)$_3$(μ-dppm)$_2$] is that the rhodium centre has a 16 electron count and is therefore electronically unsaturated. This was anticipated to enhance the reactivity of 4.2 to two-electron donors such as alkenes and acetylenes. 4.2 is seen to be less reactive toward this type of addition than the electronically saturated [Co$_2$(CO)$_4$(μ-dppm)$_2$] which reacts readily with HC≡CH under ambient conditions (section 3.3.5). Also [CoRh(H)(CO)$_3$(dppm)$_2$]$^+$ has a 16 electron rhodium centre and fails to react with HC≡CH while [Co$_2$H(CO)$_4$(dppm)$_2$]+ reacts readily with acetylene (section 3.3.2.1). It is tempting to attribute the difference in the reactivities of the cobalt-rhodium and related cobalt dimers to the presence of the rhodium. While the electron count of rhodium in the complexes [CoRh(CO)$_3$(μ-dppm)$_2$] and [CoRh(μ-H)(CO)$_3$(μ-dppm)$_2$]$^+$ is only 16, however, the position of rhodium in the periodic table makes it electron rich.

The reaction of 4.2 in CH_2Cl_2 with O_2 is accompanied by a marked change in the colour of the solution from dark red-brown to bright yellow over a period of 20 minutes. The ^{31}P NMR of the reaction solution exhibits numerous resonances, the largest by far of which is a singlet at 21 ppm. No resonances exhibiting the familiar triplet and doublet of triplets pattern of the CoRh(μ-dppm)$_2$ core are recognized and it thus appears that cluster degradation has occurred.

Chapter 7 discusses the synthesis and characterization of the complex $[(\eta^1\text{-dppm})(CO)_2Co(\mu\text{-dppm})_2BH_2]$ which has provided the first structural characterization of a simple metal-BH_2 link. The unique nature of this molecule prompted various schemes aimed at producing similar molecules from reactions of metal carbonyl complexes with $BH_3 \cdot THF$ and derivatives[57]. The addition of $BH_3 \cdot THF$ to solutions of **4.2** was monitored by ^{31}P NMR and no reaction was observed.

4.6 Experimental

[CoRh(μ-dppm)$_2$(CO)$_3$] <u>4.2</u>

A suspension of $NaBH_4$ (0.337g)in EtOH (15mL), deoxygenated by bubbling N_2, was added to a CO saturated solution of $RhCl_3\cdot(H_2O)_n$ (0.353g), $CoCl_2\cdot(H_2O)_6$ (0.321g) and dppm (2.00g) in C_6H_6/EtOH (30 mL, 1:1). The mixture was allowed to stir for 2 h under a slow CO stream and the solvent was removed under vacuum. The solid was boiled with degassed C_6H_6 (10 mL) for 2 min to convert any of the suspected intermediate, [Rh(CO)(dppm)$_2$][Co(CO)$_4$], to **4.2** and again the solvent was removed by vacuum. The residue was washed with EtOH (40 mL) and recrystallized from CH_2Cl_2/EtOH.

Yield: 40% Anal. calc. for $C_{53}H_{44}CoO_3P_4Rh$: C, 62.73 ; H, 4.37 Found : C, 63.15 ; H, 4.45.

Spectroscopic data: NMR in CD_2Cl_2; $\delta^{31}P$(labelling defined in Fig. 4.4) = 29.1[br s, PCo], 17.9[dt, $^2J(P_aP_b)$ = 72 Hz, $^1J(RhP)$ = 129 Hz, PRh];$\delta^{13}C(-45°C)$ = 214.7[br s, CoCO], 214.7[br s, CoCO], 180.7[dt, $^2J(PC)$ = 15 Hz, $^1J(RhC)$=71 Hz, RhCO]; δ^1H = 4.24[s, CH_2P]. I.R.(Nujol): ν(CO) = 1965(s), 1922(s), 1815(s) cm^{-1}.

[CoRh(μ-Cl)(μ-CO)(μ-dppm)$_2$(CO)$_2$]BPh$_4$ <u>4.4a</u>

4.2 (0.25g)was dissolved in $CHCl_3$ (5mL) and the solvent was removed by vacuum. The residue was washed with EtOH (15mL) and excess $NaBPh_4$ was added to the red EtOH washings. The resulting orange precipitate was recrystallized from CH_2Cl_2/EtOH.

Yield: 89% Anal. calc. for $C_{77}H_{64}BClCoO_3P_4Rh$: C, 67.54; H, 4.71 Found : C, 67.45; H, 4.83

The same complex was prepared when equimolar amounts of **4.2** and $HgCl_2$ were stirred in CH_2Cl_2. The solvent was removed by vacuum and the residue was washed with EtOH and the resulting red solution was filtered. Excess $NaBPh_4$ was added giving an orange precipitate which was filtered and recrystallized from CH_2Cl_2.

Spectroscopic data : NMR; $\delta^{31}P(CD_2Cl_2)$(labelling defined in Fig. 4.8) = 43.7[t, $^2J(PP)$ = 39 Hz, PCo], 24.1[dt, $^2J(PP)$ = 39 Hz, $^1J(RhP)$ = 104 Hz, PRh];$\delta^1H(d_6$-acetone) = 4.20[m, $CH_aH_bP_2$]. I.R.(Nujol) : ν(CO) 1986(m), 1962(s), 1850(m) cm^{-1}.

[$CoRhCl_2(CO)_3(\mu$-dppm$)_2$] <u>4.4a^1</u>

4.2 (0.11g) was dissolved in the minimum amount of $CHCl_3$ (3mL) and EtOH (10mL) was layered on the red $CHCl_3$ solution and allowed to diffuse slowly into the $CHCl_3$ layer. After one week large green crystals precipitated which were filtered and washed with hexane. The cationic species $[CoRhCl(CO)_3(dppm)_2]^+$ **4.4a** was isolated in high yield by addition of excess $NaBPh_4$ to the $CHCl_3$/EtOH mother liquor. Solutions of the sparingly soluble **4.4a^1** in EtOH are yellow from which the $[CoRhCl(CO)_3(dppm)_2]^+$ cation can be precipitated with the addition of excess $NaBPh_4$.

Yield: 31%

IR(Nujol): ν(CO)= 1977(s), 1962(s), 1869(m) cm^{-1}

[CoRh(μ-Br)(μ-CO)(μ-dppm)$_2$(CO)$_2$]BPh$_4$ 4.4d

4.2 (0.12g) was dissolved in the minimum amount of CHBr$_3$ (3 mL). The solvent was removed by vacuum and the residue was washed with EtOH (15mL) and excess NaBPh$_4$ was added to the red EtOH washings. The resulting orange precitate was filtered off and was recrystallized by slow diffusion of EtOH into a CH$_2$Cl$_2$ solution of the solid. After 1 week this resulted in precipitation of large red crystals of the title complex and fine yellow needles of an unidentified rhodium (η^2-dppm) complex {^{31}P NMR : δ=-32.1[d, ^{1}J(RhP)= 74.3 Hz]}. The red crystals were easily separated from the mixture by handpicking and were used for subsequent analysis and spectroscopic work.

Yield: 35% Anal. calc. for $C_{77}H_{64}BBrCoO_3P_4Rh$: C, 65.42; H, 4.56 Found : C, 65.52; H, 4.66

Spectroscopic data : NMR in d$_6$-acetone; δ^{31}P = 43.4[t, ^{2}J(PP)=43.6 Hz, PCo] 24.9[dm,^{1}J(RhP)=100.7Hz,PRh]; δ^1H = 4.45[m,$CH_aH_bP_2$]. IR(Nujol) : ν(CO)= 1997(sh), 1987(sh), 1981(s), 1964(s), 1848(m) cm^{-1}.

[CoRh(μ-I)(μ-CO)(μ-dppm)$_2$(CO)$_2$]BPh$_4$ 4.4c

4.2 (0.25g) and I$_2$ (0.063g) were dissolved in CH$_2$Cl$_2$ (20mL) giving a deep red solution which quickly turned orange. The solvent was removed by vacuum and the remaining residue was washed with repeated EtOH washings (50mL in total). Excess NaBPh$_4$ was added to the orange EtOH solution and an orange powder precitated. The solid was recrystallized from CH_2Cl_2/EtOH.

Yield: 68% Anal. calc. for $C_{77}H_{64}BCoIO_3P_4Rh$: C,63.31; H,4.42

Found : C,63.05; H,4.34.

Spectroscopic data : NMR; $\delta^{31}P$ = 45.4[t, $^2J(PP)$ = 47 Hz, PCo], 26.9[dt, $^2J(PP)$ = 47 Hz, $^1J(RhP)$ = 100 Hz, PRh]; I.R.(Nujol), ν(CO) 1997(m), 1990(m), 1970(s), 1849(m) cm^{-1}.

[CoRh(μ-S)(μ-CO)(μ-dppm)$_2$] 4.4d

4.2 (0.40g) was dissolved in CH_2Cl_2 (5mL) and S_8 (0.013g) was added. The solution was stirred for 10 min. during which time the solution turned from a deep red to a dark brown. The solution was filtered and EtOH (20mL) was layered on the solution giving large brown crystals after 1 week.

Yield: 79% Anal. calc. for $C_{53}H_{54}CoO_3P_4RhS$: C, 60.82; H, 4.24 Found : C, 60.50; H, 4.19

Spectroscopic data : NMR; $\delta^{31}P(CD_2Cl_2)$ = 23.1[dt, $^2J(PP)$ = 32 Hz, $^1J(RhP)$ = 134 Hz, PRh] 36.0[t, $^2J(PP)$ = 32 Hz, PCo]; $\delta^{13}C(CH_2Cl_2/CD_3CN)$ = 197.7[dt, $^1J(RhC)$ = 73 Hz, $^2J(PC)$ = 14 Hz, RhCO], 210.0 [t, $^2J(PC)$ = 56 Hz, μ-CO], 222.6[s, CoCO]; $\delta^1H(CD_2Cl_2)$ = 3.38[br, $CH_aH_bP_2$]. IR(Nujol) : ν(CO) 1971(s), 1958(s), 1796(m) cm^{-1}.

[CoRh(μ-H)(CO)$_3$(dppm)$_2$]X (X=BF$_4$ 4.5a, X=BPH$_4$ 4.5b)

To a red-brown solution of 4.2 (0.32g) in CH_2Cl_2 (15mL) was added HBF_4(aq) (1mL). The solution turned immediately dark brown and the solvent was removed by vacuum. Water was removed by pipette and the remaining wet solid was washed with EtOH (1ml) to remove excess water. The remaining solid was recrystallized from CH_2Cl_2/hexane to give crystalline **4.5a**. Alternatively, EtOH and hexane were allowed to diffuse slowly into the CH_2Cl_2 solutions of **4.5a** to which an excess of $NaBPh_4$ was added, to precipitate **4.5b**.

Yield : While ^{31}P NMR of the reactions of **4.2** with HBF_4(aq) indicate quantitative yields of **4.5a** recrystallized yields of either **4.5a** or **4.5b** are significantly lower (30%) due to handling losses and the solubility of **4.5a** in the EtOH used to remove the water.

Anal. calc. for $C_{53}H_{45}BCoF_4O_3Rh$: C,57.74; H,4.11

Found : C,57.42; H,4.01.

Spectroscopic data : NMR in CD_2Cl_2; $\delta^{31}P$ = 42.5[t, $^2J(PP)$ = 56.5 Hz, PCo], 23.1[dt, $^2J(PP)$ = 56.5 Hz, $^1J(RhP)$ = 111 Hz, PRh]; $\delta^{13}C$ = 206.9[s, 2 C, CoCO], 182.0[dt, 1 C, $^1J(RhC)$ = 60.7 Hz, $^2J(PC)$ = 14.5 Hz, RhCO]; δ^1H = -13.3[br, CoRh(μ-H)], 3.80[s, CH_2P_2]. I.R.(Nujol) : ν(CO) 1981(s), 1946(sh), 1933(m) cm^{-1}.

Complex 4.6

To a dark brown CH_2Cl_2 solution of **4.5b** was bubbled O_2 (5min). After a period of several hours the solution turned bright yellow. **4.6** was never recrystallized in pure form except once from a ^{13}CO enriched sample of **4.5b** in which case the crystalline sample was used for an unsuccessful X-ray diffraction study and therefore a recrystallized yield has not been determined.

^{31}P NMR (CD_3CN/CH_2Cl_2) : δ = 37.7[t,$^2J(PP)$=17.2 Hz, PCo] 18.4[dt, $^2J(PP)$=17.2 Hz, $^1J(RhP)$=128.2 Hz, PRh].

IR(Nujol)(^{13}CO enriched sample): $\nu(^{12}CO)$ = 1981.1(s),1934.8(s); $\nu(^{13}CO)$ = 1967.6(m), 1923.3(m).

Complex 4.7

A sample of **4.2** which showed signs of surface decomposition was dissolved in undegassed CH_2Cl_2 giving a red brown solution and aqueous HBF_4 was added. The solution immediately turned bright yellow (in contrast to the dark brown solutions of **4.5a** normally obtained when fresh samples of **4.2** and degassed CH_2Cl_2 are used). A ^{31}P NMR spectrum of the reaction solution reveals near quantative yields of **4.7**. The solvent was removed by vacuum and the water was removed by pipette. The excess water was removed by washing with EtOH (1ml). The remaining solid was redissolved in CH_2Cl_2 and the solution was concentrated by N_2 to precipitate solid **4.7**.

Anal. calc. for $C_{76}H_{67}B_2Cl_2F_8O_2P_6Rh_2$: C, 53.46 ; H, 3.95 Found : C, 52.68 ; H, 4.08.

Spectroscopic data : NMR in d_6-acetone; $\delta^{31}P$(labelling defined in Fig. 4.11) = 63.6[dd,$^2J(PP)$=40.3 Hz, $^2J(PP)$=22.8 Hz, PCo], 28.0[ddd, $^2J(PP)$=40.3 Hz, $^2J(PP)$=316.5 Hz, $^2J(RhP)$=124.4 Hz], 16.9[ddt, $^2J(PP)$=22.8 Hz, $^2J(PP)$=316.5 Hz, $^1J(RhP)$=132.6 Hz]; δ^1H = 4.032[s,Co(PCH_2P)Rh], 4.60[s, Rh(PCH_2P)Rh]. IR(Nujol) : $\nu(CO)$= 1983.1 cm^{-1}. FAB-MS : m/z

1532, 1417; Calc. for $C_{75}H_{67}Cl_2CoO_2P_6Rh$[P] : 1532, P-$COCl_2$(O)(H) 1417.

cis-[$RhCl_2(\eta^2$-dppm$)_2$]BF_4 4.8

Hexane was allowed to slowly diffuse into solutions of 4.7 to give a mixture of pink crystals and yellow crystals of 4.8. 4.8 was separated from the pink complex by acetone in which the pink complex is insoluble and pure 4.8 was precipitated with hexane.

Spectroscopic data: NMR in CD_2Cl_2; $\delta^{31}P$ = -30.6[dt, $^2J(PP)$ = 30.5, $^1J(RhP)$ = 96.3], -46.1[dt, $^2J(PP)$ = 30.5 Hz, $^1J(RhP)$ = 75.0]. FAB-MS : m/z = 941, 906, 871; Calc. for $C_{50}H_{44}Cl_2Rh$ [P] : 941, P-Cl 906, P-Cl_2 871.

[CoRh(μ-H)(μ-PPh_2)(μ-dppm$)_2$(CO$)_2$] 4.9

To a solution of 4.2 (0.78g) in CH_2Cl_2 (5mL) was added PPh_2H (2 drops). A layer of EtOH was allowed to diffuse into the CH_2Cl_2 reaction solution over a period of days to give crystals of 4.9. Yield: ^{31}P NMR of the reaction mixture shows essentially quantitative yields of 4.9 however recrystallized yields were small (<20%).

NMR data for 4.6: $\delta^{31}P$(d_6-acetone)(labelling defined in Fig. 4.16) = 26.0[m, 2P, RhP], 43.9[m, 2P, CoP], 211[m, 1P, μ-PPh_2], $\delta^1H(CD_2Cl_2)$ = -15.49[br s, CoRh(μ-H)], 2.91[m, CH_aHP_2] 1.78[m, CHH_bP_2].

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Chapter 5 : Synthesis and Characterization of complexes $[CoM(\mu\text{-dppm})_2(CO)_5]$ and $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})M(CO)_4]$ (M=Mn,Re).

5.1 Introduction

Devising systematic syntheses of heteronuclear clusters is a popular pursuit of organometallic chemists and methods employed include the addition of nucleophilic metal fragments to metal-metal bonds[1] or use of metal fragments which are isolobal with agents known to complex to metal-metal bonded complexes[2] (eg. $H^+ = ML^+$ {M=Cu,Ag,Au}). More often than not, however, serendipitous discoveries of heteronuclear clusters are made when mixtures of metal complexes are treated under refluxing or pyrolysis conditions, for example. Bridging phosphines such as dppm have been incorporated into heterobimetallics for two reasons. Firstly, approaches to the systematic synthesis of complexes containing $MM^1(\mu\text{-dppm})$ units involving (η^1-dppm) and/or (η^2-dppm) precursors have proved to be widely successful (section 1.4). Secondly, incorporation of bridging ligands can allow the study of the chemistry of these species without cluster degradation. Such degradation is a common problem in studying the chemistry of unbridged species since metal-metal bond cleavage often occurs due to the frequently polar or dative nature of many $M\text{-}M^1$ bonds[3].

The interest in heteronuclear, and particularly heterodinuclear, clusters is due to the unique chemistry offered by adjacent metals with differing electronic properties. Numerous $MM^1(\mu\text{-dppm})$ complexes of group VIIIb metals have been synthesized and there is current interest in "early-late" heterobimetallics of this type. This term applies to bimetallics containing transition elements widely separated in the periodic table. A more functional definition is dinuclear complexes containing a group VIIIb metal and a metal from earlier in the transition series. Due to their relative positions in the periodic table, the different metals display very different chemistry and their imposed proximity in $MM^1(\mu\text{-dppm})$ complexes can lead to interesting ligand activation chemistry. One possible application of this type of system is in the dual activation of polar molecules such as CO via the formation of a $\eta^2\text{-C=O}$ ligand[4]. It was thought that the oxophilicity of the early transition metals and the relative softness and affinity of late transition metals for carbon would be ideal for this type of activation.

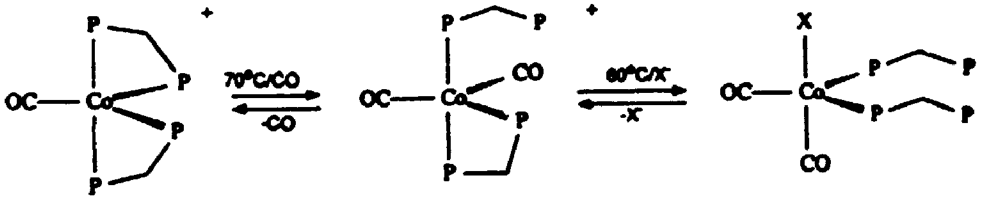
Phosphine bridged heterobimetallics containing elements from the cobalt triad with "early" transition elements have usually been prepared from the reactions of $M(\eta^2\text{-dppm})$ (M=Rh,Ir) complexes (section 1.4). Examples include the complexes $[RhM(CO)_4(\mu\text{-dppm})_2]$ (M=Mn,Re)[5] and $[(CO)_3M^1(\mu\text{-dppm})_2M(CO)X]$ (M^1=Cr,Mo,W; M=Rh,Ir)[6]. Treatment of mer,cis-$[MnCl(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$ with $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2(\text{p-toluidine})]$ in the presence of CO and PF_6^- gives the complexes $[Cl(CO)_2Mn(\mu\text{-dppm})_2M(CO)_2]PF_6$

(M=Rh,Ir)[7]. Other MnM(μ-dppm)$_2$ (M=Rh,Ir) complexes were prepared using mer,cis-[MnCl(CO)$_2$(η^1-dppm)(η^2-dppm)] as a reagent. There is no precedent for a complex containing the MnCo(μ-dppm) unit. Dimers containing a cobalt atom and a group VIIb element include the binary carbonyls [CoM(CO)$_9$] (M=Mn[8,9],Re[9] or Tc[10]) produced by the nucleophilic displacement of halide from [XM(CO)$_5$] by the [Co(CO)$_4$]$^-$ anion. Similarly, the complexes [MCo(CO)$_5$(μ-CO)(DAB)] (M=Mn,Re) are prepared by the reaction of [Co(CO)$_4$]$^-$ with [M(CO)$_3$Br(DAB)][11]. [CpCo(μ-NO)$_2$MnCpPMe$_3$], which contains the rare double nitrosyl bridge, is prepared from the treatment of Na[CpCoNO], prepared in situ by the Na/Hg reduction of [(CpCoNO)$_2$], with [CpMn(CO)(NO)PMe$_3$]BF$_4$[12].

5.2 Synthesis of the complexes [CoM(μ-dppm)$_2$(CO)$_5$] (M=Mn,Re)

In light of the evidence for the intermediacy of [Rh(CO)(η^2-dppm)$_2$][Co(CO)$_4$] in the formation of neutral [CoRh(CO)$_3$(μ-dppm)$_2$] (section 4.2) and the conversion of [Co(CO)(η^2-dppm)$_2$][Co(CO)$_4$] to [Co$_2$(CO)$_4$(μ-dppm)$_2$] (section 2.4.2), it was hoped that replacement of [Co(CO)$_4$]$^-$ with other metal carbonyl anions would provide a general synthetic route to reduced dppm bridged heterobimetallics containing cobalt. M. Cowie coincidentally came up with the same approach to synthesize successfully RhM(μ-dppm)$_2$ (M=Co,Fe,Ru,Cr,Mo,W,Mn,Re) complexes utilizing the ring strain in [Rh(η^2-dppm)$_2$]X[5]. As Cowie has recognized, obvious substitutes for [Co(CO)$_4$]$^-$ are [M(CO)$_5$]$^-$ (M=Mn,Re) ions, which are readily prepared by the Na/Hg reduction of the binary carbonyls $[M_2(CO)_{10}]$. This could in theory provide dppm substituted derivatives of the mixed metal binary carbonyls $[CoM(CO)_9]^{8,9,10}$.

In fact, acceptable yields of $[CoM(\mu\text{-dppm})_2(CO)_5]$ are obtained by refluxing the $[M(CO)_5]^-$ anion, prepared from $[M_2(CO)_{10}]$, with $[Co(CO)(dppm)_2]BPh_4$ under a CO atmosphere in the presence of a halide ion. The halide and CO are present in order to facilitate the ring opening of the chelating dppm ligands according to the established chemistry of the $[Co(CO)(dppm)_2]^+$ cation[13] as shown in equation 5.1.



(5.1)

$[Co(CO)(dppm)_2]^+$ has been shown to be much less reactive than the rhodium and iridium analogues used extensively to make dppm bridged heterobimetallics and it was hoped that formation of a bis-monodentate dppm complex would increase the reactivity of the Co(I) species.

The first attempt at synthesizing a $CoMn(\mu\text{-dppm})_2$ type complex using the $[Co(CO)(\eta^2\text{-dppm})_2]^+$ cation was done in the absence of a source of halide and CO to facilitate the η^2-dppm ring openings. The solvent was removed from the reaction mixture by vacuum and the residue was washed with EtOH and recrystallized from CH_2Cl_2/EtOH to produce large red and orange crystals of $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$ and an unidentified complex 5.1. Crystals of 5.1 were handpicked for ^{31}P NMR and IR spectra.

The ^{31}P NMR spectrum of 5.1 (Figure 5.1) reveals two sets of resonances at δ=81.8[dd] and 28.0[ddd] consistent with bridging dppm on manganese and cobalt respectively. The splitting of the resonances is more consistent with two μ-dppm functions than a single dppm bridge which would exhibit simple doublets for each resonance and an interpretation of the ^{31}P NMR spectrum of 5.1 based on the $CoMn(\mu\text{-dppm})_2$ core is given in the experimental section and in Figure 5.1. The IR spectrum of 5.6 reveals both terminal and bridging carbonyl ligands. 5.1 was isolated in a small yield, it was not completely characterized, and the reproducibility of the synthesis of 5.1 was not established.

5.3 Characterization of $[CoMn(CO)_5(\mu\text{-dppm})_2]$ 5.2

5.3.1 Structure of 5.2

Complex 5.2 crystallizes from CH_2Cl_2/EtOH to give dark red air sensitive crystals of suitable quality for X-ray diffraction[14]. An ORTEP representation of the molecular structure and selected bond distances and angles of 5.2 can be found in Figure 5.2 and Table 5.1 respectively. The

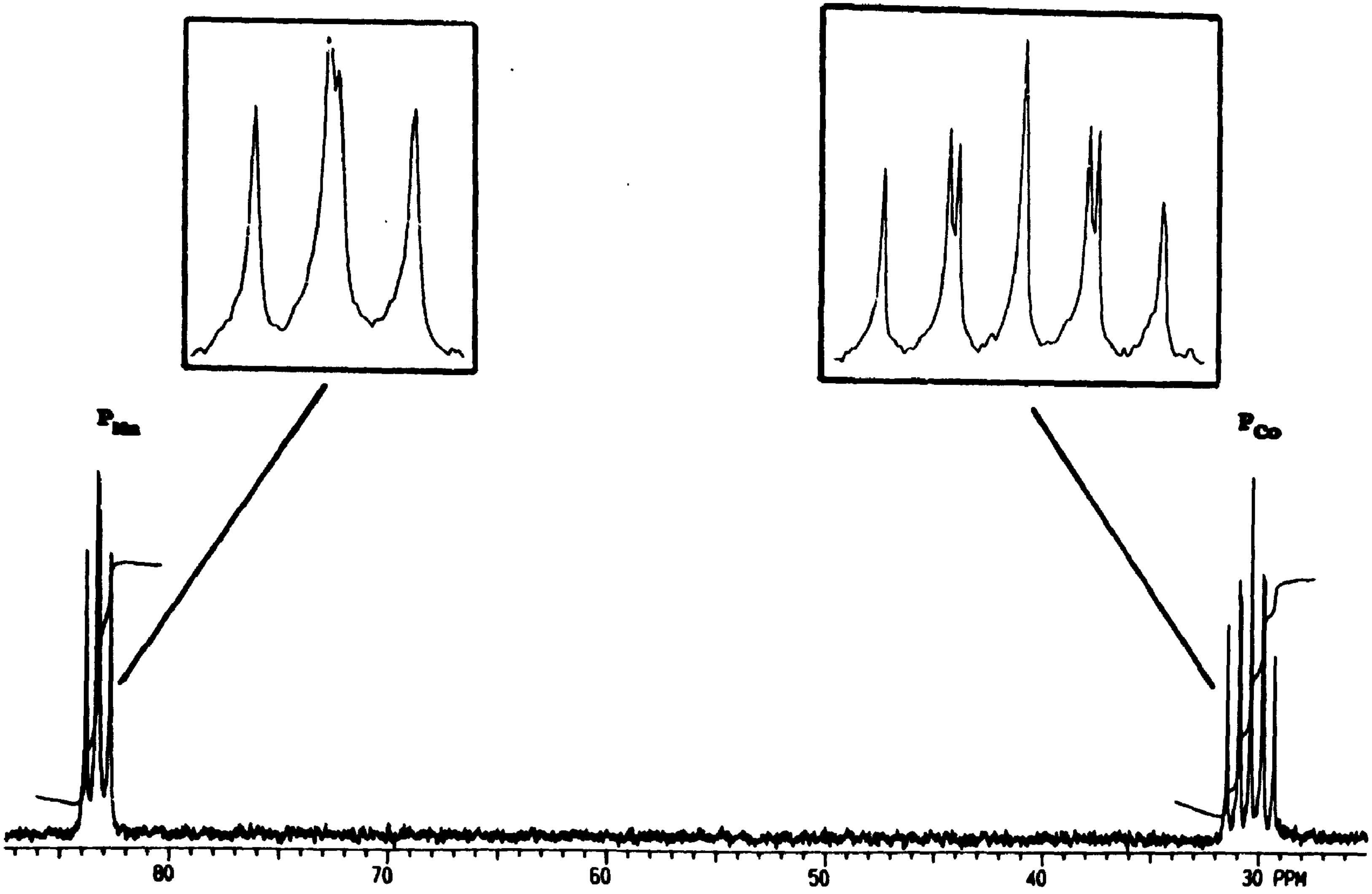


Figure 5.1: ^{31}P NMR spectrum of 5.1

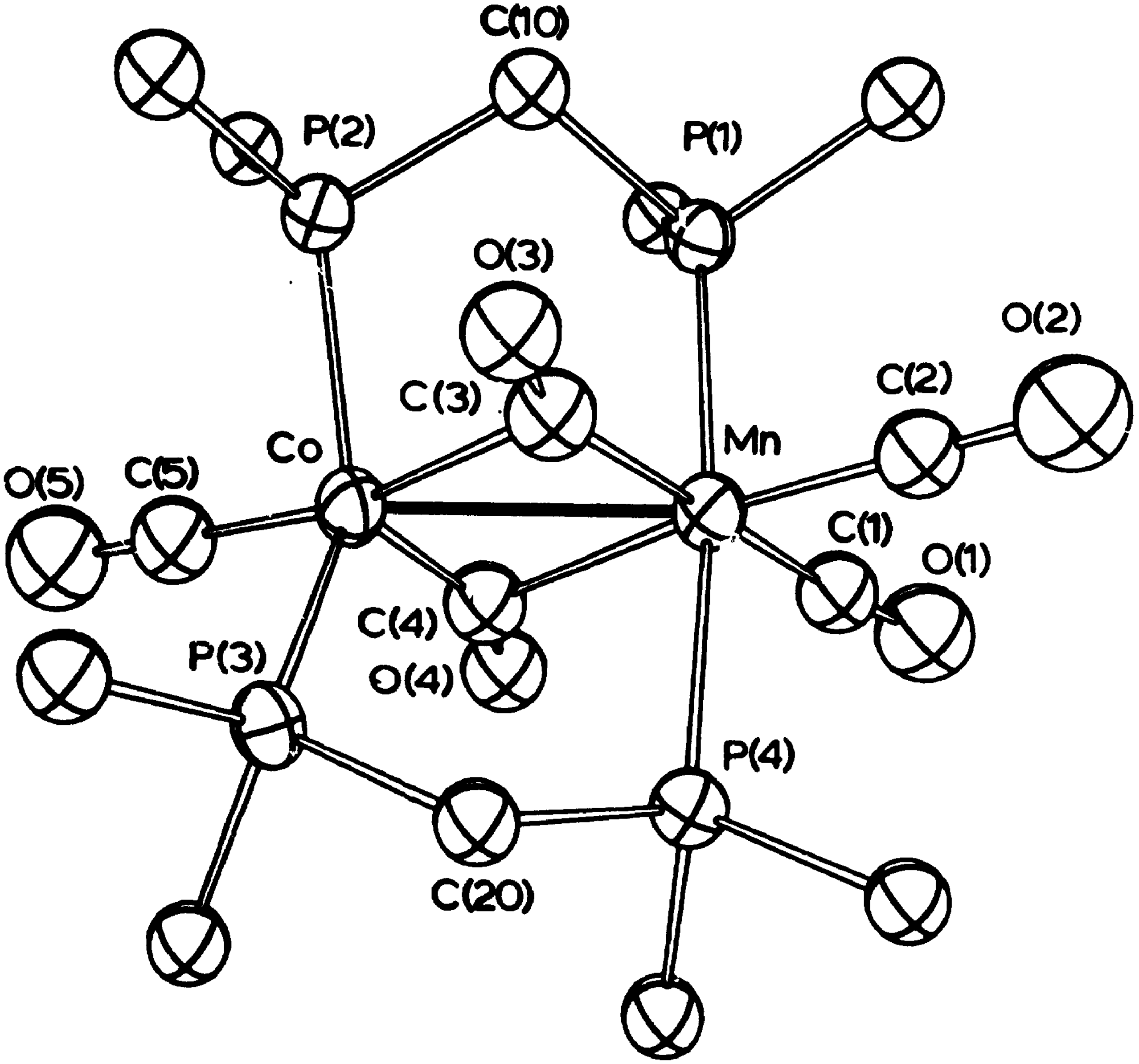


Figure 5.2: ORTEP representation of 5.2

Table 5.1: Selected bond distances and angles in **5.2**

Bond	Distance(Å)	Angle	Degrees(°)
Mn-Co	2.726(1)	C(5)-Co-C(3)	162.2(3)
P(3)-Co	2.214(2)	C(5)-Co-P(3)	93.0(2)
P(2)-Co	2.216(2)	C(5)-Co-P(2)	92.9(2)
C(5)-Co	1.732(7)	C(5)-Co-C(4)	94.8(3)
C(4)-Co	1.766(6)	C(3)-Co-P(3)	81.3(2)
C(3)-Co	2.277(6)	C(3)-Co-P(2)	78.5(2)
P(4)-Mn	2.319(2)	C(3)-Co-C(4)	103.1(3)
P(1)-Mn	2.300(2)	P(2)-Co-C(4)	118.9(2)
C(1)-Mn	1.786(6)	P(2)-Co-P(3)	130.68(7)
C(4)-Mn	2.400(6)	P(3)-Co-C(4)	109.3(2)
C(3)-Mn	1.879(6)	P(4)-Mn-P(1)	172.08(7)
C(3)-O(3)	1.186(6)	C(4)-Mn-C(2)	171.9(3)
C(4)-O(4)	1.184(7)	C(3)-Mn-C(1)	177.9(3)
C(2)-O(2)	1.169(7)	P(4)-Mn-C(2)	91.2(2)
C(5)-O(5)	1.171(7)	P(1)-Mn-C(2)	90.7(2)
		C(4)-Mn-P(1)	91.1(2)
		C(2)-Mn-C(1)	89.0(3)
		Co-C(3)-O(3)	124.9(5)
		Mn-C(3)-O(3)	153.7(5)
		Co-C(4)-O(4)	151.9(5)
		Mn-C(4)-O(4)	127.8(5)

geometry about each metal, ignoring the metal-metal interaction, is best described as distorted octahedral and TBP for the manganese and cobalt atoms respectively. Similar geometries are found for homodinuclear M(0) dimers containing cobalt such as $[Co_2(\mu\text{-dppm})_2(CO)_4]$ (section 2.4.3.1) and manganese in $[Mn_2(CO)_6(\mu\text{-PP})_2]$ complexes[15]. At the manganese, the two phosphines occupy trans positions on the octahedron with a P(4)-Mn-P(1) angle of 172.08(7). Trans phosphines at a manganese atom are also found in the complex $[RhMn(CO)_4(\mu\text{-dppm})_2]$[5]. The trans carbonyls subtend angles at the manganese atom in 5.2 as follows: C(4)-Mn-C(2)=171.9(3)° and C(3)-Mn-C(1)=177.9(3)°. Assigning a geometry to the cobalt atom is more tentative due to the distortion from ideal TBP geometry. For example, the C(5)-Co-C(3) angle of 162.2(3)° deviates significantly from the 180° expected for trans sites in a trigonal bipyramid. Also the equatorial ligands subtend angles as follows: P(2)-Co-P(3)=130.68(7)°, P(2)-Co-C(4)=118.9(2)° and P(3)-Co-C(4)=109.3(2)° instead of 120° as in a regular TBP structure. The phosphines are found in equatorial sites which is consistent with the tendency of more basic ligands to occupy equatorial sites in other reduced TBP systems.

The two metal-centred polyhedra are fused through two asymetrically bridging CO ligands, which occupy cis positions on the manganese octahedron and one axial and one equatorial site on the five coordinate cobalt atom respectively.

The structure contains a roughly planar $(CO)Co(\mu$-$CO)_2Mn(CO)_2$ arrangement. From the M-C-O angles and the M-C distances of the bridging carbonyls it is apparent that these ligands are not symmetrically bridging. The criteria for semibridging CO are based on differences in M-C-O angles and M-C distances of the bridge in question. These criteria are met in 5.2 with a M-C-O difference of 28.8° for the C(3)O(3) ligand and 24.1° for the C(4)O(4) ligand and M-C differences of 0.398Å for C(3)O(3) and 0.634Å for C(4)O(4) and thus these ligands can be considered semibridging.

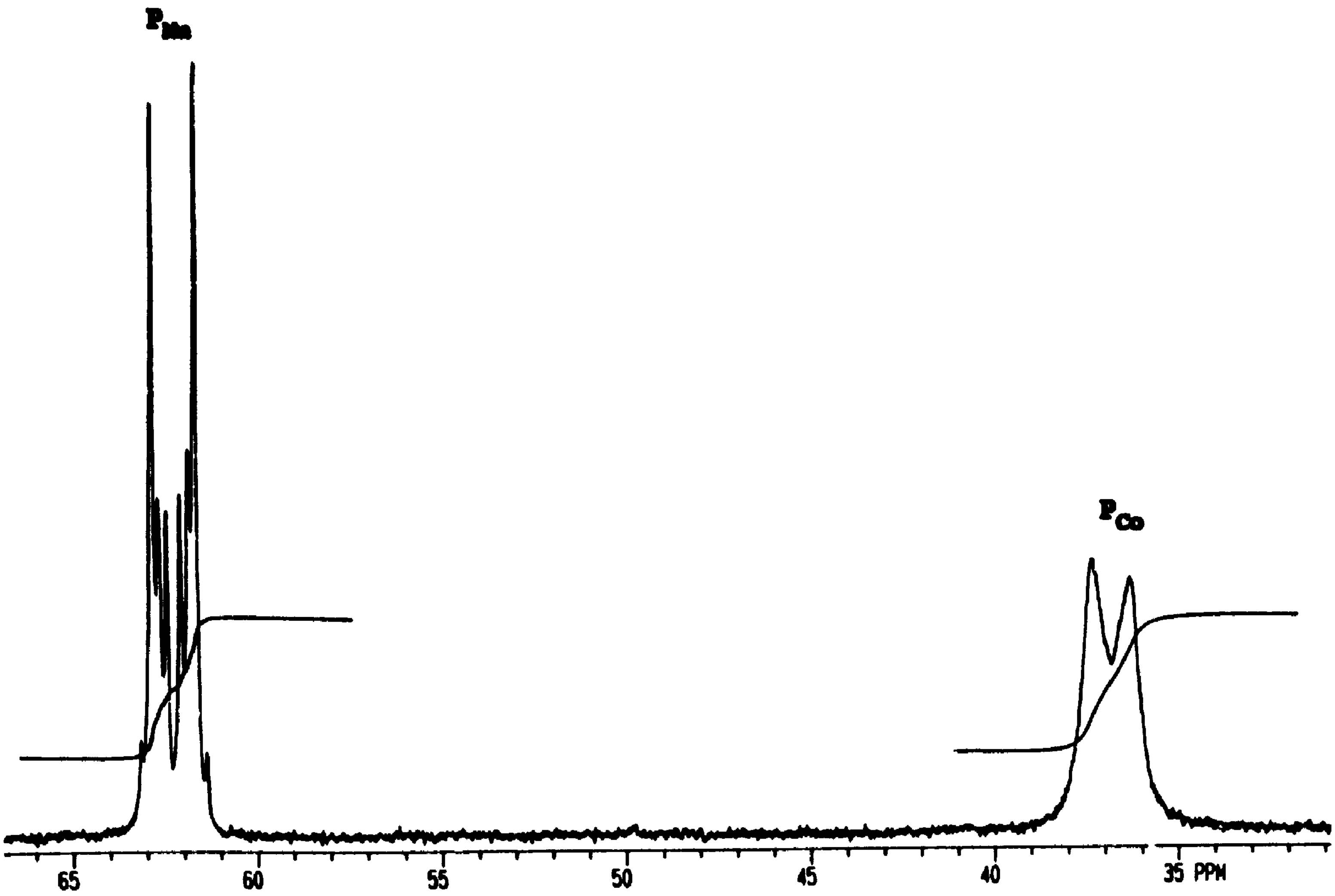
The Co-Mn distance of 2.726(1)Å in 5.2 is indicative of metal-metal bonding interaction. Several other clusters containing metal-metal bonded cobalt-manganese fragments have been structurally characterized. Some single M-M bond distances are 2.444(1)Å in $[CpCo(\mu\text{-}NO)_2MnCp(PMe_3)]$[12], 2.561Å(average) in $[(\eta^5\text{-}C_5H_4Me)MnCo_2(\eta^5\text{-}C_5H_4Me)(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$[1], 2.639(3)Å in $[CoMn(CO)_5(\mu\text{-}CO)(DAB)]$[11] and 2.656(4)Å in $[(\mu\text{-}{}^tBuP)FeCo(CO)_6Mn(CO)_4]$[16]. The 2.726(1)Å Co-Mn distance in 5.2 is well outside of the previous known range of Co-Mn distances yet is still indicative of a Co-Mn interaction which is required for diamagnetism for a Co(0)-Mn(0) dimer. Alternatively, a dative $M(-I)\rightarrow M(I)$ interaction has been used to explain the observed weak M-M interactions in similar complexes $[RhM(\mu\text{-}dppm)_2(CO)_n]$ (M=Co[3],Rh[17],Ir[18];n=3 M=Mn,Re[3];n=4).

The structure of $[RhMn(CO)_4(\mu\text{-}dppm)_2]$[3] is fundamentally different than that of 5.2 as it contains no bridging carbonyls and also contains one less carbonyl. The difference in the chemical formula of complexes [$MMn(dppm)_2(CO)_n$] (M=Co,n=5; M=Rh,n=4) reflects the tendency of rhodium to obtain a 16 electron square planar environment as opposed to cobalt which almost always forms 18 electron complexes when in a low oxidation state. This fundamental difference in the chemistry of cobalt and rhodium has also been used to explain[19] the difference in the structure and formulation of the dimers [$CoM(\mu\text{-}dppm)_2(CO)_n$] which have n=4 when M=Co and n=3 when M=Rh.

The geometries about the manganese and rhodium atoms in [$RhMn(CO)_4(dppm)_2$] are also clearly defined as TBP and square planar respectively. The respective metal geometries and the long Rh-Mn distance make a stronger case for the presence of a Mn(-I)→Rh(I) dative bond than for a Mn(-I)→Co(I) bond in 5.2.

5.3.2 NMR spectra of 5.2

[$CoMn(CO)_5(\mu\text{-}dppm)_2$] is readily soluble in toluene, benzene, acetone, THF, and CH_2Cl_2 and characterization by NMR was therefore possible. A second order ^{31}P NMR spectrum is expected due to the magnetic inequivalence of the two sets of chemically equivalent ^{31}P nuclei in the AA^1XX^1 spin system. In the ^{31}P spectrum of 5.2 (Figure 5.3), two sets of resonances at δ=59.6(m) and δ=34.3(m,br) integrating as 1:1, are assigned to the phosphorus atoms on manganese and cobalt respectively. These assignments are based on comparisons



P_{Mn}
P_{Co}
65
60
55
50
45
40
35 PPM

with other dppm bridged manganese and cobalt systems such as $[Mn_2(CO)_5(\mu\text{-dppm})_2]$[20] ($\delta$=69.5), $[Mn_2H(CO)_6(\mu\text{-dppm})_2]^+$ [21] (δ=59.1), $[Cl(CO)Mn(\mu\text{-dppm})_2(\mu\text{-H})(\mu\text{-CO})Rh(CO)]$[7] ($\delta$=69.7) for PMn and $[Co_2(CO)_4(\mu\text{-dppm})_2]$[22] ($\delta$=32.3) and $[CoRh(CO)_3(\mu\text{-dppm})_2]$[19]($\delta$=29.1) for PCo.

At room temperature, the second order splitting is observed in the P(Mn) resonance while only a broad doublet is observed for P(Co). At -90 C, however, some second order splitting is seen in the δ=34.3 signal. Both metal nuclei have quadrupole moments (I=7/2 for ^{59}Co and 5/2 for ^{55}Mn) which can broaden ^{31}P resonances through nuclear quadrupolar coupling of the ^{31}P nucleus to the metal atom. Presumably the sharpening of the $^{31}P(Co)$ resonance is not due to freezing out of fluxionality but rather is consistent with lower quadrupolar broadening at lower temperatures according to the phenomenon known as thermal decoupling[23].

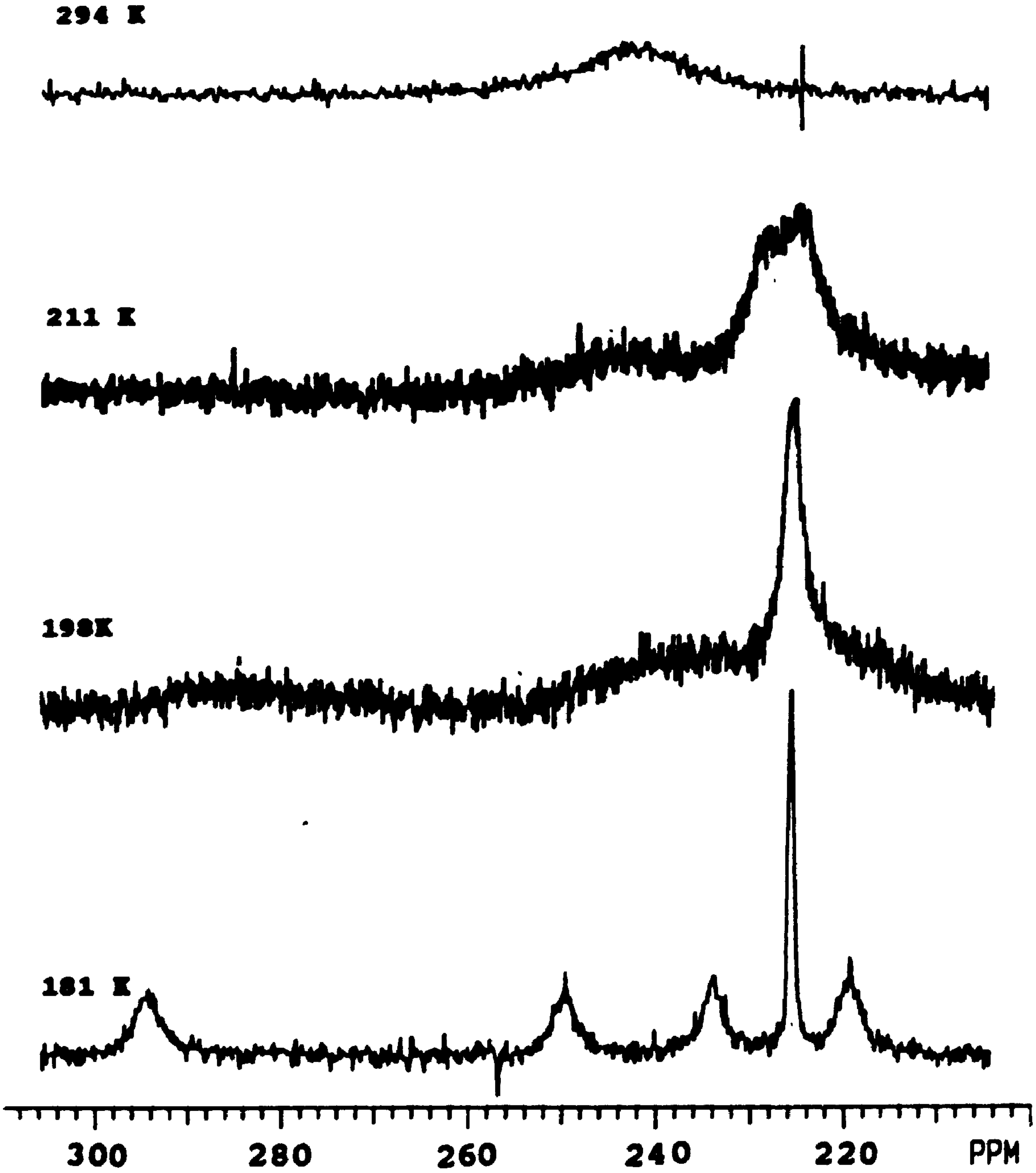
Due to the asymmetry in the solid state structure, two ^1H resonances are expected for the chemically non equivalent methylene ($CH_aH_bP_2$) protons on dppm. However, a broad singlet at δ=5.33, which integrates correctly as 1:10 when compared to the phenyl protons, is observed indicating chemical equivalence. This is indicative of a fluxionality involving exchange of carbonyls as outlined in section 5.3.2.1.

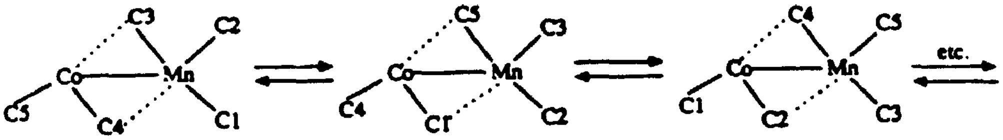
5.3.2.1 Variable temperature ^{13}C NMR studies of 5.2

^{13}CO enrichment of $[CoMn(CO)_5(dppm)_2]$ was accomplished by stirring a CH_2Cl_2 solution of the compound under a ^{13}CO atmosphere for 24 hours. The solvent was removed by vacuum and the solid was recrystallized from CH_2Cl_2/EtOH. From comparison of selected ν(CO) stretches in the I.R. spectra of normal and ^{13}CO enriched samples, the degree of enrichment was determined to be approximately 50%. Both before and after the variable temperature ^{13}C NMR experiment (Figure 5.4), a ^{31}P NMR spectrum of the sample was recorded to confirm the purity of the sample.

At room temperature a single broad resonance in the ^{13}C NMR spectrum appears at δ=239 indicating the effective equivalence of all five carbonyl ligands. At -90°C five resonances at δ=294.2, 248.7, 232.9, 224.5 and 218.2, all of equal area, are resolved, consistent with the solid state structure of $[CoMn(CO)_5(dppm)_2]$ in which all carbonyls are inequivalent. The complex is evidently fluxional and a mechanism consistent with the above observations is a delocalized merry-go-round exchange of carbonyl ligands around the cobalt-manganese template. Equation 5.2 illustrates this process with the carbon atoms in the roughly planar $CoMn(CO)_5$ frame numbered as in the crystal structure. This type of concerted migration has also been observed in $[Co_2(CO)_4(\mu\text{-dppm})_2]^{24}$, $[Fe_2(CO)_5[\mu\text{-}(EtO)_2POP(OEt)_2]_2]^{25}$ and $[Mn_2(CO)_6(\mu\text{-dppm})_2]^{20}$.

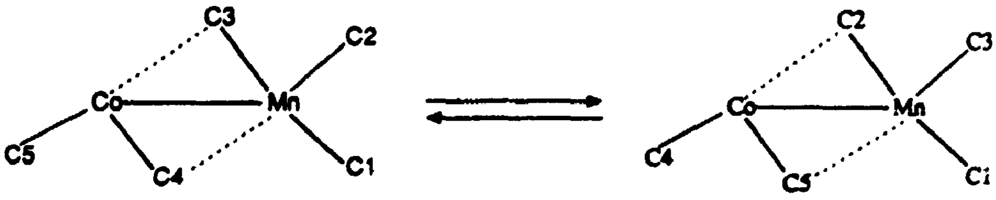
Figure 5.4: Variable temperature ^{13}C NMR spectra of 5.2





(5.2)

The appearance of the low temperature spectrum is interesting in that four of the resonances are very broad while the one at δ=224.5 is very sharp by comparison. A possible explanation for this is that one of the carbonyls is unique and "freezes out" before the other four which are undergoing a second type of exchange. By examining the planar $(CO)Co(\mu\text{-}CO)_2Mn(CO)_2$ model once again it is apparent that a localized exchange between terminal and semibridging ligand can occur on each metal exchanging C2-C3 and C4-C5 pairs (equation 5.3).



(5.3)

Thus it appears that the sharp signal is due to the C1 ligand. This mechanism however does not exchange C5-C3 or C2-C4 ligands which would be necessary to make the remaining four ligands equivalent. Therefore, one would expect to see three sets of resonances for the C1, C3-C2 and C5-C4 sets of ligands at a temperature somewhere between room temperature and -90 C. To this end spectra have been obtained at -62.5°, -75° and -80° C which are consistent with the localized exchange of C3-C2 and C5-C4 ligands as proposed above. At -62.5° C three broad resonances appear. One is centred at δ=256 ppm which is attributed to the coalesced resonances at δ=294 and 218 (294+218/2=256) observed in the low temperature limiting spectrum. The other two broad, overlapping signals are assigned to coalesced δ=249 and 233 (249+233/2=241ppm) signals, and the 225ppm resonance which is sharp in the -90° C spectrum. At -75° C the 225 ppm signal assigned to the C1 ligand sharpens considerably. The 256 ppm signal seen in the -62.5° C spectrum has decoalesced to the point where a broad signal appears at 280 ppm and a hump appears at the upfield side of the sharpening 225 ppm signal. Also at this temperature the coalesced peak due to the 249 and 233 ppm signals is still present as a broad hump at 240 ppm. The type of localized exchange occurring in 5.2 as demonstrated by variable temperature ^{13}C NMR is observed for $[Mn_2(CO)_5(dppm)_2]$[20], which contains an unsymmetrical $\mu:\eta^2$ four electron donor carbonyl ligand. The mechanism of fluxionality involves a wagging motion which results in disruption of the CO bridge as illustrated in equation 5.4. Also, [$MnCo(CO)_6(DAB)$] complexes[11] contain six unique carbonyl ligands with a semibridging ligand more strongly bonded to the cobalt atom but only four ^{13}C resonances are observed in the temperature region -50° to 50° C; three being assigned to the terminal carbonyls on manganese and the fourth to the two terminal and one semibridging carbonyls on cobalt time averaged by a localized scrambling[26].

Another interesting feature of the limiting low temperature ^{13}C NMR spectrum of 5.2 is the odd chemical shift of the resonance at δ=294.2 ppm. Most carbonyl ligands have chemical shifts which fall in the range δ=190-260 ppm, with the downfield part of that range being associated with bridging carbonyls. As the crystal structure of 5.2 reveals only semi-bridging ligands the shift of 294.2 ppm is even more unusual. A shift of 294.2 ppm is unprecedented and is indicative of an unusual environment encountered by one of the carbonyls. From looking at the solid state structure of the compound it is not obvious which ligand is responsible for this extreme downfield shift. Related cobalt and manganese carbonyl complexes exhibit ^{13}CO shifts in the range 190-260 ppm as seen in Table 5.2.

5.4 Reactions of 5.2

Although no complexes have been completely characterized, a preliminary study of the chemistry of 5.2

Table 5.2: ^{13}CO resonances in cobalt and manganese carbonyl complexes

complex	$\delta^{13}C$(ppm)	ref.
$[Co_4(CO)_8(dppm)_2]$	260.1, 258.2, 206.9, 203.2, 201.7	29
$[Co_4(CO)_8(dmpm)_2]$	260.5, 259.8, 259.4, 258.1, 250.7, 250.0, 210.0, 208.5, 203.8, 203.1	29
$[Co_4(CO)_8(dmm)_2]$	258.7, 249.3, 199.4,197.7	29
$[Mn_2(CO)_{10}]$	223.1, 212.9	27
$[Mn_2(CO)_5(dppm)_2]$	239.8, 237.5, 233.8, 226.8, 224.9	20
$[C_6H_5Mn(CO)_5]$	211.1, 209.1	27
$[MeC_5H_4Mn(CO)_3]$	226	27
$[CoMn(CO)_6(L)]$ (L=iPr-N=CH-CH=N-iPr)	209.3, 218.5, 222.2, 223.3	26
$[Cp(CO)Mn(\mu\text{-}CO)_2Rh(CO)Cp]$	252.2[2(μ-CO)], 227.6[(CO)Mn]	28

toward oxidative addition of inorganic reagents has provided a number of complexes that are tentatively assigned structures in Scheme 5.1 based on ^{31}P NMR and IR spectra and related chemistry observed for other complexes $[CoM(CO)_n(\mu\text{-}dppm)_2]$ (M=Co,n=4; M=Rh,n=3).

The spectral parameters measured for the addition products **5.2a-d** are remarkably similar and are summarized in Table 5.3. The ^{31}P NMR data exhibit very narrow ranges of the PCo and PMn resonances and the $^{2}J(PP)$ couplings in the pseudo triplets observed for these resonances are all within 1 Hz of each other. The IR spectra measured for **5.2a,c** and **d** all contain three terminal carbonyl and one bridging carbonyl signals. These similarities in spectral parameters suggests similar structures for the products **5.2a-d** as indicated in Scheme 5.1.

5.5 Synthesis and characterisation of $[(CO)_2(\eta^1\text{-}dppm)Co(\mu\text{-}dppm)Mn(CO)_4]$ 5.3

5.5.1 Synthesis of 5.3

By adjusting reaction conditions from those used to prepare good yields of **5.2**, moderate yields of **5.3** are produced. In particular NaI is used in place of LiCl to induce the ring opening reaction of the η^2-dppm ligands in $[Co(CO)(dppm)_2]^+$, the manganese to cobalt ratio is reduced and the time of reaction of $[Mn_2(CO)_{10}]$ with the Na/Hg amalgam is reduced from 12 to 2 hours. It is probable that **5.3** is an intermediate in the formation of **5.2**. The

Scheme 5.1: Addition chemistry of **5.2**

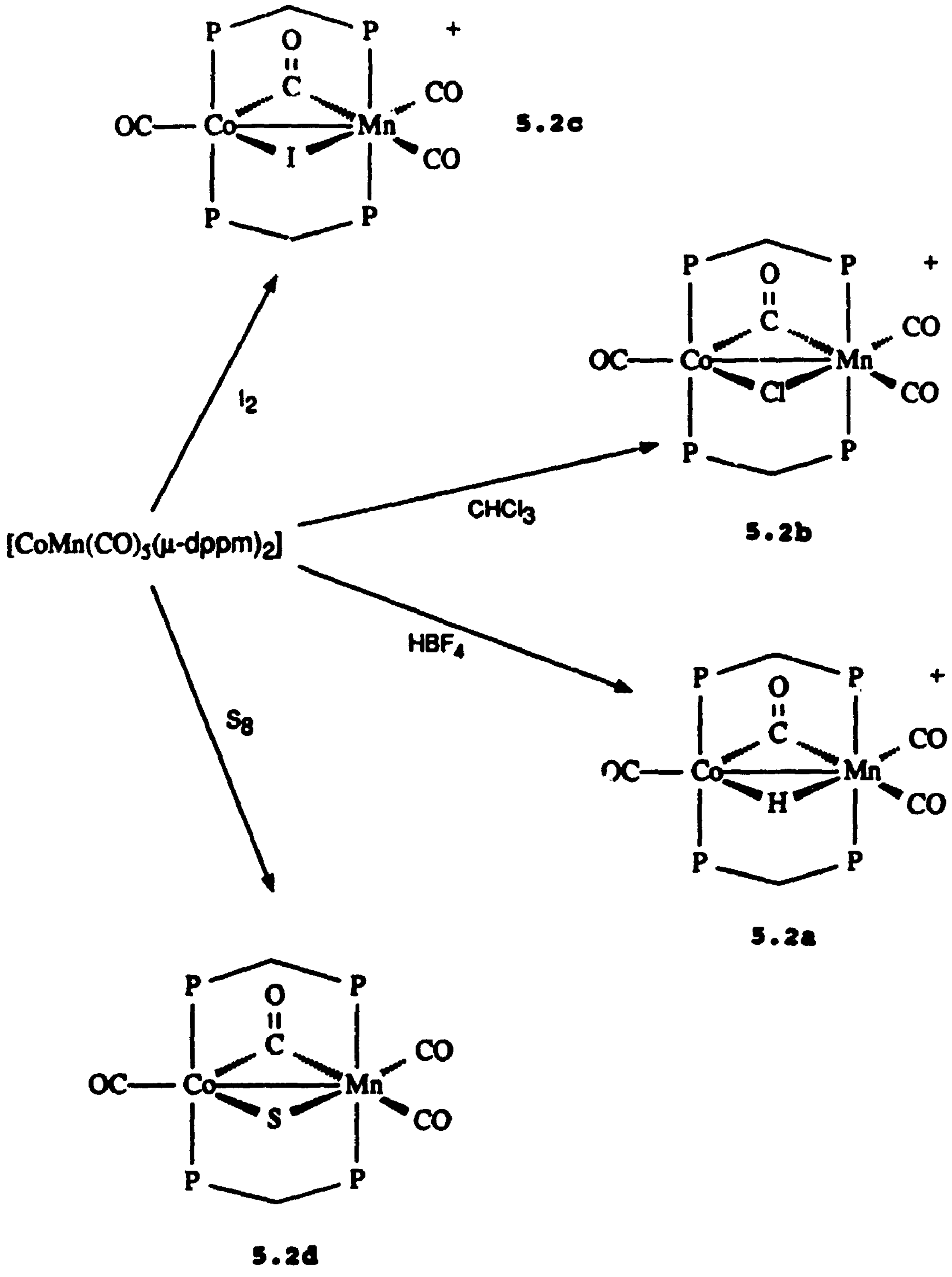


Table 5.3: ^{31}P NMR and IR data for 5.2 and derivatives

Complex	δPCo(ppm)	δPMn(ppm)	$^2J(P_{Co}P_{Mn})$ (Hz)	ν(CO)(cm^{-1})
5.1	28.0	80.8	-	1968(m), 1933(s), 1815(m), 1777(m)
5.2	34.3	59.6	-	1954(m), 1937(m), 1902(w), 1885(s), 1759(w), 1700(s)
5.2a	38.4	52.1	40	1996(w), 1971(s), 1902(s), 1807(m)
5.2b	39.7	52.9	41	-
5.2c	41.8	51.4	40	1991(w), 1968(s), 1916(s), 1802(m)
5.2d	35.6	57.4	41	1948(s), 1927(s), 1865(s), 1773(m)

formation of a Co(0)-Mn(0) dimer presumably proceeds through nucleophillic attack of $[Mn(CO)_5]^-$ on the Co(I) centre which results in the formation of a cobalt-manganese bond and and loss of a two electron donor from the cobalt. The formation of 5.3 provides evidence that the halide is the leaving group.

5.5.2 Characterisation of 5.3

The IR spectrum of 5.3 contains a number of signals between 2058 and 1863 cm^{-1} which are associated with terminal $\nu(CO)$ stretches. The assignment of the lowest frequency signal at 1863.5 cm^{-1} as a bridging or semibridging ligand is precluded by comparison to the $\nu(CO)$ values of the semibridging carbonyls in 5.2 (1759 and 1700 cm^{-1}).

The ^{31}P NMR spectrum of 5.3 in CH_2Cl_2 bears a striking resemblance to that of $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$ 7.2 as seen in Table 5.4. Thus it appears that both 5.3 and 7.2 contain the $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})X]$ unit ($X=BH_2$ or $Mn(CO)_4$). In both molecules the resonances associated with the quadrupolar ^{59}Co and ^{55}Mn in the case of 5.3 or $^{11/10}B$ in 7.2 are broadened relative to the resonance due to the free end of the η^1-dppm ligand which is very sharp and well resolved.

The ^{31}P NMR spectrum of 5.3 also reveals increasing amounts of 5.2 as a function of time. 5.2 forms in solution as the IR spectrum of the sample used to run the ^{31}P NMR

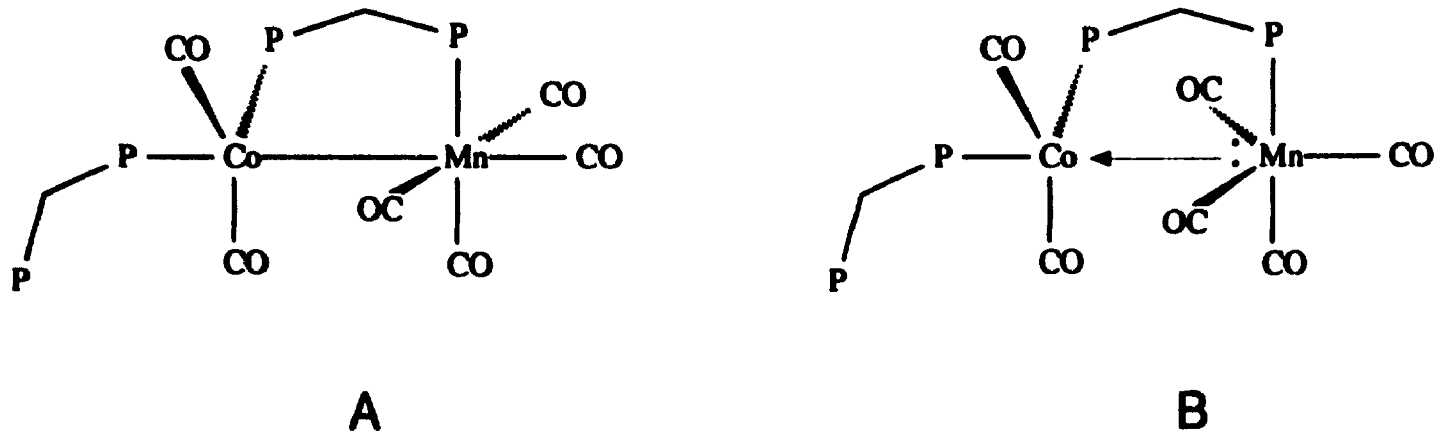
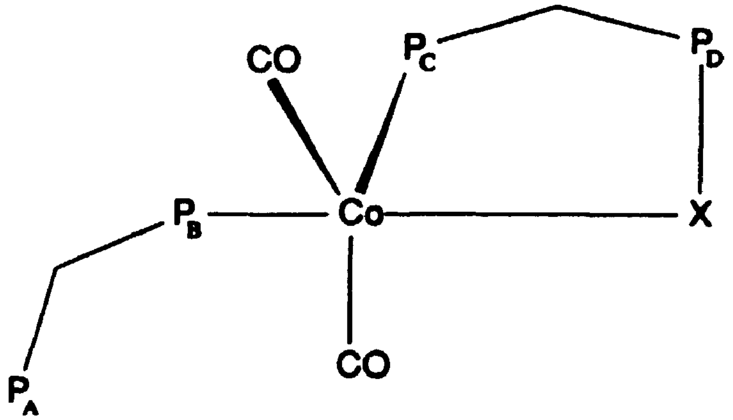


Figure 5.5: Structural limits and metal-metal bonding in 5.3

Table 5.4: Comparison of ^{31}P spectral parameters in $(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})X$ complexes. ($X = Mn(CO)_4$, $Re(CO)_4$ or BH_2)



X	δP_A (ppm)	δP_B (ppm)	δP_C (ppm)	δP_D (ppm)	$^2J_{AB}$ (Hz)	$^2J_{CD}$ (Hz)	J_{BC} (Hz)
BH_2	49.5	18.1	46.9	-30.6	155	28	0
$Mn(CO)_4$	53.8	30.2	52.5	-30.8	105	20.5	0
$Re(CO)_4$	30.6	-2.87	30.6	-28.5	144	63	115

contains none of the strong 1700 cm^{-1} stretch characterist of 5.2.

A crystal structure of 5.3 would be of interest as it could shed some light on the nature of the cobalt-mangane bond. Two extreme cases may be considered. If the bond is dative then the manganese atom should have TBP geometry w a lone pair donated to the cobalt atom comprising the six coordination site. This type of stucture is seen in the related complex $[RhMn(\mu\text{-dppm})_2(CO)_4]^5$ in which the three terminal carbonyls on the manganese atom are found in the trigonal plane of the TBP manganese arrangement. If the cobalt-manganese bond in 5.3 is more covalent than dative an octahedral geometry at the manganese atom should resul The two limiting structures, illustrating these two extre interpretations of the metal-metal bonding in 5.3, are sh in Figure 5.5.

Crystals of 5.3 were obtained directly from the EtOH washings of the crude reaction solid however they were no of suitable quality for X-ray diffraction. Recrystallizat from another solvent system was not attempted due to the ease of conversion of 5.3 to 5.2 in solution.

5.6 Characterisation of $[CoRe(CO)_5(\mu\text{-dppm})_2]$ 5.4

The IR spectrum of 5.4 contains ν(CO) stretches betwe 2010 and 1840 cm^{-1}. It is tempting to assign the 1840 cm^{-} signal to a bridging carbonyl, but this value is very hig when compared to those assigned to the semibridging carbonyls (1700, 1760 cm^{-1}) in the structurally characterized [CoMn(μ-dppm)$_2$(CO)$_5$]. Also low ν(CO) values for terminal carbonyls are common in complexes of electron rich third row transition elements. The general appearance of the spectrum of 5.4 is also very similar to that of 5.3 which contains only terminal carbonyls. Thus it is very likely that 5.4 contains only terminal carbonyls as in the possible structures drawn in Figure 5.6.

The cis and trans arrangements of the phosphines on the cobalt and rhenium are proposed due to this sort of arrangement in [CoMn(μ-dppm)$_2$(CO)$_5$] and [RhM(μ-dppm)$_2$(CO)$_4$]^5 (M=Mn,Re) which contains trans phosphines on both the rhodium and M centres. The geometry about the the rhenium atom is represented as being octahedral but, depending on the polarity of the cobalt-rhenium bond, the trans carbonyls on rhenium could bend toward the cobalt-rhenium axis. In the extreme case of a dative Mn(-I)→Co(+I) interaction a TBP geometry, reminiscent of the [Re(CO)$_5$]$^-$ anion, is expected for the rhenium atom. The complexes [RhM(CO)$_4$(dppm)$_2$] (M=Mn,Re) exhibit nearly regular TBP geometry at the M site and it would be interesting to obtain a crystal structure of 5.4 to resolve this point.

Complex 5.4 is readily soluble in most organic solvents and thus characterization by NMR was possible. The ^{31}P NMR spectrum of 5.4 consists of two sets of resonances at δ=23.6 (br) and -3.82 (m) assigned to the phosphorus atoms on cobalt and rhenium respectively (Figure 5.7). The -3.82 ppm

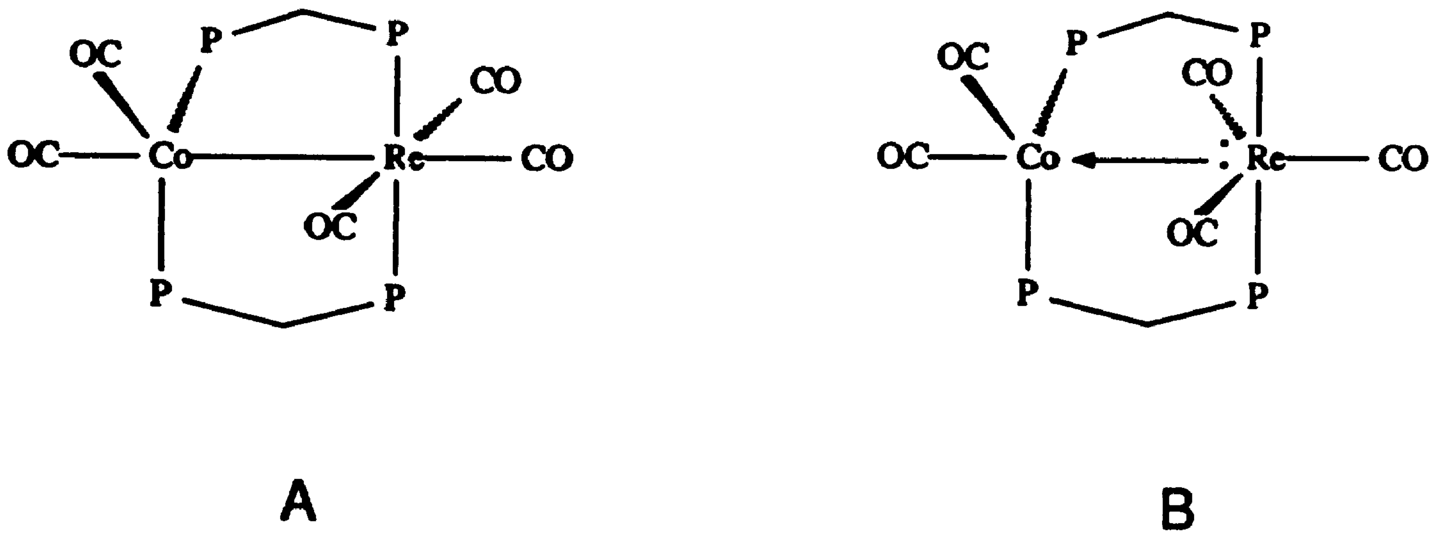


Figure 5.6: Structural limits and metal-metal bonding in 5.4

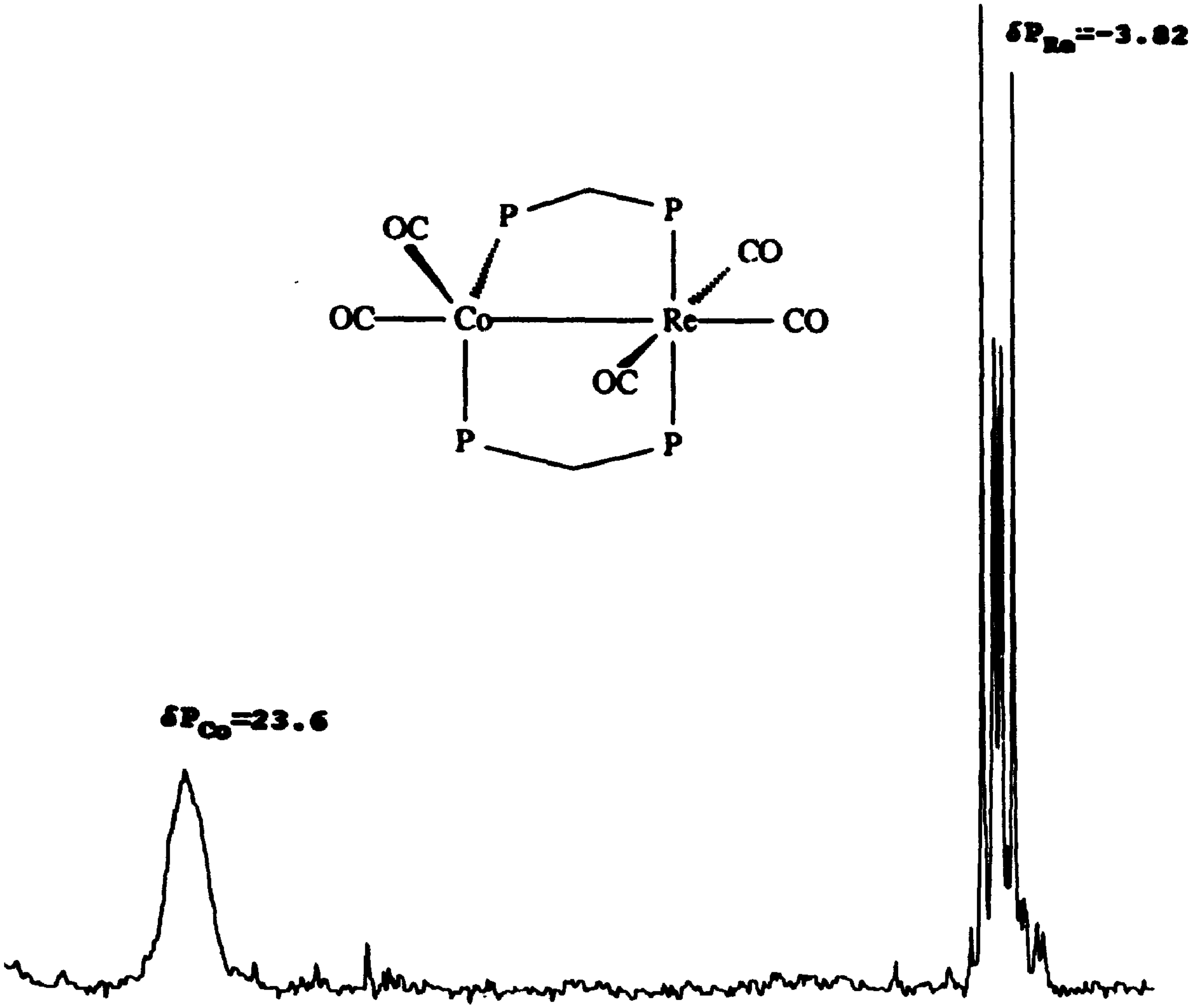
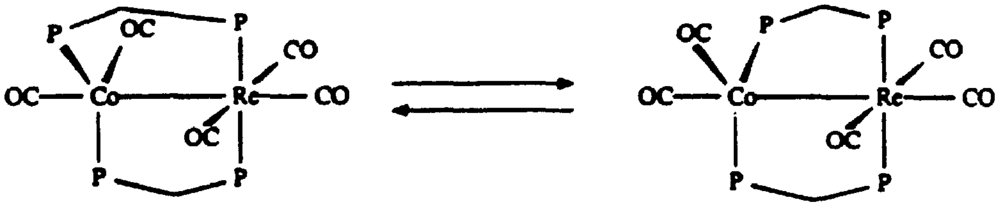


Figure 5.7: ^{31}P NMR spectrum of 5.4

shift is close to those seen in other similar systems such as $[RhRe(CO)_4(\mu\text{-dppm})_2]^5$ (δPRe=6.2). The chemical shift of 23.6 ppm is consistent with a μ-dppm ligand on cobalt as seen in $[Co_4(\mu\text{-dppm})_2(CO)_8]^{29}$ (δ=24.3). The broadness of the PCo resonance in 5.4 is also observed in 5.3, 5.2, and $[CoRh(CO)(\mu\text{-dppm})_2]$.

The room temperature ^{1}H NMR spectrum contains a singlet resonance at 4.43 ppm which is in the region associated with the methylene protons on dppm. However, in the proposed structures of $[CoRe(CO)_5(\mu\text{-dppm})_2]$ with phosphorus donors cis and trans on the cobalt and rhenium atoms respectively, chemical equivalence of the dppm methylene protons is possible only if some fluxional process is operating. One possible fluxional process is illustrated in Equation 5.4.



(5.4)

At -90°C the ^{1}H singlet at 4.43 ppm broadens significantly, indicating the beginings of decoalescence.

5.7 $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})Re(CO)_4]$ 5.5

As in the preparation of 5.2, an intermediate in the formation of 5.4, namely $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})Re(CO)_4]$ 5.5 has been identified by ^{31}P and ^1H NMR. The ^{31}P NMR spectrum of 5.5 consists of four sets of resonances, two of which are superimposed, as observed in the other complexes $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})X]$ ($X=BH_2$ or $Mn(CO)_4$) (Table 5.4). The P_B and P_C resonances of 5.5 are shifted significantly from those seen in 5.3 and 7.2. This can probably be attributed to the the proximity of the electron rich rhenium atom to the cobalt centre attached to P_B and P_C. The P_B and P_C resonances are superimposed at $\delta=30.6$ ppm which is not surprising since these resonances for 5.3 and 7.2 are also very close. The P_D resonance ($\delta=2.50$) is assigned to the phosphorus atoms on rhenium consistent with shifts seen for other μ-dppm complexes containing rhenium such as $[RhRe(CO)_4(\mu\text{-dppm})_2]$ ($\delta=6.2$,PRe)^5. The P_D atom is split by both P_B and P_C and in this respect is different from 5.3 and 7.2 in which the $^3J(P_BP_D)$ coupling is not observed. In the P_D multiplet observed for 5.5 the larger coupling of 145 Hz is attributed to $^2J(P_CP_D)$ and the smaller coupling of 115 Hz is attributed to $^3J(P_BP_D)$.

The ^1H NMR spectrum of 5.5 exhibits two multiplets at $\delta=4.03$ and 3.78 which is expected for the $CH_2P_aP_b$ and $CH_2P_cP_d$ methylene protons on dppm. This portion of the spectrum also closely resembles that of 7.2.

^{31}P NMR of reaction mixtures produced by refluxing $[Mn(CO)_5]^-$ and $[CoI(CO)_2(\eta^1\text{-dppm})_2]$, generated <u>in situ</u> by reaction of [Co(CO)(η^2-dppm)$_2$]BPh$_4$ with CO and NaI, show that 5.5 is present as a major species and that no 5.4 is present. It should thus be possible to isolate pure 5.5 in the solid state.

5.8 Experimental

Complex 5.1

$[Mn_2(CO)_{10}]$ (0.125g) was added to distilled THF (30mL) and stirred over a Na/Hg amalgam (0.052g Na, 5mL Hg) for 40 min. The resulting greyish suspension was pipetted into a solution of $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$ in THF (25mL) and the mixture was refluxed for 10 minutes. The solvent was removed by vacuum and the residue was washed with EtOH (30 mL) and recrystallized from CH_2Cl_2/EtOH to give mixtures of $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$ and small amounts of 5.1.

$\delta^{31}P$ NMR ($CH_2Cl_2\backslash CD_3CN$) = 80.8[dd, J(PP)= 70.7, 62.9 Hz, PMn], 28.0[ddd, J(PP)= 132, 70.7, 62.9 Hz, PCo].

IR(Nujol) : ν(CO) = 1968(m), 1933(s), 1898(m), 1815(m), 1777(m) cm^{-1}..

$[CoMn(CO)_5(dppm)_2]$ <u>5.2</u>

$[Mn_2(CO)_{10}]$ (0.86g) in freshly distilled THF (20 mL) was stirred over a Na\Hg amalgam (0.59g Na/40g Hg) for 12 hours. The resulting pale green suspension was pipetted into a solution of $[Co(CO)(dppm)_2]BPh_4$ (2.40g) and LiCl (0.20g) in THF (40 mL) that had been refluxed under CO for 30 minutes. The mixture was refluxed under CO for an additional 45 minutes then under N_2 for 2 hours. The solvent was removed by vacuum and the resulting solid was washed with EtOH (30 mL) and recrystallized from C_6H_6/EtOH.

Yield : 48% Anal. calc. for $C_{55}H_{44}CoMnO_5P_4$: C,64.59; H,4.34 Found : C,63.35; H,3.52.

Spectroscopic data : NMR(CD_2Cl_2); $\delta^{31}P$= 59.6[m, PMn], 34.3[br,m, PCo]; $\delta^{13}C$= 294.2, 248.7, 232.9, 224.5, 218.2; $\delta^{1}H$= 5.33[s, PCH_2P]. IR(Nujol): ν(CO) = 1954(m), 1937(s), 1902(w), 1885(s), 1759(w), 1700(s) cm^{-1}.

Complex 5.2a

To a solution of **5.2** (0.041 g) in CH_2Cl_2 (10 mL) was added HBF_4(aq) (1ml) and the mixture was stirred for 5 minutes. The solvent was removed by vacuum and the wet solid was washed with EtOH (10 mL). The remaining solid was recrystallized from CH_2Cl_2/hexane.

^{31}P NMR (CD_2Cl_2): δ= 52.1[t, $^2J(PP)$=40 Hz, PMn], 38.4[t, $^2J(PP)$=40 Hz, PCo]

IR(Nujol): ν(CO)= 1996(w), 1971(s), 1902(s), 1807(m) cm^{-1}.

Complex 5.2b

A sample of **5.2** was dissolved in $CHCl_3/CD_2Cl_2$ for ^{31}P NMR which revealed that **5.2** had reacted to give **5.2b** as a primary product.

^{31}P NMR ($CHCl_3/CD_2Cl_2$): δ= 52.9[t, $^2J(PP)$=41 Hz, PMn] 39.7[t, $^2J(PP)$=41Hz]

Complex 5.2c

5.2 (0.040g) and I_2 (0.10g) were stirred in CH_2Cl_2 (10mL) for 1 hour. The solvent was removed by vacuum and the residue was washed with EtOH (10 mL). The remaining solid was recrystallized from CH_2Cl_2/EtOH.

^{31}P NMR (CH_2Cl_2/CD_3CN): 51.4[t, $^2J(PP)$=40 Hz, PMn], 41.8[t, $^2J(PP)$=40 Hz, PCo]
IR(Nujol) : ν(CO) : 1991(w), 1968(s), 1916(s), 1802(m) cm^{-1}.

Complex 5.2d

5.2 (0.044 g) and S_8 (0.005 g) were stirred in CH_2Cl_2 (10 mL) for 30 minutes. The solvent was removed by vacuum and the residue was washed with EtOH (10 mL). The remaining solid was recrystallized from CH_2Cl_2/EtOH to give a mixture of 5.2d and unreacted 5.2.
^{31}P NMR (CH_2Cl_2/CD_3CN): δ= 57.4[t, $^2J(PP)$=40.6 Hz, PMn], 35.6[br,PCo]
IR(Nujol): ν(CO)= 1948(s), 1927(s), 1865(s), 1773(m) cm^{-1}.

[(CO)(η^1-dppm)Co(μ-dppm)Mn(CO)$_4$] <u>5.3</u>

[$Mn_2(CO)_{10}$] (0.70 g) was added to distilled THF (30 mL) and stirred over a Na/Hg amalgam (0.37g Na, 3mL Hg) for two hours. The resulting grey-green suspension was pipetted into a THF solution (40 mL) of [Co(CO)(dppm)$_2$]BPh_4 (2.73g) and NaI (0.36g) that had refluxed under CO for 45 minutes. The solution was refluxed under N_2 for an additional 30 minutes and the solvent was removed by vacuum. The resulting solid was washed with EtOH (25 mL). Over a 24 hour period dark red crystals of 5.3 were precipitated from the EtOH washings.
Yield : 31% Anal. calc. for $C_{56}H_{44}CoMnO_6P_4$: C,64.01; H,4.22
Found : C,63.75; H,4.26.

Spectroscopic data : NMR; $\delta^{31}P(CH_2Cl_2/CD_3CN)$ (resonances as labelled in Table 5.4) = 53.8[d,br, $^2J(P_CP_D)$= 105 Hz, P_C], 30.2[d, $^2J(P_CP_D)$= 105 Hz, P_D], 52.5[br, P_B], -30.8[d, $^2J(P_AP_B)$= 20.5 Hz, P_A].

IR(Nujol): ν(CO)= 2058(w), 2024(m), 1962(s), 1952(m), 1931(s), 1892(m), 1864(m) cm^{-1}.

FAB-MS : m/z = 1050, 912, 883, 855, 827; Calc. for $C_{56}H_{44}CoMnO_6P_4$[P] : 1050, P-4CO 910, P-$Mn(CO)_4$ 883, P-$Mn(CO)_4$-CO 855, P-$Mn(CO)_4$-2CO 827.

The solid that remained after the EtOH washings of the reaction mixture was recrystallized from CH_2Cl_2/EtOH to give mixtures of [Co(CO)(dppm)$_2$]BPh_4 and 5.2.

[CoRe(CO)$_5$(μ-dppm)$_2$] <u>5.4</u>

[$Re_2(CO)_{10}$] (1.11 g) was stirred, under N_2, in a solution of distilled THF (30 mL) over a Na/Hg amalgam (0.092g Na/5mL Hg) for 16 hours. The resulting orange solution was pipetted into a solution of [Co(CO)(dppm)$_2$]BPh_4 (1.00g) and NaI (0.19g) that had refluxed under a CO atmosphere for 20 minutes. The solution was refluxed for an additional 10 minutes under N_2 and the solvent was removed by vacuum. The solid residue was recrystallized from C_6H_6/EtOH.

Yield : 15%

NMR ($d_6$acetone); ^{31}P NMR : δ=23.6 [br,PCo], -3.82 [m,PRe]; ^1H NMR : δ=4.43 [s,CH_2P_2]; IR(Nujol) : ν(CO); 2010(m), 1979(w), 1923(s), 1885(s), 1840(m).

FAB-MS : 1042; Calc. for $C_{55}H_{44}CoReP_4O_5$[P] = 1153, P-4CO

1041.

$[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})Re(CO)_4]$ **5.5**

In the above preparation of 5.4 , a ^{31}P NMR spectrum of the residue left by removal of the solvent by vacuum, in CH_2Cl_2/CD_3CN, reveals 5.5 to be a major component with none of 5.4 evident. Subsequent recrystallization of the solid from C_6H_6/EtOH led to a mixture of 5.4 and a small amount of 5.5 which was used for ^{31}P and ^1H NMR of 5.5.

Spectroscopic data : NMR(d_6-acetone); $\delta^{31}P$(resonances as labelled in Table 5.4)= 30.6[br, P_C], -2.50[dd, $^2J(P_CP_D)$= 145 Hz, $^3J(P_BP_D)$= 115 Hz, P_D], 30.6[br, P_B], -31.5[d, $^2J(P_AP_B)$= 63 Hz, P_A]; δ^1H = 3.78 and 4.03[m, $P_ACH_aH_bP_B$, $P_CCH_aH_bP_D$].

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Chapter 6 : P-C Bond Cleavage in Dppm ; Synthesis and Characterization of Complexes $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)_n(CO)_{6-2n}]$ (n=1 **6.1** or 2 **6.2**) and $[Ni_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)_2(CO)_2]^+$ **6.3**

6.1 Introduction

With the synthesis of complexes 6.1, 6.2 and 6.3 from Co(II)/dppm/$NaBH_4$/CO reaction systems came the recognition that the synthesis of (μ-PR_2) complexes generally involves secondary phosphines or derivatives and that P-C bond cleavage in tertiary phosphines is rare and usually requires more forcing conditions. Thus the following discussion briefly outlines the properties of phosphide ligands and methods of synthesis of phosphido complexes.

6.1.1 Bonding modes of phosphides

The terms phosphide or arsenide can be used to describe any derivative of the trianions P^{3-} or As^{3-}. In this discussion they will designate dialkyl derivatives and emphasis will be placed on the phosphorus containing species, PR_2^-. The interest in the coordination chemistry of PR_2^- has increased dramatically in the last decade. This is due in part to the versatility of this class of ligand and to the recognition that P-C bond cleavage in tertiary phosphines may be a deactivation pathway for phosphine containing homogeneous catalysts. Two reviews have appeared recently which discuss these aspects of phosphide chemistry[1,2].

There are two lone pairs of electrons on the phosphide and thus a number of interactions with a metal are possible. The three bonding modes of phosphides thus far identified are illustrated in Figure 6.1[1].

Examples of **B**, which contains a P-M multiple bond and a planar MPR_2 arrangement are not commonly found in the literature. The reaction of $[Cp_2MCl_2]$ (M = Zr, Hf) with two equivalents of $LiPR_2$ (R = Et, cyclohexyl,Ph) provides $[Cp_2M(PR_2)_2]$ whose ^{31}P nmr spectra indicate that both types of terminal PR_2^- coordination **A** and **B** are present and they interconvert in solution at room temperature[3]. The crystal structures of complexes $[Cp_2M(PR_2)_2]$ reveal that one phosphorus atom has a pyramidal geometry as in **A** with a lone electron pair, while the other is part of a planar MPR_2 arrangement with a significantly shorter P-M distance as in **B**. There are several other examples of type **A** terminal phosphide complexes. These types of complexes behave as tertiary phosphines and can coordinate to another metal by forming a phosphido bridge. Terminal phosphides have therefore proved to be particularly useful in the synthesis of heterobimetallic complexes and will be discussed later in this context.

The vast majority of characterized phosphide complexes contain a bridging phosphido group as in **C**. This is due to the fact that the phosphido bridge forms strong bonds with metals yet is flexible enough to allow for a wide range of metal-metal distances and metal-phosphorus-metal bond

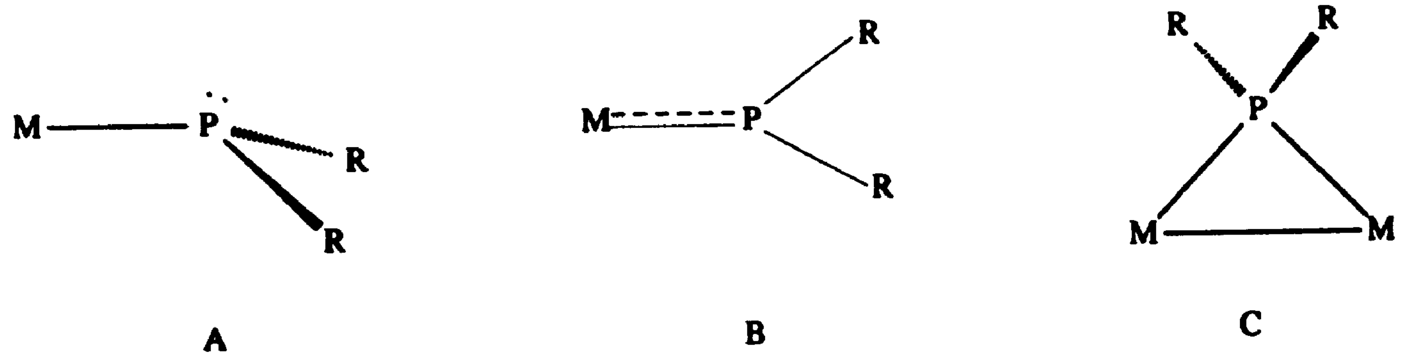


Figure 6.1: Bonding modes of phosphides; PR_2^-

angles[1].

6.1.2 Synthesis of metal-phosphido complexes

6.1.2.1 Synthesis from secondary phosphines

Most μ-PR_2 complexes are derived from the secondary phosphines PR_2X, where X is a hydrogen or a halogen. The P-H bond in dialkyl phosphines can be cleaved to facilitate the formation of a phosphido bridge. For example, $[Re_2(CO)_{10}]$ and PPh_2H react at 200°C to produce $[Re_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$[4]. $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$ and $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ are prepared similarly[5,6]. $[Rh_4(CO)_{12}]$ reacts with $Bu_2{}^tPH$ in refluxing toluene producing either $[Rh_6(\mu\text{-}Bu_2{}^tP)_4(CO)(\mu\text{-}CO)_2(\mu\text{-}H)_2]$ or $[Rh_2(CO)_2(PBu_2{}^tH)(\mu\text{-}H)(\mu\text{-}PBu_2{}^t)]$ depending on the reaction stoichiometry[7]. In some cases the hydride is not retained in the adduct as illustrated in equation 6.1 below[8].

$$2[V(CO)_6] + 2Ph_2PH \rightarrow [V(CO)_4(\mu\text{-}PPh_2)]_2 + H_2 + CO \qquad (6.1)$$

Reaction of two equivalents of PPh_2H with $[Co_2(CO)_8]$ provides the oligomeric complex $[Co(\mu\text{-}PPh_2)(CO)_3]_n$ in a 85-90% yield[9].

Another interesting reaction is that between the $[Ir(dppe)_2]^+$ cation and PH_3[5]. The phosphine oxidatively adds such that both fragments form terminal ligands in the resulting complex $[Ir(PH_2)(H)(dppe)_2]^+$. This is a rare example of the addition occurring at a single metal site increasing its oxidation state by two.

There is also an example of a bis-secondary phosphine adding to a metal complex providing an unusual bridged phosphido type species. $[PtCl\{PhP(CH_2)_3P(C_6H_{11})_2\}]_2$, results from the reaction of $PtCl_2\{Ph(H)P(CH_2)_3P(C_6H_{11})_2\}$ in THF[10].

Halophosphines, PR_2X, are another class of secondary phosphines that will add to a metal complex. For example, when two equivalents of Ph_2PCl are added to a room temperature THF solution of $Na_2[Fe_2(CO)_8]$, $[Fe_2(PPh_2)_2(CO)_6]$ is formed along with NaCl[11]. Similarly, $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ was found to be the product formed from the reaction between $Na[Mn(CO)_5]$ and PPh_2Cl[6]. In the reaction between $Na[Co(CO)_4]$ and PPh_2Cl, at -60°C, $[Co(CO)_4PPh_2]$ is formed while at room temperature dimerization occurs with loss of CO and $[Co_2(CO)_6(\mu\text{-}PPh_2)_2]$ is isolated[9].

6.1.2.2 Synthesis from metal salts MPR_2

Metal salts of phosphides react readily with transition metal complexes under mild conditions to afford bridged phosphido species in high yield. $[MCl(COD)]_2$ complexes (M = Rh,Ir) react with $LiPPh_2$ in THF to give $[M(\mu\text{-}PPh_2)(COD)]_2$ in excellent yields[12,13]. In the reaction of $LiPPh_2$ with $[Cp^*Co(\mu\text{-}Cl)]_2$ substitution occurs at only one of the bridging chloride sites to give $[(Cp^*)_2Co_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$[14]. $KPPh_2$ reacts with $[Ir(CO)_3Cl]_2$ to afford $[Ir_2(CO)_6(\mu\text{-}PPh_2)_2]$ and KCl[15]. This complex lacks the metal-metal double bond present in $[Rh_2(CO)_4(\mu\text{-}PBu_2^t)_2]$. $LiPBu_2^t$ reacts with

$[MCl_2(PMe_3)_2]$ (M = Fe,Co,Ni) in THF at -78°C to provide $[Fe(\mu\text{-}PBu_2^t)Cl(PMe_3)]_2$, $[Co_2(\mu\text{-}PBu_2^t)_2Cl(PMe_3)_2]$ and $[Ni(\mu\text{-}PBu_2^t)(PMe_3)_2]_2$ respectively[16]. $[Co(\mu\text{-}PBu_2^t)(CO)_2]_2$, which contains a rare example of a cobalt-cobalt double bond, is formed from the reaction of $[Co(CO)_4I]$ with $LiPPh_2$ in THF at -78°C[17].

6.1.2.3 Deprotonation of coordinated PR_2H ligand

Phosphide ligands can also be formed in situ by deprotonation of a coordinated secondary phosphine by a base. In many cases a terminal phosphide complex has been identified as an intermediate in the reaction. These complexes are essentially analogous to tertiary phosphines except one alkyl group has been replaced by a metal moiety. As expected they behave as phosphines and will coordinate to another metal. For example, $Li_2[W(CO)_4(PPh_2)_2]$ is generated in situ by addition of MeLi to a THF solution of $[W(CO)_4(PPh_2H)_2]$. It reacts with appropriate complexes to afford the di-phosphido bridged dinuclear complexes $[ZrW(\mu\text{-}PPh_2)_2Cp_2(CO)_4]$, $[TiW(\mu\text{-}PPh_2)_2Cp^*(CO)_4]$, $[(CO)_4W(\mu\text{-}PPh_2)_2M(PPh_3)]$ (M = Ni,Pd,Pt) and $[(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3]$[18,19,20]. When a solution of NaOMe is added dropwise to a CO saturated solution of $CoCl_2 \cdot 6H_2O$ and PPh_2H, $[Co_2(\mu\text{-}PPh_2)(CO)_4(PPh_2H)_2]$ is formed[21]. It is apparent that a strong base is normally required to deprotonate the phosphine but in the case of the reaction between $[Rh(CO)_2Cl]_2$ with PPh_2H, diethylamine is a sufficiently strong base to facilitate the formation of $[Rh_3(\mu-PPh_2)_3(CO)_5]$[22]. These reactions closely resemble reactions involving salts of phosphides which is not suprising considering that the reaction between a secondary phosphine and a strong base such as methyl lithium provides the lithium salt of the phosphide and methane.

6.1.2.4 Synthesis from P_2R_4

Diphosphines or diarsines E_2R_4 (E = As, P), containing no alkyl bridge between the two ER_2 groups, can oxidatively add across a dinuclear centre to provide two bridging phosphido or arsenido ligands. $[Co(Cp)(\mu-PPh_2)]_2$ is made by reaction of $[CpCo(CO)_2]$ with P_2Ph_4[23]. $[Fe(CO)_5]$ reacts with E_2R_4 species in C_6H_6 at 150°C to give $[Fe(CO)_3(\mu-ER_2)]_2$ (E = As;R = Me; E = P;R = Me or Ph)[15].

6.1.2.5 Synthesis from tertiary phosphines

Up to this point the phosphido ligands in the complexes discussed have been generated by the cleavage of relatively weak bonds such as P-P, P-H, or P-Cl and in the extreme case by the salt of a phosphide. There is another group of reactions, usually requiring more forcing conditions, that provides the phosphido ligand by oxidative cleavage of the stronger P-C bond. Many examples of this type of reaction involve PPh_3. For example, prolonged heating of $[PdCl(PPh_3)_3][BF_4]$ in a THF suspension at 125°C provides the trinuclear complex $[PdCl(PPh_2)_2(PPh_3)_3]BF_4$[24]. Two isomers of

$[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$, in which the cleaved phenyl group is found coordinated, are prepared from $[Pt(C_2H_4)(PPh_3)_2]$ heated in acetone[25]. This is also the case in $[(PPh_3)_3Pt_2(\mu\text{-}H)(\mu\text{-}PPh_2)(Ph)][HC(SO_2CF_3)_2]$ which derives from trans-$[(PPh_3)_2PtH[HC(SO_2CF_3)_2]$ refluxed in 2-propanol[26]. Thermal degradation of $[RhH(CO)(PPh_3)_3]$ in nonane provides a dark green complex $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$[2]. The tetranuclear cluster, $[Rh_4(\mu\text{-}PPh_2)_4(CO)_4(PPh_3)]$, is isolated when the nonane solution is kept under 60 psig of CO/H_2.

An interesting transformation of PPh_3 occurs on $[Mo(CO)_3(PPh_3)(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ under U.V. light[27]. Phenyl migration from PPh_3 to CO is followed by benzoyl migration to the acetylene yielding $[Mo_2(CO)_2(\mu\text{-}PPh_2)\{\mu\text{-}HC_2(H)C(O)Ph\}(Cp)_2]$.

There is another class of phosphine which is known to cleave to provide a phosphide ligand. Diphenyl phosphino alkyl acetylenes will under thermal conditions fracture giving phosphido-acetylide complexes. When refluxed, $[Ru_3(CO)_{11}(Ph_2PC{\equiv}CPh)]$ will form either $[Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ or a mixture of this and $[Ru_2(CO)_7(C{\equiv}CPh)(\mu\text{-}PPh_2)]$ depending on the refluxing solvent[28,29]. $Ph_2PC{\equiv}CBu^t$ added to a solution of $[Ru_3(CO)_{12}]$ followed by reflux provides $[Ru_3(CO)_6(\mu\text{-}C_2Bu^t)(\mu\text{-}\eta^2\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(PPh_2C_2Bu^t]^+$[30].

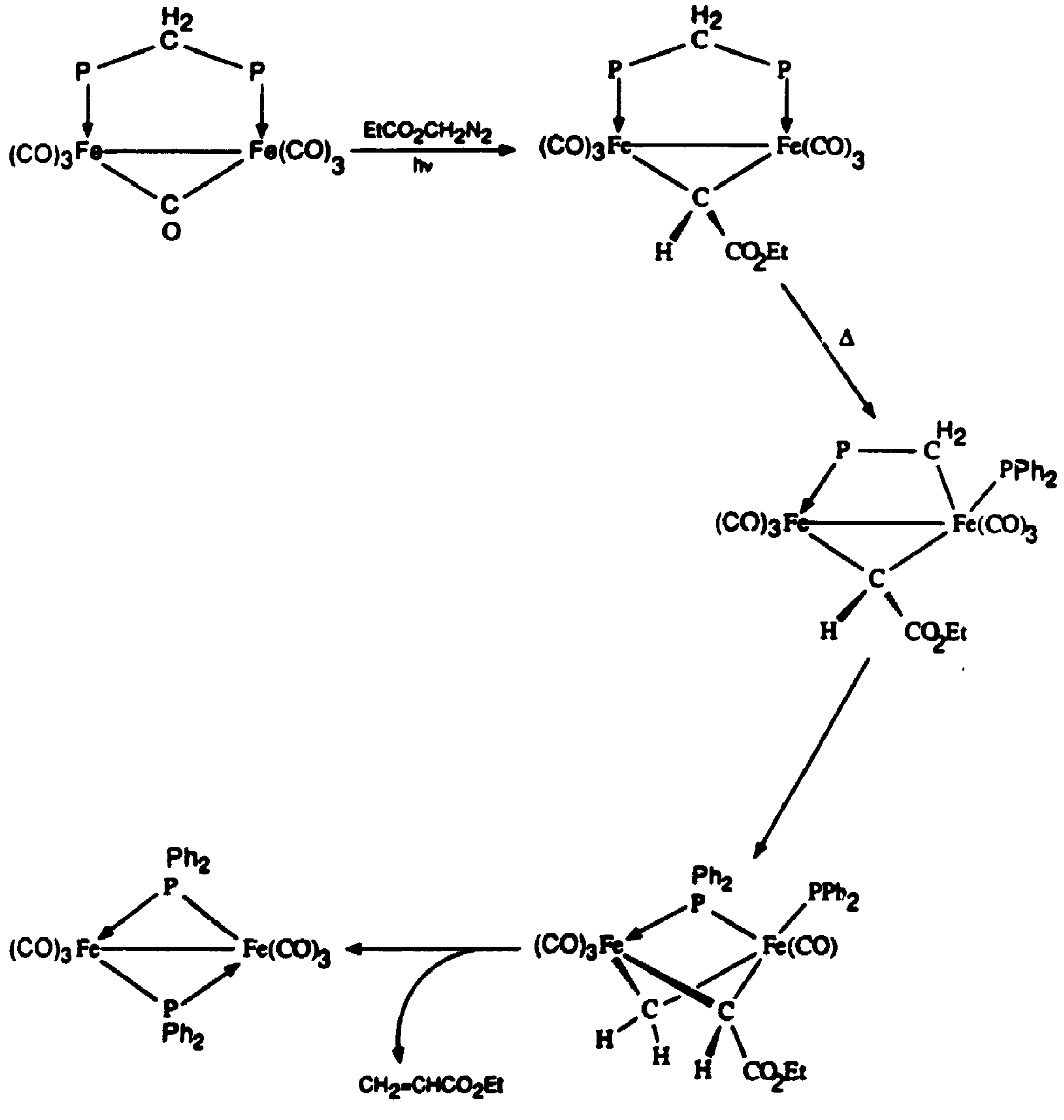
As with monotertiary phosphines, phosphides derived from ditertiary phosphines normally require harsh thermal or photolytic conditions for P-C bond cleavage. For example, when $[Co_2(CO)_6(\mu\text{-dppm})]$ is heated under 70 atm H_2 for 12 hours $[Co_2(CO)_4(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})]$ is formed[31]. Other examples of P-C bond cleavage in dppm are provided by $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ under various conditions[32]. Reaction with H_2 or $[K(HBBu_3^s)]$ give the dephenylated species $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)]$ and $[Ru_3(CO)_9(\mu_3\text{-PPhCH}_2\text{PPh}_2)]^-$ respectively. Refluxing in cyclohexane causes loss of a phenyl group at one end of the phosphine and ortho metallation at the other to yield $[Ru_3(CO)_9[\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)]$. The compound $[Mo_2(C_5H_5)_2(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(CO)_2]$ is obtained by heating of $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$ in THF at 60°C[33]. In this case both fragments of the fractured ligand are retained in the product.

Knox and coworkers have investigated P-C bond cleavage of bis-phosphines on iron dimers[34,35,36]. Refluxing $[Fe_2(CO)_7(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)]$ (R = Me, Ph) complexes in THF provides $[Fe_2(CO)_6(\mu\text{-PPh}_2)(\mu\text{-CH}_2\text{PR}_2)]$. The rate determining step in the reaction is thought to be CO loss followed by P-C bond cleavage to fulfill the electronic requirements of the metal atoms. Evidence for this is provided by the fact that the transformation occurs more rapidly for the dppm complex. The more basic dmpm ligand enhances Fe-CO backbonding thus hindering CO dissociation. In the complex $[Fe_2(CO)_5(\mu\text{-dppm})(\mu\text{-dmpm})]$ preferential P-C bond cleavage occurs in the dppm yielding $[Fe_2(CO)_4(\mu\text{-PPh}_2)(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-dmpm})]$. They also studied the thermolysis of a related complex $[Fe_2(CO)_7(\mu\text{-dppee})]$ [dppee =

1,1 bis(diphenylphosphino)ethylene]. The phosphine contains an sp^2 hybridized carbon atom in the bridge which cleaves more readily than a sp^3 hybridized carbon atom. The expected product, $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C(CH_2)PPh_2\}]$, is formed and if a third iron atom is introduced into the cluster an unprecedented second P-C bond cleavage on the same ligand occurs providing $[Fe_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(\mu_3\text{-}CCH_2)]$. Another example of double P-C bond cleavage was observed for dppm in the complex $[Fe_2(CO)_7(\mu\text{-dppm})]$[37]. Treatment of $[Fe_2(CO)_7(\mu\text{-dppm})]$ with ethyl diazoacetate under UV light and subsequent heating provide $[Fe_2(\mu\text{-}PPh_2)(CO)_6]$ and $CH_2{=}CH(CO_2Et)$ (Scheme 6.1).

Recently a number of reports of base induced P-C bond cleavage in a chelating dppm ligand under extremely mild conditions have appeared in the literature. When $[PtCl_2(dppm)]$ is treated with NaOH in organic solvents such as Me_2SO and MeCN, or liquid ammonia at -50°C both cis and trans isomers of $Pt_2(\mu\text{-}X)_2(POPh_2)_2(PMePh_2)_2$ (X =OH, NH_2)are formed[38,39]. Two types of mechanisms for the P-C bond cleavage are considered, both involving nucleophillic substition by OH^- at the phosphorus atom. One mechanism provides a carbanion which can then be protonated to give the $PMePh_2$ and PPh_2O groups while the other involves ylide formation followed by tautomerism. An interesting observation is that even under forcing conditions analagous dppe complexes are not found to undergo similar transformations. This is attributed to the ring strain found

Scheme 6.1: Double P-C bond cleavage in dppm on a dinuclear iron complex



in the four membered dppm chelate rings not present in five membered ring dppe chelates. As already discussed dppm is also found to undergo P-C bond cleavage while coordinated in a bridging mode where it also forms five membered rings, under fairly mild conditions (refluxing THF for example). In addition to the ring strain associated with dppm, a contributing factor is probably that in dppm the two P-C bonds on the methylene bridge are mutually polarizing while in dppe each carbon atom in the hydrocarbon bridge contains only one polar P-C bond. In a similar study, the reaction of $[PtCl_2(dppm)]$ with $[S(O)Me_3]Cl$ and NaOH under phase transfer catalyzed conditions gave $[Pt(PPh_2Me)(PPh_2OH)]\{(CH_2)_2SOMe\}Cl]$[40]. Again the dppe analogue did not react under these conditions.

With tridentate phosphines such as triphos, facile P-C bond cleavage is more common. $[Ru_3(CO)_{12}]$ reacts with $CH(PPh_2)_3$ under ambient conditions to form $[Ru_2(CO)_4(\mu\text{-}Cl)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ among other products in which P-Ph bond cleavage and bis(diphenylphosphino)methanide ligand formation have occured[41]. In the presence of zinc and CO $[IrCl(CO)_2(CH_3C_6H_4NH_2\text{-}p)]$ reacts with triphos to provide $[Ir_3(CO)_6(Ph)(\mu_3\text{-}PPh)(\mu\text{-}dppm)]$ as a major product[42]. The triphos ligand contains much weaker P-C bonds than ditertiary or monotertiary phosphines so it is not surprising that ligand fragmentation is facile.

6.1.3 ^{31}P NMR shifts of phosphido complexes

There are a number of factors affecting the ^{31}P chemical shift of bridging phosphido ligands, for which a wide range of shifts is known, and these are discussed in a review article by Carty[1]. For example, different metals will have different shieldings on a ^{31}P nucleus as will different oxidation states of a given metal. Also a metal-metal interaction will increase the deshielding of the ^{31}P nucleus. Changes in the stereochemisry at the phosphorus atom, that is changes in the R-P-R and M-P-M bond angles, will have an effect on the chemical shift. The nature, number and orientation of other ligands will influence the electron density on the metal and hence the deshielding effect the metal has on the ^{31}P nucleus. The electronic nature of the M-P interaction is another factor which influences the shift of the phosphide ligand. Finally the nature of the substituents on the phosphorus atom can have a dramatic effect on the shielding experienced by a ^{31}P nucleus. The variation among these factors results in a wide range of ^{31}P chemical shifts for known complexes from -181.6 for $[Pt(\mu\text{-}PPh_2)(dppe)]_2Cl_2$ to 461.4 ppm for $[CpCr_2(CO)_8(\mu\text{-}PF_2)]$.

6.2 Synthesis and characterization of complexes $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)_n(CO)_{6-2n}]$ (n=1 6.1, n=2 6.2) and $[Ni_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)_2(CO)_2]BPh_4$ 6.3

6.2.1 Synthesis of 6.1, 6.2 and 6.3

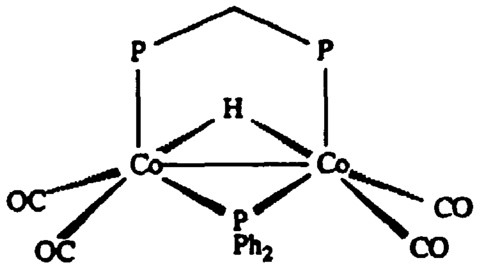
The cleavage of P-C bonds in dppm to provide (μ-PPh$_2$) ligands has been observed under various conditions. For example, when NaBH$_4$ is added slowly (between 5-30 min.) to CO saturated solutions of Co(II) and dppm, [Co$_2$(CO)$_4$(μ-dppm)$_2$)] or [Co(CO)(η^2-dppm)$_2$][Co(CO)$_4$] are produced. However, when the NaBH$_4$ is added quickly (<1 min.), at temperatures down to 0°C, 6.1 is produced in a significant yield. If NaBH$_4$ is added to solutions of Co(II) and dppm followed by passage of CO, again at temperatures down to 0°C, mixtures of 6.1 and 6.2 (approximately 2:5) are precipitated. When NiCl$_2\cdot$6H$_2$O is added prior to passage of CO to the above solutions at temperatures of 0°C or greater 6.3 is precipitated. 6.3 was also detected by ^{31}P NMR in Ni(II)/dppm/BH$_4^-$/CO reaction systems along with a variety o other products which made the isolation of pure 6.3 difficult. From a synthetic viewpoint, the preparations of the phosphido complexes described above are significant because of the extremely mild conditions found to effect P- bond cleavage, and the convenience of a "one pot" synthesis An interesting observation is that with analogous dppe reaction systems no (μ-PPh$_2$) complexes are isolated. With more forcing conditions, namely refluxing of [Co$_2$(CO)$_4$(μ-dppm)$_2$] in toluene under H$_2$, 6.2 is the major product.

The P-C bond in dppm, until very recently, was thought to be very stable. P-C bond cleavage is now recognized as a deactivation pathway for dppm containing catalysts and a fe examples of facile dppm cleavage can be found in the literature. In most cases the ligand cleaves to provide the μ-PPh_2 ligand and the fate of the remaining fragment (-CH_2PPh_2) is μ-CH_2PPh_2 ligand coordination or formation of $MePh_2P$. For example, the complex $[Fe_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_6]$ is produced from the heating of $[Fe_2(CO)_7(\mu\text{-}dppm)]$[34]. Under the conditions used to effect dppm cleavage in this work, the μ-CH_2PPh_2 moiety has not yet been identified nor have any $PMePh_2$ complexes been isolated. Also, no free $PMePh_2$ has been detected in any of the reaction mixtures. This is surprising given that the (μ-PPh_2) complexes are formed in significant yields and assuming single P-C bond cleavage in dppm, then the remaining fragment should therefore be evident by ^{31}P NMR. One possibility is that two PPh_2^- ligands are produced per dppm. Such cleavage is not unprecedented, for example in the product formed from 1,1 bis(diphenylphosphino)ethylene on a trinuclear cluster. P-C bonds at an sp^2 carbon atom are expected to be easier to cleave than at an sp^3 carbon atom, although double P-C bond cleavge is seen in the complex $[Fe_2(CO)_7(\mu\text{-}dppm)]$ (Scheme 6.1). More work is needed to determine the mechanism of (μ-PPh_2) formation in **6.1**, **6.2** and **6.3**.

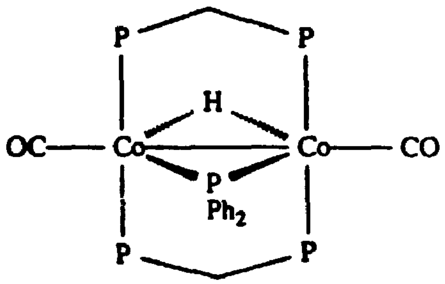
6.2.2 Characterization of 6.1, 6.2 and 6.3

The complexes **6.1**, **6.2** and **6.3** (Figure 6.2) were characterized[43] by ^{31}P and ^1H NMR and IR. **6.1** had been previously prepared by heating of $[Co_2(CO)_6(\mu\text{-}dppm)]$ under

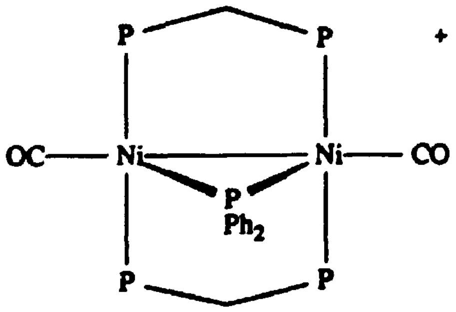
Figure 6.2: Complexes 6.1, 6.2 and 6.3



6.1



6.2



6.3

70 atm. H_2 and its reported ^{31}P and ^{1}H NMR agree with those found for **6.1** prepared by the $NaBH_4$ reduction of Co(II) in the presence of dppm and CO.

The ^{31}P NMR of **6.2** consists of a doublet at $\delta=47.6$ and a quintet at $\delta=215.6$. These shifts are close to those found for **6.1** and other μ-PPh_2 complexes. The ^{1}H NMR of **6.2** contains a symmetrical multiplet at $\delta= -17.8$, consistent with a μ-H group. The ^{31}P NMR of **6.3** is similar to those of **6.1** and **6.2**, consisting of a doublet at $\delta=15.6$ and a quintet at $\delta=239.8$.

6.3 Experimental

$[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)(CO)_4]$ 6.1

To a solution of $CoCl_2 \cdot 6H_2O$ (0.55g) and dppm (2.04g) in EtOH/toluene (4:1, 50mL) was added $NaBH_4$ (0.20g) in EtOH (15mL) dropwise over 15 minutes and the resulting brown suspension was filtered. CO was passed through the solution for 30 minutes during which time a mixture of crystalline **6.1** and **6.2** precipitated.

$[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)_2(CO)_2]$ 6.2

A solution of $CoCl_2 \cdot 6H_2O$ (0.833g) and dppm (2.79g) in degassed EtOH/C_6H_6 (1:1/30mL) was treated with CO for 5 minutes. $NaBH_4$ (0.400g) in degassed EtOH (30 mL) was added dropwise over 1 minute, and the mixture was stirred under CO for 30 minutes. The initial dark green solid formed (0.960g), was shown[47] by ^{31}P NMR integration to be approximately a 7:3 mixture of **6.1** and dppm monoxide. The mixture was recrystallized from CH_2Cl_2/EtOH to give pure **6.1**.

Yield : 20% Anal. calc. for $C_{64}H_{55}Co_2O_2P_5$: C,68.09; H,4.91

Found : C,68.60; H,4.76

Later crops from the crude reaction mother liquor contain increasing amounts of $[Co_2(CO)_4(\mu\text{-}dppm)_2]$

Spectroscopic data: NMR($CDCl_3$); $\delta^{31}P$= 47.6[d, $^2J(P_aP_b)$=64.2 Hz, $Co_2(\mu\text{-}P_aPh_2CH_2P_aPh_2)$], 215.6[q, $^2J(P_aP_b)$= 64.2 Hz, $Co_2(\mu\text{-}P_bPh_2)$]; δ^1H= 17.75[m, $^2J(P_aH)$=$^2J(P_bH)$= 29.2 Hz, $Co_2(\mu\text{-}H)$].

IR(Nujol) : ν(CO) = 1921 cm^{-1}.

$[Ni_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)_2(CO)_2]BPh_4$ 6.3

$NiCl_2 \cdot 6H_2O$ (0.55g) was added to the reaction filtrate from the preparation of 6.2 above prior to the passage of CO, and then CO was passed through the solution for 90 minutes. Hexane (40 mL) was added to the resulting purple solution and the mixture was cooled in a freezer for 96 hours. The dark purple solid which precipitated which was dissolved in EtOH and excess $NaBPh_4$ was added to give crude 6.3 which was recrystallized from CH_2Cl_2/EtOH.

Yield : 19% Anal. calc. for $C_{88}H_{74}BNi_2O_2P_5 \cdot CH_2Cl_2$: C,69.77; H,5.00. Found : C,70.07; H,5.22.

Spectroscopic data : NMR; $\delta^{31}P$ = 15.6[d, $^2J(P_aP_b)$= 57.5 Hz, $Ni_2(\mu\text{-}P_aPh_2CH_2P_aPh_2)$], 239.8[q, $^2J(P_aP_b)$= 57.5 Hz, $Ni_2(\mu\text{-}P_bPh_2)$].

IR(Nujol) : ν(CO) = 1996 cm^{-1}.

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Chapter 7 : Synthesis and Characterisation of $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})(BH_2)]$.

7.1 Introduction

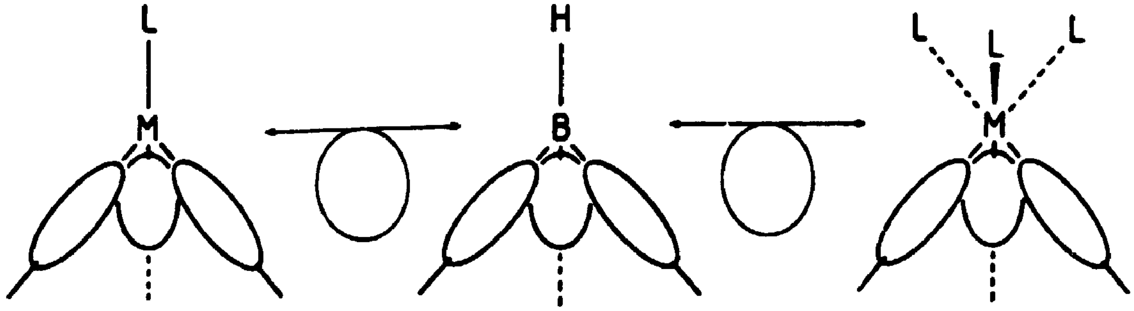
The title complex represents an example of an elusive class of compounds having a simple metal-BH_2 bond. To place this in context, a brief review of metal complexes containing small borane fragments will be given. This review is also justified by the general synthetic use of $NaBH_4$ in this thesis, and by the isolation of numerous BH_4^- metal complexes in the absence of CO (section 2.1).

7.1.1 Types of metallaboranes

There is a huge compilation of literature concerning metallaborane complexes. The explosion of research into boranes results partially from their wide use in synthetic organic chemistry[1]. It became evident that modifying boranes by substituting hydrides by other groups, such as basic metal fragments, could alter their reactivity. Also, investigation of complexes containing small borane fragments can provide insight into bonding and transformations of isoelectronic hydrocarbon fragments on metal clusters[2]. Finally, polyhedral borane clusters, once considered oddities, are now recognized as "pattern makers" in structural inorganic chemistry[3]. The binary clusters are composed largely of B-H units held together by multicentre bonding. The B-H fragment, with three vacant orbitals available for bonding, has a tetrahedral geometry and is isolobal with tetrahedral ML and octahedral ML_3 metal fragments also having three empty orbitals available for bonding (Figure 7.1)[4]. Thus, appropriate metal groups can be incorporated into polyhedral borane cages. The resulting complexes can be thought of as either extensions of polyborane clusters or as metal complexes of borane ligands[4]. Variation of metal geometry and metal substituents can permit structures not available to binary boron hydrides.

Several reviews have appeared in the literature discussing various aspects of metallaborane complexes. Classifications of metallaboranes have been made including "boron rich"[5] (M:B <1) and "metal rich" (M:B>1)[6,7]. These classifications indicate the authors' tendency to regard metallaboranes as formal metal complexes of boranes. Another group classifies the clusters according to the number of vertices in the metallaborane while relating these to analogous binary boranes. Clusters with less than eight[4] and greater than or equal to[8] eight vertices are discussed in a two part review respectively. No significance is placed on the M:B ratio but rather to electron valence pair counting and to the type of cluster formed. For example, nido type clusters with four vertices are represented by $[(CO)_3MnB_3H_9]$, $[(CO)_6Fe_2B_2H_6]$ and $[(CO)_9Co_3B(NEt_3)]$. These complexes can be thought of as metal derivatives of the binary borohydride B_4H_4.

Figure 7.1: Isolobal BH, ML and ML_3 fragments



7.1.2 Complexes of B_2H_n boranes

As just mentioned, reviews have appeared covering metal complexes of large borane or carborane clusters otherwise known as boron rich metallaboranes. For this reason and because these complexes are of little help in examining direct M-B interactions that are more readily studied in smaller clusters, this introduction will focus on metal complexes of borane fragments containing one or two boron atoms.

Complexes containing fragments derived from diborane have been prepared and are of significance because of their resemblance to clusters containing two carbon fragments. For example, the complexes $[Pt_2(PMe_2Ph)_2(B_2H_5)(B_6H_9)]$[9] and $[Cp_2Co_2(PPh_2)B_2H_5]$[10] both contain the B_2H_5 unit bound in a manner similar to a σ-π bound C_2H_3 ligand. In contrast to the bonding of the B_2H_5 in the above complexes, complexes $K[M(CO)_4(\eta^2\text{-}B_2H_5)]$ (M = Fe, Ru, Os) and $[M^1(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2\text{-}B_2H_5)]$ (M^1 = Fe, Ru) have symmetrically bound bidentate ligands and are considered to be analogues of metal-olefin complexes[11].

$B_2H_6^{2-}$, while unknown in its uncomplexed state can be found as a bidentate ligand in metal complexes. It is isoelectronic with C_2H_6 and thus these complexes can be considered models for the interaction of saturated hydrocarbons with metal surfaces. Examples of bis and tris(bidentate) coordination can be found in $[(CO)_6Fe_2B_2H_6]$[12] and $[(CO)_{10}HMn_3B_2H_6]$[13] respectively.

The substituted diborane $B_2H_4(PMe_3)_2$ acts as a bidentate ligand and forms adducts with a number of metals as discussed in section 7.1.3.2[14].

7.1.3 Complexes of BH_n boranes

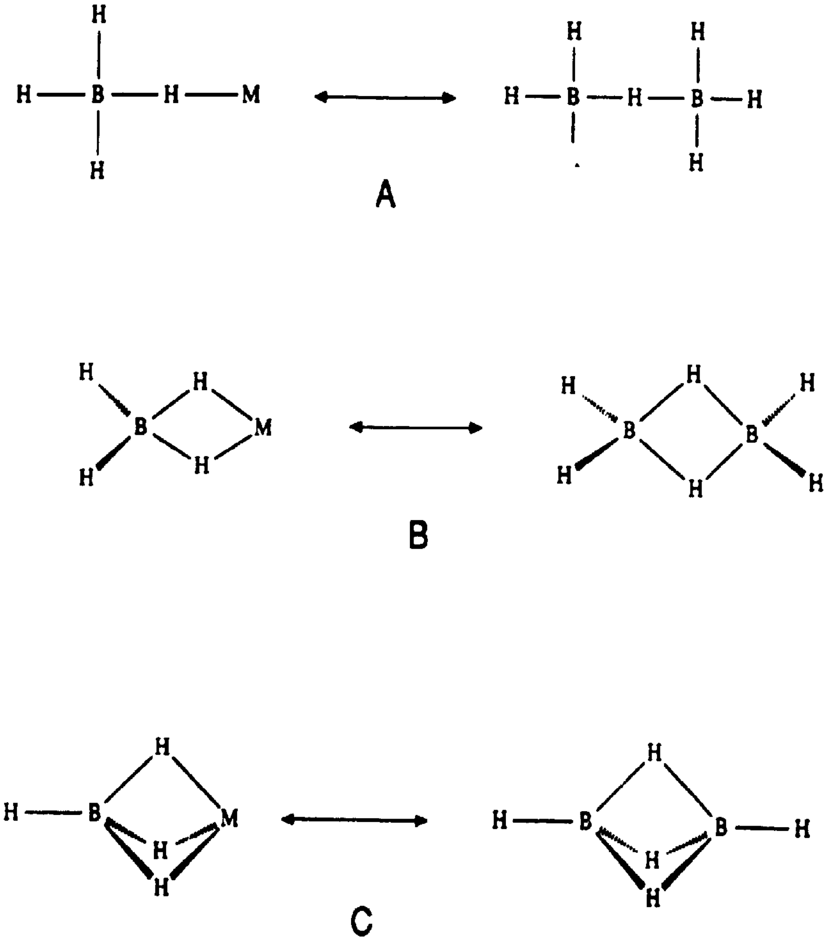
7.1.3.1 BH_4^- complexes

It is well established that the BH_4^- anion can ligate to a metal centre with participation of one, two or three hydrogen atoms and the resulting complexes can be related to binary boron hydrides[4,8]. For example, when phosphines, PR_3, are added to a solution of $[Ti(BH_4)_3(Et_2O)]$, prepared *in situ* from $TiCl_4$ and $LiBH_4$ in Et_2O, $[Ti(BH_4)_3(PR_3)_2]$ complexes are isolated[15]. The structure of the R=Me complex was determined crystallographically and it was found that two modes of BH_4^- coordination are present. One of the three equatorial BH_4^- groups is bidentate while the other two contain a single B-H-M bridge[16]. These complexes are thought to have similar bonding to and are isoelectronic with the $B_2H_7^-$ anion as illustrated in Figure 7.2a[4].

The dihydride bridged metal tetrahydroborates have similar bonding to that found in diborane, the first in the nido series of boron hydrides (Figure 7.2b).

The tetrahydroborate anion can also act as a tridentate ligand to a single metal centre and in so doing providing a model for the observed but highly unstable $B_2H_5^+$ cation which is thought to have a triply hydride bridged structure (Figure 7.2c).

Figure 7.2: BH_4^- coordination in metal complexes



Reaction of Co(II) salts with $NaBH_4$ in the presence of dppp provides the dinuclear species; $[Co_2(\mu\text{-}BH_4)_2\{\mu\text{-}PPh_2(CH_2)_5PPh_2\}_2]$[18] which contains an interesting mode of BH_4^- coordination. The crystal structure of the complex reveals that three hydrogens on each BH_4^- are involved in bonding. Two of the hydrides form B-H-M bridges while the third effectively caps a Co_2B face. Reaction of $Na[Fe(CO)_4(COCH_3)]$ with $BH_3\cdot THF$ at 70°C followed by protonation with H_3PO_4 provides $[(CO)_9HFe_3BH_4]$ in which a BH_4 caps the trinuclear face through three hydrides[19]. Thus while it can be seen that BH_4^- complexes exhibit interesting bonding properties and are interesting in their own right, they provide little insight into the nature of the M-B link of simple metal-borane adducts due to the participation of the hydrogens in bonding to the metal.

7.1.3.2 BH_3 complexes of Lewis bases

Borane, BH_3, in itself is highly unstable and dimerizes to give diborane B_2H_6. More stable adducts $BH_3\cdot L$ can be formed with the addition of Lewis bases such as phosphines, amines, oxygen or sulphur containing species or even basic metal complexes with an available lone pair of electrons. This property has been exploited to prepare borane adducts from $BH_3\cdot THF$ which is made by simply dissolving diborane in THF. The THF can be displaced by stronger bases such as phosphines. $(CH_3)_2S\cdot BH_3$ has also been used for this purpose.

There are many examples of phosphine adducts of boranes.

For example, adducts of the type $PPh_2(CH_2)_nPPh_2\cdot(BH_3)_m$ (m=2, n=1-4; m =1, n=1) have been prepared by addition of I_2 to a solution of $NaBH_4$ and the phosphine[20,21]. Phosphines with n=1 or 2 also form adducts $B_5H_9\cdot L$ with pentaborane[22]. Adducts in which the phosphine chelates a BH_2^+ fragment are prepared by addition of the phosphine to a solution of $(CH_3)_2S\cdot BH_3$ and I_2[20,21].

An interesting example of a phosphine-borane adduct acting as a ligand can be seen in $[Ni(CO)_2(BH_2\cdot PMe_3)_2]$[14]. The complex results from the reaction of $[Ni(CO)_4]$ with the $(BH_2\cdot PMe_3)_2$.

Anionic metal carbonylates have been shown to stabilize a BH_3 fragment through their Lewis basicity[23]. For example, reaction of $Na[Re(CO)_5]$ with a stoichiometric amount or excess amount of $R_2O\cdot BH_3$ gave $Na[Re(CO)_5(BH_3)_n]$ n=1 or 2 respectively. While $[Mn(CO)_5]^-$ was found to be less basic toward BH_3 than the rhenium analogue, the substituted derivative $[Mn(CO)_4PPh_3]^-$ was found to give a stable adduct. Solutions of $[Co(CO)_4]^-$ were found to absorb 0.5 moles of diborane per mole of cobalt salt, however the reaction was apparently reversible as removal of solvent gave only solvated $Na[Co(CO)_4]$.

7.1.3.3. Complexes of BX_2 fragments

Another type of metal adduct of a borane containing a single boron atom resembles B_2H_4 which is the first member of the closo family B_nH_{n+2}[4]. B_2H_4 is only known as an unstable reaction intermediate while the halide derivatives B_2X_4 and certain organic derivatives B_2R_4 are well characterized. Analogous two vertex metallaboranes, MBX_2, containing a direct M-B bond are known where X is an aromatic or electronegative substituent[4].

Many examples of this type of adduct are known including $[(CO)_4CoBCl_2]$[24]. Adducts containing a B-H bond have proved to be elusive with only an unsubstantiated claim of $[Fe(CO)_4BH_2]^-$ as a reaction intermediate appearing in the literature[6]. Recently the isoelectronic species $[Co(CO)_4BH_2\cdot THF]$ **7.1** was obtained from the low temperature reaction of $[Co_2(CO)_8]$ with $BH_3\cdot THF$ in a THF solution[25]. The reaction stoichiometry, as shown in equation 7.1, was established by monitoring H_2 gas evolution and the growth of an absorption band of **7.1** at 512 nm as a function of time during the reaction.

$$2[BH_3\cdot THF] + Co_2(CO)_8 \rightarrow 2[Co(CO)_4BH_2\cdot THF] + H_2 \qquad (7.1)$$

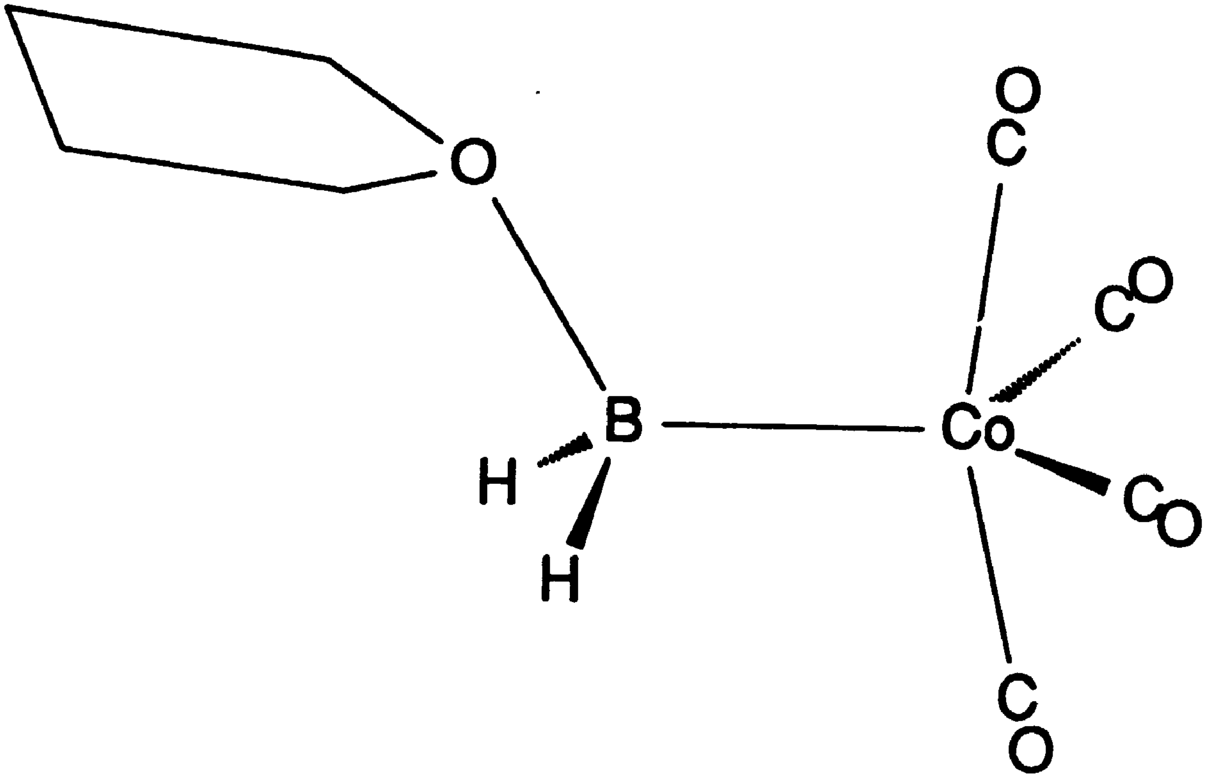
Additional spectroscopic and chemical evidence was used to confirm the reaction stoichiometry. The reaction is also accompanied by a concurrent loss of a ^{11}B nmr resonance for the $BH_3\cdot THF$ with growth of a singlet at $\delta=7.9$ indicating a single boron containing species. The formation of $[BH_2\cdot 2THF][Co(CO)_4]$ was ruled out on the basis of spectroscopic and chemical evidence. Reaction of $[Co_2(CO)_8]$ with $BH_3\cdot SMe_2$ in CH_2Cl_2 provides none of **7.1** which led to the conclusion that THF is required to stabilize 7.1 through interaction of the lone pair on the oxygen atom of THF with the boron fragment. Also, addition of NEt_3 to solutions of 7.1 results in loss of the ^{11}B resonance at $\delta=7.9$ and appearance of a broad signal at $\delta=3.6$ presumably due to the displacement of a THF by the amine which is a better Lewis base. The proposed structure of 7.1 (Figure 7.3) is derived from square based pyramidal geometry around the cobalt with the coordinated boron fragment at the apical site. The THF occupies one site on a tetrahedrally coordinated boron atom.

7.1.3.4 Miscellaneous complexes with M-B bonds

A number of polynuclear complexes have been characterized in which single boron atom containing fragments are stabilized without the involvement of B-H-M bridges. For example, in the clusters $[(CoCp)_3(\mu_3\text{-}BPh)(\mu_3\text{-}PPh)]$, which is obtained from the reaction of $[CpCo(PPh_3)_2]$ with $BH_3\cdot THF$, the BPh group caps an equilateral triangle of cobalt atoms[26]. A similar structure is found in the isoelectronic $[\{Co(CO)_3\}_3(\mu_3\text{-}BNEt_3)]$[27] and $[(\mu\text{-}H)_3(CO)_9Os_3BCO]$[28]. The B-CO bond is labile, a property which can be used in the preparation of complexes $[(\mu\text{-}H)_3(CO)_9Os_3BPMe_3]$, $[(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}CBCl_2)]$ and $[(\mu\text{-}H)(CO)_9Os_3H_2B{=}CH_2]$. A comparison of the latter with the trimetal vinylidine complex $[(\mu\text{-}H)_2Os_3(CO)_9C{=}CH_2]$ has been made.

There is also a series of trinuclear iron clusters

Figure 7.3: Proposed structure of $[Co(CO)_4BH_2 \cdot THF]$



containing single boron fragments BH_n which are related to the tetrahydroborate capped cluster $[(CO)_9HFe_3BH_4]$, already discussed. The reaction of $Na[Fe(CO)_4(COCH_3)]$ with $BH_3\cdot THF$ in the presence of $[Fe(CO)_5]$ followed by protonation with H_3PO_4 leads to $[(\mu\text{-}H)Fe_3(CO)_{10}(BH_2)]$[29]. The complex can be deprotonated at the hydride bridged Fe_2 edge to provide $[Fe_3(CO)_{10}BH_2^-]$. $[(\mu\text{-}H)Fe_3(CO)_{10}BH_2]$ and its conjugate base $[(\mu\text{-}H)Fe_3(CO)_{10}BH]^-$ are also known[30]. Alkyl derivatives of $[HFe_3(CO)_9BH_4]$, $[HFe_3(CO)_9(H_3BR)]$ are known as well as the conjugate base of the former, $[(\mu\text{-}H)Fe_3(CO)_9BH_3]^-$.

A BH_2^+ fragment is found bridging the wingtips of butterfly clusters $[HM_4(CO)_{12}BH_2]$ (M = Fe, Ru) which are isoelectronic with the carbido cluster $[HFe_4(CO)_{12}CH]$[31]. The iron cluster was observed to undergo stepwise deprotonation to give the borido cluster anion $[Fe_4(CO)_{12}B]^{3-}$. A BH_2+ fragment is also bound to what is essentially the deprotonated carbido cluster mentioned above, in $[HFe_3(CO)_{12}CBH_2]$[32]. The cluster contains no M-B-H bridges.

$BH_3\cdot THF$ reacts with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ via addition to the W-C triple bond to provide $[W_2\{\mu\text{-}MeCB(H)Et\}(CO)_4(C_5H_5)_2]$[33]. The X-ray structure of the complex reveals that the EtB-CMe group transversely bridges the W-W bond as in some alkyne complexes of tungsten[34] and cobalt[35] for example. A single B-H-W bridge was also found.

7.2 Synthesis and Characterisation of $[(CO)_2(\eta^1\text{-}dppm)Co(\mu\text{-}dppm)BH_2]$ 7.2

7.2.1 Synthesis of 7.2

The novel complex has been synthesized in a single step reaction involving the $NaBH_4$ reduction of Co(II) halide salts in the presence of CO and dppm. The compound is only isolated in small yields, however, from mixtures containing the $[Co(CO)_2(\mu\text{-dppm})]_2$ isomers as the major product. The unique nature of the elusive $M\text{-}BH_2$ unit and the potentially rich chemistry offered by this complex makes an alternative, high yield synthesis desirable. To this end several approaches have been tried. The borane adduct of dppm, $dppm\cdot BH_3$, has been detected by ^{31}P NMR in some of the reaction mixtures described above and it is possible that such a species could be an intermediate in the formation of 7.2. For example, such a species could add to a cobalt hydride or halide species with subsequent reductive elimination of H_2 or HX respectively to provide a $Co(\mu\text{-dppm})BH_2$ unit. In response to this idea a C_6H_6 solution of $dppm\cdot BH_3$ was prepared by a literature described method[20]. This solution was combined with a stoichiometric amount of $CoCl_2\cdot 6H_2O$ and dppm. To this mixture was added an EtOH solution of $NaBH_4$ under a continuous purge of CO. The reaction mixture was worked up in a manner similar to those leading to small yields of 7.2 but no trace of 7.2 was detected.

Recently Felhner et al[25] reported the characterization of $[(CO)_4CoBH_2\cdot THF]$ 7.1 which is the first example of a complex containing the $M\text{-}BH_2$ unit with a simple M-B interaction. Complex 7.1 is only stable in solution at low temperature, in contrast to 7.2 which is air stable in the solid state and is stable in solution at room temperature under N_2. Complex 7.1 could serve as a substrate for the synthesis of 7.2 via substitution of two carbonyls and the THF by a monodentate dppm and bridging dppm. Accordingly a solution of $BH_3 \cdot THF$ was added to $[Co_2(CO)_8]$ in THF in a THF/dry ice bath as outlined in the preparation of 7.1, and an appropriate amount of dppm was added. The ^{31}P nmr of the reaction mixture indicated that a complex mixture had formed and no trace of 7.2 was seen. A major component of the mixture was $dppm \cdot BH_3$, characterized by a doublet in the ^{31}P NMR spectrum at $\delta=-31.5[^2J(PP^1)=77.2\ Hz]$ and a broad resonace at $\delta=11.0$. The broadening of the ^{31}P-B signal is presumably due to the quadrupolar broadening effects of the ^{10}B and ^{11}B nuclei. The other major component exhibits a very similar pattern [$\delta=-34.5(d,\ ^2J(PP^1)=62.6\ Hz),\ 55.8(br)$] but this complex could not be fully characterized.

A second possible route to complex 7.2 is the reaction of $[CoBr(CO)_2(\eta^1\text{-dppm})_2]$, which already contains structural features found in 7.2, with $BH_3 \cdot THF$. Displacement of THF by a phosphorus donor of a η^1-dppm ligand and subsequent reductive elimination of HBr would give 7.2. However, this reaction was also unsuccessful[37]. A likely problem of both of the above methods is that they require cleavage of a B-H bond from the BH_3 unit. Complex 7.2 can be thought of as having a $Co^{(-1)} \rightarrow BH_2^{(+1)}$ core and perhaps a better approach would be to prepare a BH_2^+ derivative such as $[(\eta^2$-dppm$)BH_2]^+$ [20] and reacting it with $[Co(CO)_4]^-$.

7.2.2 Characterisation of 7.2

7.2.2.1 Structure of 7.2

7.2 is found as a minor component of a mixture containing mainly the isomers of $[Co(CO)_2(\mu$-dppm$)]_2$. Large yellow crystals of 7.2 of suitable quality for a X-ray diffraction study were handpicked from the mixture. The structure determination of 7.2 is of significance because it represents the first structural characterization of a simple M-BH_2 interaction. An ORTEP representation of the structure of 7.2 can be seen in Figure 7.4.

The geometry about the cobalt atom can be described as distorted trigonal bipyramidal with the carbonyl ligands and one end of the μ-dppm at equatorial sites and the η^1-dppm and BH_2 at axial sites. Selected bond angles demonstrating the geometry of the cobalt atom are listed in Table 7.1. Distortion from axial-equatorial angles of 90° in a regular TBP is seen by angles P(1)CoP(2)=101.91(3)°, BCoC(3)=82.4(2)°, and BCoC(4)=75.5(2)°. This distortion probably arises from steric interaction between phenyl groups on the axial dppm with equatorial ligands, resulting in displacement of the equatorially bonded atoms away from P(4).

An interesting feature in the structure of 7.2 is the long Co-B distance of 2.232(6)Å. It is difficult to make

Figure 7.4: ORTEP representation of 7.2

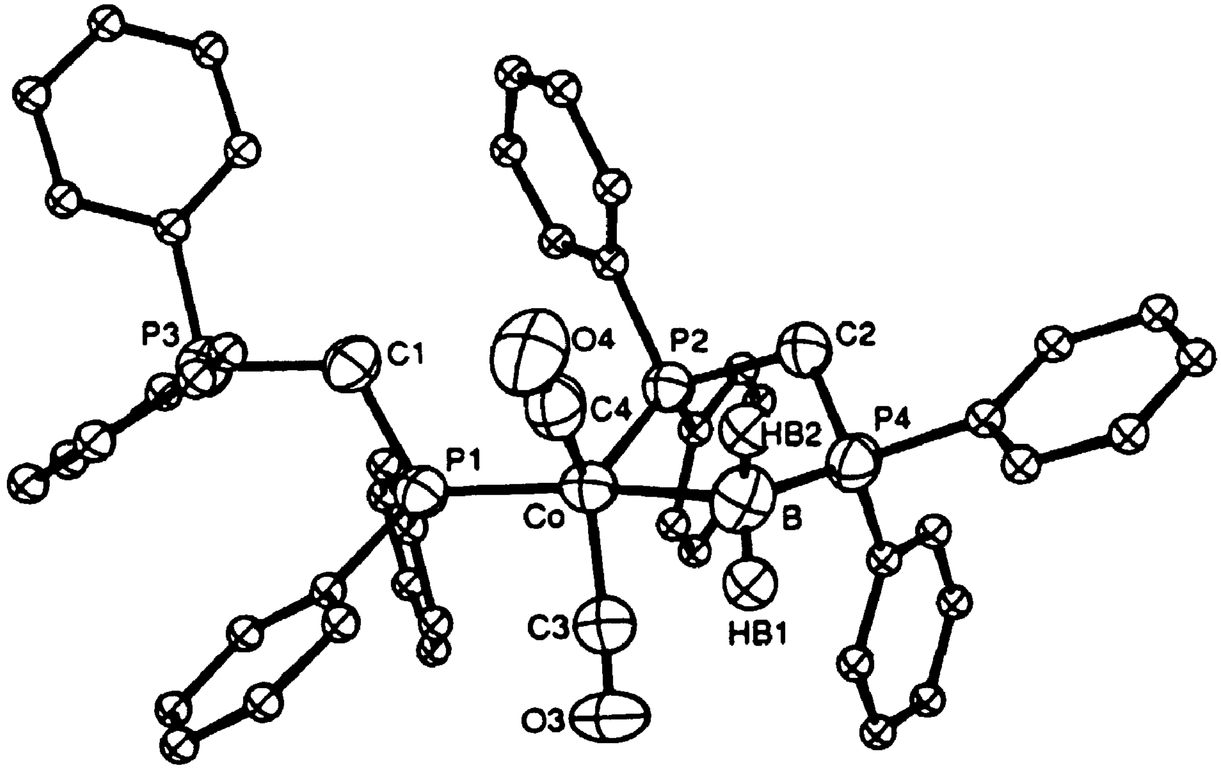


TABLE 7.1. Selected Distances and Angles in 7.2

Bond	Distance(Å)	Angle	Degrees(°)
Co-P(1)	2.193(1)	P(1)-Co-B	164.3(2)
Co-P(2)	2.298(1)	P(1)-Co-C(4)	95.30(16)
Co-C(3)	1.746(5)	P(1)-Co-C(3)	93.56(18)
Co-C(4)	1.738(5)	P(1)-Co-P(2)	101.91(3)
Co-B	2.232(6)	P(2)-Co-B	93.1(2)
P(4)-B	1.912(6)	C(3)-Co-B	82.4(2)
C(4)-O(4)	1.150(7)	C(4)-Co-B	75.5(2)
C(3)-O(3)	1.147(6)	P(2)-Co-C(3)	119.93(21)
P(1)-C(1)	1.847(5)	C(3)-Co-C(4)	127.2(3)
P(2)-C(2)	1.873(5)	Co-B-P(4)	103.9(3)

comparisons to other structurally characterized species because of the lack of this unique metal-boron type of interaction in the literature. Most complexes contain "metal rich" or "boron rich" cores or boron-hydride bridged structures. However it is still apparent that most first row transition metal-boron bonds fall in the range 2.00-2.15Å. For example, $[HFe_4(CO)_{12}BH_2]$ contains a BH_2 unit bridging the wingtips of the Fe_4 butterfly arrangement[31]. The Fe-B distances range from 1.974(6)-2.047(6)Å. In $[(\eta^5\text{-}C_5H_5Co)_2(\mu\text{-}PPh_2)B_2H_5]$ the bonding of the B_2H_5 unit to the cobalt dimer is likened to that in $\mu\text{-}\eta^2$-ethylene complexes and Co-B distances are 2.110(9), 2.025(8), and 2.138(9)Å[10]. $[Co_4(BH)_2(\mu_3\text{-}H)_2]$ is one in a series of octahedral $Co_{6-n}B_n$ clusters and the Co-B distances range from 2.009(8) to 2.070(8)Å[36]. The long Co-B distance in 7.2 is indicative of a weak interaction probably polarized in the sense $Co^{\delta-}\rightarrow B^{\delta+}$. In the extreme case it can be considered as a dative bond with $Co(CO)_2L_2^-$ as a two electron donor and BH_2L^+ as an acceptor. Spectroscopic evidence for this type of formulation includes the $\nu(CO)$ values of 1925 and 1865 cm^{-1} in the IR spectrum of 7.2 compared to those in related dinuclear Co(0) complexes such as $[Co_2(CO)_4(\mu\text{-dppm})_2]$ with $\nu(CO)$ in the region 1929-2000 cm^{-1}. Also the pale yellow colour of 7.2 is more reminiscent of $Co(CO)_4^-$ and derivatives than the characteristic intense colours of Co(0) and Co(I) complexes.

If the $Co(-1)\rightarrow BH_2(+1)$ model is considered valid the geometry around the cobalt atom can be reinterpreted. In other systems with the posulated dative Co(-1)→M interactions, the geometry of the cobalt atom is interpreted in terms of a distorted tetrahedron and a long Co-M distance is found. The Co(-1) fragment acts as a two electron donor to the neighbouring M fragment and distortions arise from the interactions of the ligands on M with three of the ligands on cobalt. This leads to closing of the tetrahedral angles subtended by these three ligands at the cobalt atom with the fourth ligand. Also, the approach of the Co(-1) fragment on M makes the fourth ligand roughly colinear with cobalt and M giving the appearence of a distorted TBP. This treatment, when applied to 7.2, does not agree with the geometry demonstrated at the cobalt atom in 7.2 as the angles P(1)CoP(2)=101.91(3)°, P(1)CoC(3)=93.56(18)°, P(1)CoC(4)=95.30(16)° are closer to 90° expected for TBP than the 109° expected for tetrahedral geometry. However the bonding is interpreted, the structure is significantly different from the square based pyramid proposed for 7.1 on the basis of spectroscopic data. This difference is reconcilable however given that TBP and SP structures are known to have similar energies.

The two hydrogen atoms on boron were located by the X-ray structure determination and were successfully refined. The geometry around the boron atom is roughly tetrahedral as expected for a four coordinate boron.

7.2.2.2 Spectroscopic characterisation of 7.2

The IR spectrum of 7.2 exhibits $\nu(CO)$ stretches at 1925(m) and 1865(s) cm^{-1} consistent with the two terminal carbonyls found in the solid state structure of 7.2. These stretches, particularly the one at 1865 cm^{-1}, are at the low end of the range observed for terminal carbonyls. This indicates that there is considerable backbonding from cobalt to the π^* orbital of CO resulting in a lower C–O bond order and a correspondingly low $\nu(CO)$ value. This electron density must originate from the metal centre and hence the low $\nu(CO)$ values support the $Co(-1) \rightarrow BH_2^+$ formulation.

$\nu(BH)$ stretches at 2380(w) and 2310(w) cm^{-1} are also observed in the IR spectrum of 7.2.

7.2 is freely soluble in most organic solvents and thus characterization by NMR was possible. The ^{31}P NMR spectrum of 7.2 (Figure 7.7) exhibits four sets of resonances integrating 1:1:1:1 at δ=-33.0[d,$^2J(P_AP_B)$=28 hz, P_A], 47.1[br, P_B], 15.7[d,$^2J(P_CP_D)$=155 Hz, P_D], 44.5[d,$^2J(P_CP_D)$=155 Hz, P_C]. The number of signals is consistent with the four chemically distinct phosphorus atoms in the solid state structure of 7.2. The ^{31}P NMR of 7.2 is remarkably similar to [(η^1-dppm)(CO)$_2$Co(μ-dppm)Mn(CO)$_4$] and the spectral parameters for complexes [(η^1-dppm)(CO)$_2$Co(μ-dppm)X] {X=BH$_2$, Mn(CO)$_4$, Re(CO)$_4$} are summarized in Table 5.4. The resonance due to the free end of the η^1-dppm ligand (P_A) was easy to assign due to the similarity of the δ=-33.0 shift and $^2J(PP)$ coupling constant to numerous other η^1-dppm complexes characterized by ^{31}P NMR. Also it was the sharpest of the four signals, consistent with it being the only one not coordinated to a cobalt or boron and hence it is free from the quadrupolar broadening effects seen in the other signals.

The δ=15.7 and 44.5 resonances appear as an AB type pair of doublets and thus can be assigned to the phosphorus atoms of the bridging dppm. The remaining resonance can therefore be assigned to P_B. The assignment of the AB doublets is tentative. However, the P_B and P_C resonances are expected to have similar shifts as seen in related complexes $[(\eta^1\text{-dppm})(CO)_2Co(\mu\text{-dppm})M(CO)_4]$ (M=Mn or Re) and thus the δ=44.5 and δ=15.7 resonances are assigned to P_C and P_D respectively. The low temperature spectrum of **7.2** remains essentially unchanged down to -90°C with sharpening of the resonances according to the quadrupolar thermal decoupling model described in section 1.1.3.1.

The ^1H NMR spectrum of **7.2** consists of two sets of AB type resonances assigned to the $P_ACH_aH_bP_B$ and $P_CCH_aH_bP_D$ sets of methylene protons on the dppm ligands. The respective signals cannot be assigned unambiguously to the different dppm ligands. The combined signals from these protons integrate 1:10 to the phenyl protons as expected. The absence of any signal for the B-H protons down to -30 ppm is presumably due to the multiplicity of the signal and quadrupolar broadening from the attached ^{11}B or ^{10}B nucleus and possibly from the neighbouring ^{59}Co nucleus.

The FAB-MS of 7.2 contains peaks at 898, 884, 870 and 841 assignable to the parent ion plus two hydrogens, (P+2H) {P=$(CO)_2$(dppm)$_2$CoBH_2}, P-BH_2+H, P-CO+2H and P-2CO+H respectively. Also, there was excellent agreement between the observed and calculated envelope structures at m/z = 841 (P-2CO+H) confirming the presence of a single boron atom.

The ^{11}B NMR spectrum of 7.2 exhibits a broad singlet resonance at -25.9 ppm.

7.3 Experimental

$[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})(BH_2)]$ 7.2

A solution of $NaBH_4$ (0.12g) in EtOH (10 mL), which had a stream of N_2 passing through it, was added dropwise to a solution of $CoBr_2\cdot 6H_2O$ (0.44g) and dppm (1.00g) in C_6H_6/EtOH (30 mL,1:1) over 30 minutes. The mixture was stirred under a continuous stream of CO for four hours, then the solvents were removed by vacuum and the solid washed with EtOH (40 mL) and recrystallized from CH_2Cl_2/EtOH. Large yellow crystals of the title complex were separated from black crystals of $[Co_2(CO)_4(\mu\text{-dppm})_2]$ by handpicking. A mixture of black and yellow crystals was also precipitated from the EtOH washings overnight. These were recrystallized from CH_2Cl_2/EtOH to obtain large enough crystals for separation by hand.

Yield : <5%

Spectroscopic data : NMR(CD_2Cl_2); $\delta^{31}P$(labelling defined in Table 5.4) = -33.0 [d, $^2J(P_AP_B)$= 28, P_A]; 47.1 [br, P_B]; 15.7 [d, $^2J(P_CP_D)$ = 155, P_D]; 44.5 [d, $^2J(P_CP_D)$ = 155, P_C]; $\delta^{11}B$ = -25.9 [br s], δ^1H = 2.28 and 3.40 [m, PCH_aH_bP]. IR: ν(CO) = 1925 (m), 1865 (s) cm^{-1}, ν(BH) = 2380 (w), 2310 (w) cm^{-1}. FAB-MS: m/z = 898, 884, 870, 841; Calc. for $C_{52}H_{46}BCoO_2P_4$: 896, P-BH_2 883, P-CO 868, P-2CO 840. There was excellent agreement between the observed and calculated (for P-2CO + H) envelope structures at m/z = 841, thus proving the presence of a single boron atom. EI-MS: confirms ^{11}B and ^{10}B at m/z = 11 and 10 in required ratio.

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Chapter 8 : Conclusions

8.1 Synthetic methods

The main synthetic method used in this work is the reduction of metal halide salts in the presence of CO and phosphines by $NaBH_4$ and this provides a unique, often advantageous, approach to the preparation of metal-phosphine carbonyl complexes. For example, complexes $[CoM(CO)_n(\mu\text{-dppm})_2]$ (M=Co,n=4 **8.1**; M=Rh,n=3 **8.2**) have been prepared in this manner in good yields. Related complexes $[Co_2(CO)_4L_4]$, where L_4 is a tetradentate or two bidentate phosphines, nave been synthesized from reactions of $[Co_2(CO)_8]$ with the appropriate phosphine (section 1.3.5.2). In the case of dppm, however, only disubstitution occurs to give $[Co_2(CO)_6(\mu\text{-dppm})]$ and thus the "one pot" method above offers a route to a phosphine derivative of $[Co_2(CO)_8]$ not available by a conventional method. Also, all the materials used in the synthesis of $[Co_2(CO)_4(\mu\text{-dppm})_2]$ are easily handled in air, and with the exception of $NaBH_4$, are not moisture sensitive, as opposed to $[Co_2(CO)_8]$ which is both air and moisture sensitive.

Related complexes $[M_2(CO)_3(\mu\text{-dppm})_2]$ (M=Ir or Rh) cannot be prepared by substitution of the binary carbonyls, which are unstable, but rather are made in multistep reactions[1,2]. For example, when $[Rh(\mu\text{-Cl})(CO)_2]_2$, prepared from $RhCl_3$ under a hot stream of CO, is treated with two equivalents of dppm, $[Rh_2(\mu\text{-dppm})_2Cl_2(CO)_2]$ is produced. Subsequent reduction with $NaBH_4$ leads to $[Rh_2(CO)_3(\mu\text{-dppm})_2]$. $[RhIr(CO)_3(\mu\text{-dppm})_2]$ is also produced in a multistep reaction[3]. The borohydride reduction method is not likely to completely displace such multistep syntheses but, when good yields are obtained in a single step, the advantages are obvious.

Two surprises emerged from these Co(II)/dppm/NaBH$_4$/CO reaction systems, namely the isolation of [(CO)$_2$(η^1-dppm)Co(μ-dppm)BH$_2$] (Chapter 7), containing a cobalt-boron bond, and the synthesis of μ-PPh$_2$ complexes by cleavage of a dppm ligand under mild conditions (Chapter 6).

8.2 Reactivity of the [Co(CO)(η^2-dppm)$_2$]$^+$ cation 8.3

A possible mechanism of formation of [Co$_2$(CO)$_4$(μ-dppm)$_2$] 8.1 was postulated to involve a complex, [Co$_2$(μ-dppm)$_2$Cl$_3$], isolated from Co(II)/dppm/NaBH$_4$ reaction systems not involving CO[4]. It now appears that [Co(CO)(η^2-dppm)$_2$][Co(CO)$_4$] 8.4 is not an intermediate in the formation of 8.1.. This mechanism had been suggested by the established loss of CO from 8.4 to give 8.1, but it now seems that 8.4 is formed from the reaction of 8.1 with CO. In the case of [CoRh(CO)$_3$(μ-dppm)$_2$] 8.2, there is evidence for the formation of [Rh(CO)(η^2-dppm)$_2$][Co(CO)$_4$] but it is not clear if this is a reaction intermediate. Regardless of whether or not the complexes [M(CO)(dppm)$_2$][Co(CO)$_4$] (M=Co or Rh) are precursors to neutral dimers [CoM(CO)$_n$(μ-dppm)$_2$] in the NaBH$_4$ reductions, their demonstrated tendency to form binuclear complexes with loss of CO prompted an investigation into the chemistry of the [Co(CO)(η^2-dppm)$_2$]$^+$ cation 8.3 towards metal carbonyl anions as a possible general synthetic route to dppm bridged heterobimetallics containing cobalt.

Encouragement for this pursuit was also provided by the success of using related rhodium and iridium complexes with chelating dppm as precursors to heterobimetallic complexes[5] (section 1.4).

Thus the reactivity of the 8.3 was investigated towards other metal complexes (section 2.4.4.2). It was determined that the cation was much less reactive than the rhodium and iridium analogues towards (η^2-dppm) ring opening reactions in the formation of $MM^1(\mu$-dppm$)_2$ type heterobimetallics. The success of the rhodium and iridium complexes in this pursuit is presumably due to the greater ring strain experienced in the four membered $M(\eta^2$-dppm) ring for the larger metals. With more basic metal fragments such as $[M(CO)_n]^-$ (M=Co,n=4; M=Mn or Re,n=5), the complexes $[CoM(CO)_n(\mu$-dppm$)_2]$ (M=Co,n=4 8.1; M=Mn 8.5 or Re 8.6,n=5) are formed and the intermediate complexes $[(CO)_2(\eta^1$-dppm$)Co(\mu$-dppm$)M(CO)_4]$ were also identified. With $[Co(CO)(\eta^2$-dppm$)_2]^+$ the opening of the η^2-dppm must be facilitated by the presence of a nucleophillic metal fragment such as $[M(CO)_n]^-$. The heavier elements tend to form 16 electron complexes, and this can be achieved by loss of one phosphorus donor of a dppm ligand in $[M(CO)(\eta^2$-dppm$)_2]^+$. In combination with the increased ring strain in the chelate complexes of the larger elements as discussed above, this causes the rhodium and iridium complexes to be more reactive than the cobalt complex.

The sequential opening of both η^2-dppm rings was also observed in $[Co(CO)(dppm)_2]^+$ in the presence of CO and halide respectively. This property was used to increase the yields of [$CoM(CO)_5(\mu$-dppm$)_2$] (M=Mn or Re) by the in situ formation of [$CoX(CO)_2(\eta^1$-dppm$)_2$] from [$Co(CO)(\eta^2$-dppm$)_2]^+$ and subsequent reaction with [$M(CO)_5]^-$.

8.3 Fluxionality in metal-phosphine-carbonyl complexes

Five types of fluxional processes were observed by ^{31}P, ^1H and ^{13}C NMR in this work. For example, in TBP Co(I) complexes [$Co(CO)(\eta^2$-dppm$)_2]^+$ **8.3** and [$Co(CO)_2(\eta^1$-dppm$)(\eta^2$-dppm$)]^+$ **8.7**, chemical equivalence of equatorial and axial phosphorus donors of the η^2-dppm ligands is observed at room temperature by ^{31}P NMR. The most likely mechanism of fluxionality is a polytopal rearrangement such as Berry psuedo rotation as seen in other TBP structures such as [$Fe(CO)_5$]^6. The fluxionality of **8.7** was frozen out at -65°C while **8.3** remains fluxional down to -90°C.

8.3.1 Fluxionality in complexes [$CoM(CO)_n(\mu$-dppm$)_2$]
(M=Co,n=4; M=Rh,n=3; M=Mn or Re,n=5)

Four types of fluxionality were observed in [$CoM(CO)_n(\mu$-dppm$)_2$] complexes which can be thought of as phosphine substituted derivatives of the binary carbonyls [$Co_2(CO)_8$], [$CoRh(CO)_7$] and [$CoM(CO)_9$] (M=Mn or Re).

a. Delocalized exchange : In both [$Co_2(CO)_4(\mu$-dppm$)_2$] **8.1** (equation 3.3) and [$CoMn(CO)_5(\mu$-dppm$)_2$] (equation 5.2) chemical equivalence of all carbonyls is observed in their respective room temperature ^{13}C spectra, consistent with a merry go round exchange of carbonyl ligands. The limiting structures of 8.1; $[Co_2(CO)_4(\mu\text{-dppm})_2]$ and $[Co_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})_2]$, are observed at -70°C while the related system $[Co_2(CO)_8]$ remains fluxional down to -150°C.

b. Wagging of $M(CO)_n$ unit : In $[CoRh(CO)_3(\mu\text{-dppm})_2]$ 8.2 the weakly semibridging and terminal carbonyls on the cobalt atom are found to be equivalent at room temperature consistent with the wagging of the $Co(CO)_2$ unit (equation 4.3) as also seen in the complex $[Mn_2(CO)_5(\mu\text{-dppm})_2]^7$ which contains a $(\eta^2\text{-}\mu\text{-}CO)$ bridge. The process in 8.2 is frozen out at -45°C and three chemically distinct carbonyls are observed.

c. Pairwise exchange : In addition to the merry go round mechanism of fluxionality observed for $[CoMn(CO)_5(\mu\text{-dppm})_2]$, a second type of fluxionality was observed (equation 5.3). At -62.5 °C three ^{13}C resonances are observed in the carbonyl region consistent with pairwise exchange of two sets of carbonyls on cobalt and manganese giving rise to two resonances respectively and a frozen carbonyl providing the third resonance. In the unbridged isomer of 8.1, $[Co_2(CO)_4(\mu\text{-dppm})_2]$, the persistence of chemical equivalence of all carbonyls and dppm methylene protons down to -90°C is contrary to the solid state structure of $[Co_2(CO)_4(\mu\text{-dppm})_2]$. Thus another form of fluxionality was proposed involving rotation about the Co-Co axis (equation 3.3). With $[CoRe(CO)_5(\mu\text{-dppm})_2]$ a fluxional process, which results in the exchange of the axial and equatorial carbonyls on the cobalt atom (equation 5.4), has been proposed.

d. Inversion of hydride bridge : In complexes [$Co_2(\mu$-H)$(CO)_4(\mu$-dppm$)_2]^+$ chemical equivalence of all carbonyls, consistent with inversion of the hydride bridge through the metal-metal bond is observed down to -90°C (equation 3.5). Similarly in the ^{13}C NMR spectrum of [CoRh(μ-H)$(CO)_3(\mu$-dppm$)_2]^+$ the carbonyls on cobalt exhibit a single resonance down to -90°C consistent with a rapid hydride inversion through the metal-metal axis (equation 4.4).

8.4 Reactivity of complexes [CoM$(CO)_n(\mu$-dppm$)_2$] (M=Co,n=4; M=Rh,n=3; M=Mn,n=5)

All of the complexes noted above exhibit reactivity towards inorganic oxidizing agents such as I_2, S_8 and mineral acids. It was initially hoped that the complexes [CoM$(CO)_n(\mu$-dppm$)_2$] (M=Co,n=4; M=Rh,n=3) would be good candidates for homogeneous catalysis. For example, the related carbonyl [$Co_2(CO)_8$] is catalytically active in the hydrogenation or hydroformylation of alkenes and [CoRh$(CO)_7$] is suspected as the active catalyst in mixtures of [$Rh_4(CO)_{12}$] and [$Co_2(CO)_8$] (section 4.1). However, **8.1** and **8.2** display limited reactivity towards organic substrates. For example, only **8.1** reacts with acetylene under ambient conditions and neither **8.1** or **8.2** reacts with ethylene under ambient conditions. The complexes fail to react with H_2 under ambient conditions while in refluxing toluene, **8.1** reacts with H_2 to give [$Co_2(\mu$-H)$(\mu$-$PPh_2)(\mu$-dppm$)_2(CO)_2$]. Thus the complexes [CoM$(CO)_n(\mu$-dppm$)_2$] are probably not good candidates for homogeneous catalysis at least under ambient conditions.

The greater reactivity of $[Co_2(CO)_4(\mu\text{-dppm})_2]$ towards unsaturated molecules is carried over into the protonated derivatives $[CoM(\mu\text{-H})(CO)_n(\mu\text{-dppm})_2]^+$ (M=Co,n=4; M=Rh,n=3). The rhodium derivative is unreactive towards acetylene while the cobalt complex reacts quickly with acetylene. These observations are suprising because of the electronic unsaturation associated with the 16 electron rhodium atom in $[CoRh(CO)_3(\mu\text{-dppm})_2]$ which should make complexation with unsaturated organics more favourable than with the saturated cobalt complexes.

8.5 Comparison of chemistry of complexes $[MM^1(CO)_n(\mu\text{-dppm})_2]$ ($M=M^1=Co$, n=4 <u>8.1</u>; $M=M^1=Rh$, n=2 or 3[2]; $M=M^1=Ir$, n=3 or 4[1]; $M=Co, M^1=Rh$ <u>8.2</u>, n=3; $M=Rh$, $M^1=Ir$, n=3[3])

The characterization of this series of complexes containing paired combinations of elements of the cobalt triad, extended by the synthesis of **8.1** and **8.2** in this work, allows for some comparisons to be made about the respective elements in similar chemical environments. It is apparent from the formulations and the structures of the parent materials that cobalt attains a 18 electron count while rhodium attains a 16 electron count in heterodinuclear complexes and in the unstable $[Rh_2(CO)_2(\mu\text{-dppm})_2]$. Iridium is intermediate between these two and has an 18 electron count in $[Ir_2(CO)_4(\mu\text{-dppm})_2]$ and $[RhIr(CO)_3(\mu\text{-dppm})_2]$ and does not form $[Ir_2(CO)_2(\mu\text{-dppm})_2]$. $[Ir_2(CO)_3(\mu\text{-dppm})_2]$, however, contains a 16 electron iridium atom. These trends are also evident in species derived from complexes $[MM^1(CO)_n(\mu\text{-dppm})_2]$. For example, the halide derivatives $[M_2(\mu\text{-X})(\mu\text{-CO})(\mu\text{-dppm})_2(CO)_2]^+$ are known for M=Co (section 3.3.1), Rh or Ir but in the case of rhodium and iridium[8], loss of CO can occur to give complexes with 16 electron metal centres. Similar chemistry is observed for singly protonated derivatives. For example, complexes $[M_2(\mu\text{-H})(CO)_4(\mu\text{-dppm})_2]^+$ are known for cobalt (section 3.3.2) and iridium[1], $[M_2(\mu\text{-H})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]^+$ (M=Rh[9] or Ir[1]) reversibly lose the μ-CO group, and $[RhM(\mu\text{-H})(CO)_3(\mu\text{-dppm})_2]^+$ {M=Co(section 4.4.1.3) or Ir[3]} have both 16 electron (Rh) and 18 electron (M) metals.

8.6 Suggestions for future work

8.6.1 Synthesis of heterobimetallics complexes containing the CoM(μ-dppm) group

Success in synthesizing dppm bridged heterobimetallics has been achieved by reacting the $[Co(CO)(\eta^2\text{-dppm})_2]^+$ cation with anionic carbonyl complexes $[M(CO)_5]^-$, and the complexes $[Co(CO)(dppm)_2][Co(CO)_4]$ and $[Rh(CO)(dppm)_2][Co(CO)_4]$ have been shown to lose CO to form complexes $[CoM(CO)_n(\mu\text{-dppm})_2]$ (M=Co, n=4; M=Rh, n=3) respectively. Coincidentally M.Cowie[5] recognized that the ring strain associated with η^2-dppm ligands could be used in the reaction of $[RhCl(\eta^2\text{-dppm})_2]$ with $[Co(CO)_4]^-$, $[M(CO)_5]^-$ (M=Mn or Re), $[HM(CO)_4]^-$ (M=Fe, Ru or Os) and $[HM(CO)_5]^-$ (M= Cr, W) to prepare heterobimetallics $[CoRh(CO)_3(\mu\text{-dppm})_2]$, $[RhM(CO)_4(\mu\text{-dppm})_2]$, $[RhMH(CO)_3(\mu\text{-dppm})_2]$

(M=Fe,Ru or Os) and $[RhM(CO)_4(\mu\text{-dppm})_2]$ (M=Cr or W) respectively. Thus the $[Co(CO)(dppm)_2]^+$ cation could be reacted with other anionic metal carbonylates as mentioned above with related rhodium systems to prepare cobalt heterobimetallics with a more diverse range of metals. Another possibility not reported by Cowie is the reaction of the $[M(CO)(\eta^2\text{-dppm})_2]^+$ cations with $[V(CO)_6]^-$ which could provide interesting complexes $[CoV(CO)_6(\mu\text{-dppm})_2]$ or $[RhV(CO)_5(\mu\text{-dppm})_2]$.

8.6.2 Further studies on the chemistry of complexes $[CoM(CO)_n(\mu\text{-dppm})_2]$

The preliminary study of $[CoMn(CO)_5(\mu\text{-dppm})_2]$ **8.5** indicates that it is a good substrate for oxidative addition. Complexes resulting from the reaction of **8.5** with S_8, HBF_4, $CHCl_3$ and I_2 still have to be characterized completely. Presumably the rhenium analogue will present similar chemistry.

8.6.3 P-C bond cleavage in dppm

One of the surprises in the $Co(II)/dppm/CO/NaBH_4$ reaction systems was the isolation of complexes $[Co_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})_n(CO)_{6-2n}]$. Not much work has been done to elucidate the mechanism of the P-C bond cleavage resulting in the above complexes and there is a possibility that a rare double P-C bond cleavage[10,11] to provide two PPh_2 units is operating. The best approach to this problem is probably one of elimination by an intensive ^{31}P NMR investigation of the reaction mixtures leading to the μ-PPh$_2$ complexes above in search of -CH$_2$PPh$_2$ or MePh$_2$P units resulting from single P-C bond cleavage.

8.6.4 Synthesis of [(CO)$_2$(η^1-dppm)Co(μ-dppm)BH$_2$]

The second surprise in the Co(II)/dppm/CO/NaBH$_4$ reaction system was the isolation of a novel complex [(CO)$_2$(η^1-dppm)Co(μ-dppm)BH$_2$] 8.8. The complex was only isolated in small yields in a mixture of compounds, however, and it would be desirable to obtain sufficient quantities of the material to investigate the potential reactivity of the molecule. Fehlner's[12] related complex [Co(CO)$_4$BH$_2$·THF], for example, undergoes an interesting series of transformations on its way to forming complexes [(CO)$_9$Co$_3$C(CH$_2$)$_n$OH] (n=4 or 5). To this end, several approaches have been used without any success (section 7.2.1). Another approach to the synthesis of 8.8 could involve the reaction of [η^2-dppm·BH$_2$]$^+$, prepared from dppm added to (CH$_3$)$_2$S·BH$_3$ and I$_2$[13], with [Co(CO)$_4$]$^-$ and an equivalent of dppm. This approach probably has a good chance at success because the BH$_2^+$ and Co$^-$ fragments are already present and no redox chemistry has to take place. The formation of 8.8 is only observed under conditions used to produce [Co(CO)(dppm)$_2$][Co(CO)$_4$] (ie. slow addition of NaBH$_4$) and it is possible 8.8 does form through the reaction of [Co(CO)$_4$]$^-$ with a species such as [η^2-dppm·BH$_2$]$^+$. This method of synthesis could also be applied to other metal carbonylates such as [M(CO)$_5$]$^-$ (M= Mn or Re) to provide dppm derivatives of the postulated complexes $[M(CO)_5BH_3]^-$ [14]. With a dianionic carbonylate such $[Fe(CO)_4]^{2-}$ two equivalents of $[\eta^2\text{-dppm}\cdot BH_2]^+$ could provide a neutral derivative containing two $(\eta^2\text{-dppm}\cdot BH_2)$ ligands.

8.8 also offers a possible modification of the reactivity of the borane fragment by incorporation of another metal into the cluster via the η^1-dppm function.

8.7 References

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APPENDIX 1

DETAILS OF INSTRUMENTS AND CHEMICALS USED IN EXPERIMENTS

Nuclear Magnetic Spectroscopy

^1H NMR spectra were recorded on a Varian XL-200 spectrometer. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded on a Varian XL-300 spectrometer. ^1H and $^{13}C\{^1H\}$ chemical shifts were measured relative to Me_4Si. $^{31}P\{^1H\}$ chemical shifts were measured relative to 85% H_3PO_4.

IR Spectroscopy

All IR spectra were run as nujol mulls between NaCl plates on a Bruker IR/32 FT-IR spectrophotometer equipped with an IBM 9000 computer.

Mass Spectrometry

Mass spectra were obtained from a Finnigan MAT 8230 mass spectrometer.

Elemental Analysis

Elemental analyses were carried out at Lakehead University.

Source of Chemicals

All metal salts, metal carbonyls, phosphines, solvents, deuterated solvents, ^{13}CO and miscellaneous chemicals were purchased from Aldrich, Strem, Fischer or BDH and used without further purification with the exception of the THF used in the Na/Hg production of $[M(CO)_5]^-$ from $[M_2(CO)_{10}]$ (M = Mn or Re). In this case the solvent was distilled over Na/benzophenone under a N_2 atmosphere prior to use.