THE CHEMISTRY OF COBALT AND NICKEL COMPLEXES WITH BIS(DIPHENYLPHOSPHINO)METHANE AND CO LIGANDS

BY

WEI XU ©

SUBMITTED TO

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Author's Statement

Although the chemistry recorded in this thesis is my research work completed under the guidance of my two supervisors, Dr. A. N. Hughes and Dr. D. G. Holah, it is necessary to note that the language and grammar of the thesis have been extensively modified by my two supervisors.

ABSTRACT

Reactions of $CoX(\eta^1\text{-dppm})_3$ (X = Cl, Br) with CO lead in sequence to $CoX(CO)_2(\eta^1\text{-dppm})_2$, $[Co(CO)_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})]X$ and $[Co(CO)(\eta^2\text{-dppm})_2]X$, all of which have been isolated and fully characterized. The series of reactions can be reversed under CO at elevated temperatures. The related complex $[Co(CO)_4(\eta^1\text{-dppm})]X$ is formed by a modification of the procedure.

The mechanism of the reduction of Co^{II} by $NaBH_4$ in the presence of CO and dppm which can give any one or more of several Co^I, Co^0 or Co^{-I} complexes depending upon experimental conditions, has been elucidated by a detailed study of the possible individual steps of the reaction.

The heterobinuclear complexes $[NiCu(CO)_2(MeCN)_2(\mu\text{-dppm})_2]ClO_4.0.4CH_2Cl_2$ and $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$ have been synthesized by reactions of $Ni(CO)_2(\eta^1\text{-dppm})_2$ with $Cu(MeCN)_4ClO_4$ and by reactions of the $Ni^{II}/dppm/NaBH_4/CO/CuCl_2$ system respectively. The X-ray crystal structure of $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$ is reported. The crystals of this compound are triclinic with unit cell dimensions of a, 11.411(7) Å; b, 14.937(6) Å; c, 17.045(6) Å; α, 79.66(3)°; β, 76.34(5)°; γ, 71.27(4)° and volume 2656.4(22) $Å^3$. The heterobimetallic complexes $[CoRh(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]X$ (X = Cl, Br and BPh_4) have been prepared from the reactions of $CoX(\eta^1\text{-dppm})_3$ (X = Cl, Br) or $CoX(CO)_2(\eta^1\text{-dppm})_2$ (X = Cl, Br), $[Co(CO)(\eta^2\text{-dppm})_2]X$ (X = Br, BPh_4) with $Rh_2(CO)_4Cl_2$.

Several possible synthetic routes to the interesting complex $[Co(CO)(\eta^1\text{-dppm})(\mu\text{-dppm-}BH_2)]$, previously isolated in very low yield, have been studied with a view to (1) increasing the yields and (2) establishing the mechanism of formation. However, no new route to the formation of this complex was discovered.

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ABBREVIATIONS

Me	Methyl
Et	Ethyl
Ph	Phenyl
Pr^i	Isopropyl
Cy	Cyclohexyl
Bu^t	t-butyl
Bu^n	n-Butyl
MeOH	Methanol
EtOH	Ethanol
PPh_3	Triphenylphosphine
dppm	Bis(diphenylphosphino)methane
dppe	1, 2-Bis(diphenylphosphino)ethane
dppp	1, 3-Bis(diphenylphosphino)propane
dppb	1, 4-Bis(diphenylphosphino)butane
COD	1, 5-cyclooctadiene
Py	Pyridine
THF	Tetrahydrofuran
dmpm	Bis(dimethylphosphino)methane
Cp	η^5-Cyclopentadienyl
mes	Mesityl, 2,4,6-$Me_3C_6H_2$

Phen	1,10-Phenanthroline
en	Ethylenediamine
dien	Diethylenetriamine
Pz	Pyrazolyl
tripod	Tris(diphenylphosphino)methane
BEN	$PhCH=NCH_2CH_2N=CHPh$
bipy	Bipyridyl
2MeQuin	2-Methylquinolin-8-ol
tmed	N,N,N',N' - tetramethylethlenediamine
Diphos (=dppe)	1,2 - Bis(diphenylphosphino)ethane
DMF	N,N' - dimethylformamide
DMSO	Dimethyl Sulfoxide
dpdm	(Dimethylphosphino)- (diphenylphosphino)methane
vpp	1,2 - Bis(diphenylphosphino)ethylene

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INTRODUCTION

Monodentate phosphine ligands can form a large variety of complexes with transition metal ions. These ligands can bind strongly to many transition metals in various oxidation states and are commonly used to stabilize organometallic complexes, especially those in which the metal is in a low oxidation state.[1,2]

Phosphines of the type $R_2P(CH_2)_nPR_2$ can act either as dicoordinating ligands in chelate or binuclear complexes or as monocoordinating ligands leaving one end free. Since metal-phosphorus bonds are often very strong, bridging diphosphine ligands can lock two metal atoms together. Such interactions are often involved in both heterogeneous and homogeneous catalysis using binuclear or cluster complexes as catalysts. The role of the phosphine is then to prevent dimer dissociation to monomer or to promote binuclear reactions.[1] These particular properties lead to special interest for us to isolate and characterize such complexes and to study their catalytic properties.

As mentioned above, these bidentate phosphine ligands can also coordinate through only one of the phosphorus atoms leaving the other phosphorus atom dangling which provides a free and active centre for further reactions. The potential of such complexes in the formation of homo- and hetero-nuclear bimetallic complexes has been recognized.[3,4,5] Dppm, synthesized first by Issleib and Mueller in 1959,[6] is presently playing a key role as a small bite bidentate ligand in di- and polynuclear chemistry. This ligand is remarkably versatile in its behaviour, one of the more important aspects of which is allowing the stabilization of binuclear metal-metal bonded complexes.[1,2]

This versatility makes dppm a very useful ligand in metal complex chemistry.

Brief reference has already been made to the general range of the bidentate phosphines $Ph_2P(CH_2)_nPPh_2$, but there is a fundamental difference between the type of product formed when n = 2 - 6 than when n = 1 (dppm). Chelate complex formation is not favoured when n = 1. Bao and his colleagues[7] confirmed that the stability and reactivity of these chelate compounds depend upon their chelating ring strain. Thus, the relative stabilities of $[CpCo(\eta^2\text{-}L)I]I$ ($L = Ph_2P(CH_2)_nPPh_2$, n = 1 - 4) is $n = 2 > n = 3 > n = 1 >> n = 4$.[7] Since the optimum ring size for a metal having a bond angle of 90° is five, dppe is an excellent chelating ligand while dppm can only chelate to a metal to form a four-membered ring with some ring strain. Therefore, dppm has a greater tendency to act either as a monodentate ligand or as a bridging bidentate ligand.[2]

This thesis is concerned with the properties of cobalt or nickel complexes with dppm and CO ligands and the following discussion outlines the background chemistry against which the research described in the Results and Discussions section was carried out.

I. COBALT AND NICKEL COMPLEXES WITH dppm AND CO

A large number of phosphine-substituted carbonyl cobalt complexes have been prepared.[8,9,10] Some well documented coordination geometries of these complexes are listed in ref. 10. Phosphine ligands in complexes can stabilize both lower oxidation such as Co^I and higher oxidation states such as Co^{III}. The special bridging properties of dppm also made the synthesis of many heterobimetallic complexes possible. In the following section, we will discuss synthetic methods and the properties of the cobalt and nickel complexes with dppm or dppm/CO ligands. The various applications of these complexes also will be briefly discussed.

1. Co-dppm Complexes

It has been accepted for a long time that metal chelates of dppm would be unstable because of the strained four-membered ring. However some work has shown that dppm is quite versatile and can apparently form quite stable chelate complexes.[11] For example, there is some evidence from solution electronic spectra and conductivities for the existence of monomeric pseudotetrahedral $[CoX_2(dppm)]$,[11] five-coordinate $[CoX(dppm)_2]X$ (X = Cl, Br, I, NCS, ClO_4, $SnCl_3$)[12] and a trigonal bipyramidal low-spin species, $CoCl_2L_2$ (L = dppe, dppm)[13] in solution. These complexes were isolated and characterized in the solid state by microanalysis and magnetic properties.[14] Many other Co^{II}-dppm complexes[15,16] were synthesized. Because of the paramagnetic properties of Co^{II}, the structures of these Co^{II} complexes were seldom fully characterized and structural evidence comes mainly from solution spectra such as EPR, IR, single crystal EPR[14] and electronic spectra.[11,13] X-ray data are generally absent in this area.

Substitution of the triphenylphosphine ligands on $CoX_2(PPh_3)_2$ by the tertiary diphosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 1 - 3) in benzene has been reported.[11] As expected the chelating effect of the three diphosphines is different. Thus, for dppe and dppp the simple replacement reaction occurs as equation **[1]** shows.[11]

$$\mathbf{CoBr_2(PPh_3)_2 + 2L \rightleftharpoons [CoBr(\eta^2\text{-}L)_2]Br + 2PPh_3} \qquad [1]$$

$$\mathbf{L = dppe,\ dppp}$$

The overall constant for the equilibrium is 1.06×10^5 for dppe and 1.2×10^3 for dppp reflecting the difference in sizes of the chelating rings.[11] On the other hand for dppm, a more complicated reaction occurs. Initially, a bridging mode of coordination on two metal atoms forms and this is followed by the formation of a chelating dppm ring without disruption of the bridged system as shown in **scheme 1**.

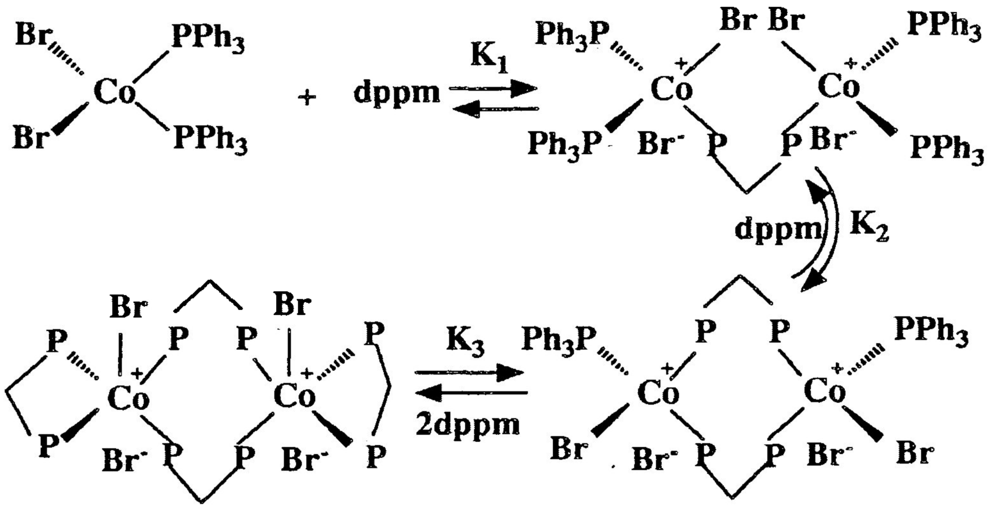
In the meanwhile, the Holah and Hughes group has been interested for some time in reactions between Co^{II} and Ni^{II} ions and $NaBH_4$ or $NaBH_3CN$ in the presence of a variety of bidentate phosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 1 - 6).[17,18,19] Reactions of Co^{II} with $NaBH_4$ in the presence of dppm are very sensitive to reaction conditions and are difficult to control. Depending upon the rate of addition of $NaBH_4$, the reaction of CoX_2 (X = Br, Cl) with $NaBH_4$ or $NaBH_3CN$ in the presence of dppm can give a variety of products as equation [2] shows.[18]

$$\mathbf{CoX_2.6H_2O + dppm + NaBH_4 \longrightarrow Co_2X_3(dppm)_2,\ 1,}\ \text{and/or}$$

$$\mathbf{CoX(\eta^1\text{-}dppm)_3,\ 2,}\ \text{and/or}\ \mathbf{[CoH(\eta^2\text{-}dppm)_2X]Y,\ 3,} \qquad [2]$$

(For 1 and 2, X = Cl, Br; for 3, X = Cl, Br, ClO_4; Y = ClO_4, BH_3CN, BPh_4)

Scheme 1. Reactions of $Co(PPh_3)_2Br_2$ with dppm



Product **1** is a dark green paramagnetic compound and so far no crystals suitable for X-ray analysis have been obtained. Its exact structure is therefore uncertain but the empirical formula and the bridging tendency of dppm are consistent with **1** being an A-frame type binuclear complex with mixed Co^{I}-Co^{II} oxidation states. However, the high-spin arrangement of both cobalt atoms (μ = 6.1BM) casts some doubt on this suggestion.

Complex **2** can be obtained directly from the $Co^{II}/NaBH_4$/dppm reaction or from recrystallization of **1** from ethanol and the structure of this complex was established by X-ray crystallography. This complex is the first published example of a complex containing three monodentate dppm ligands on one metal ion.[18]

In addition to the complexes **1** and **2**, an unexpected complex **3**, which has a single peak close to $\delta = 0$ in its ^{31}P NMR spectrum and which shows similar electronic spectra to related Co^{III} species, can be isolated under certain conditions.[18] The complex, $[CoH(\eta^2\text{-dppm})_2Cl]Cl$, is an ionic six-coordinated species, and it can react smoothly with $NaBPh_4$ to produce $[CoH(\eta^2\text{-dppm})_2Cl]BPh_4$. In a related study, it has been shown that the reaction between Co^{II} perchlorate and $NaBH_3CN$ in the presence of bidentate phosphines L, $L = Ph_2P(CH_2)_nPPh_2$ ($n = 1 - 4$), only gives the Co^{III} species, $[CoH(\eta^2\text{-}L)_2(BH_3CN)]ClO_4$, when $n = 1$.[19] Furthermore, reactions involving $NaBH_3CN$ are slower than those in which $NaBH_4$ is used and therefore easier to handle.[20]

2. Co-dppm-CO Complexes

Substitution of carbon monoxide in cobalt carbonyl complexes by phosphine ligands (e.g. equation [3][21]) has been studied[22,23] extensively and much of the interest in the substitution reactions of cobalt carbonyls stems from modification of the hydroformylation catalyst $HCo(CO)_4$ with phosphine ligands.[9,24]

$$Co_4(CO)_{12} + PPh_3 \xrightarrow[\text{or } ClCH_2CH_2Cl]{\text{In Heptane}} Co_4(CO)_8(PPh_3)_4 \qquad [3]$$

As discussed below, most cobalt complexes containing both carbonyl and dppm have been prepared from related reactions.[22,25,26]

It is well known that the reaction of certain phosphine and phosphite ligands L with dicobalt octacarbonyl leads to rapid disproportionation at room temperature yielding $[Co(CO)_3L_2][Co(CO)_4]$ which can be transformed into $[Co_2(CO)_6L_2]$ (L = PPh_3, PBu_3, and other phosphines).[9,23] Similarly, bidentate phosphines, L (L = dppm, dmpm, dppe), react with $Co_2(CO)_8$ rapidly to give the salt $[Co(CO)_3(\eta^1\text{-}L)]^+[Co(CO)_4^-]$ as indicated by IR spectroscopy. The species is not stable and the salt slowly loses CO to give the corresponding neutral dimer $Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-}L)$ even in the solid state.[25,26]

King and his colleagues[27] have prepared some novel metal-CO-phosphine complexes using $MeN(PF_2)_2$, which is clearly related structurally to dppm. For example, the reaction between $Co_2(CO)_8$ and $MeN(PF_2)_2$ proceeds rapidly at or below room temperature in the absence of ultraviolet irradiation to give a dark purple complex $Co_2(CO)_2[MeN(PF_2)_2]_3$, **4**, with an A-frame structure.[27]

When complex **4** is exposured to UV irradiation in the presence of dppe, one CO ligand is replaced by a dppe as shown in equation **[4]**.[27]

$$\mathbf{Co_2(CO)_2[MeN(F_2P)_2]_3 + dppe \xrightarrow{UV} Co_2(CO)(\eta^1\text{-}dppe)[MeN(F_2P)_2]_3} \qquad [4]$$

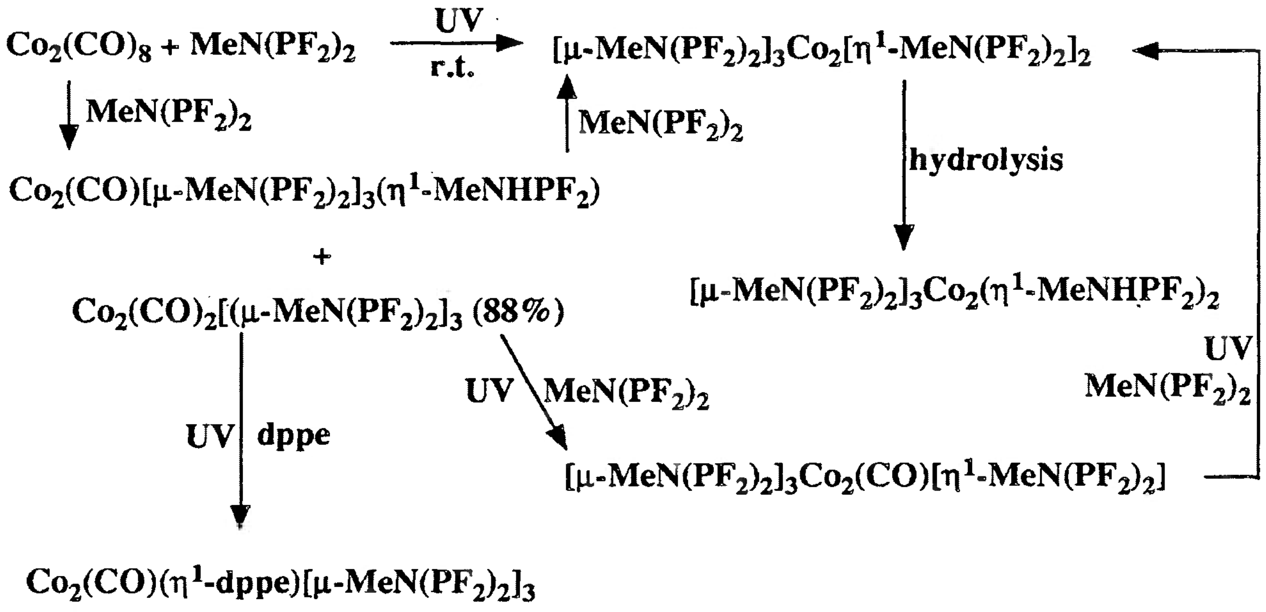
Direct UV irradiation of $Co_2(CO)_8$ in the presence of excess $MeN(PF_2)_2$ at room temperature in diethyl ether, however, results in the complete displacement of all carbonyl groups to give a black complex, $[MeN(PF_2)_2]_5Co_2$ (see **scheme 2**). The structure was revealed by X-ray diffraction to contain three bridging $MeN(PF_2)_2$ and two monodentate $MeN(PF_2)_2$ ligands.[27] This compound undergoes hydrolysis and loses $-PF_2$ groups to give the purple dimer $[MeN(PF_2)_2]_3Co_2(MeNHPF_2)_2$. The reaction is a clear demonstration of the hydrolytic stability of bidentate $MeN(PF_2)_2$ ligands in contrast to that of the monodentate $MeN(PF_2)_2$ ligands that contain an uncoordinated PF_2 group. Reaction of $Co_4(CO)_{12}$ with $MeN(PF_2)_2$ results in the replacement of CO groups by the phosphine to give products of the type $Co_4(CO)_{12-2n}[MeN(PF_2)_2]_n$, where n can be 2, 3, 4, 5, by appropriate selection of the reaction conditions.[27] In these reactions, substitution of CO groups appears to be relatively easy until $Co_4(CO)_4[MeN(PF_2)_2]_4$ is reached and further substitution then requires ultraviolet irradiation as shown in **Scheme 2**.[27]

Similar reactions were observed in tetracobalt carbonyl clusters as indicated in equation **[5]**.[28]

$$\begin{aligned}&\mathbf{[Co_4(CO)_{10}(\mu_4\text{-}PPh)_2] + L \longrightarrow [Co_4(CO)(\mu\text{-}CO)(\mu_4\text{-}PPh)_2\{\mu\text{-}MeN(PF_2)_2\}_4]}\\&\qquad\mathbf{+\ [Co_4(CO)_6(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2(\mu\text{-}dppm)]} \qquad \mathbf{[5]}\\&\qquad\qquad\mathbf{L = MeN(PF_2)_2 \text{ or } dppm}\end{aligned}$$

The cobalt carbonyl complexes used can also be polynuclear. Thus, Darensbourg and his colleagues[29] found that dppm can stereoselectively replace apical CO ligands in $Co_4(CO)_9$(tripod) to give $Co_4(CO)_7$(μ-dppm)(tripod), in which one triangular Co_3 face is rigidly held by the capping tridentate phosphine ligand and metal-metal bond fission

Scheme 2. Reactions of $Co_2(CO)_8$ with $MeN(PF_2)_2$



$$Co_4(CO)_{12} + MeN(PF_2)_2 \longrightarrow Co_4(CO)_{12\text{-}2n}[\mu\text{-}MeN(PF_2)_2]_n \ (n = 2, 3, 4, 5)$$

is therefore greatly retarded.[29] Trinuclear carbonyl cobalt clusters can also be used to synthesize Co-CO-dppm clusters as shown in equation [6].[30,31,32]

$$[(\mu_3\text{-}CMe)Co_3(CO)_9] \xrightarrow{\text{dppm}} [(\mu_3\text{-}CMe)Co_3(CO)_7(\mu\text{-dppm})],\ 5,\ + \\ [(\mu_3\text{-}CMe)Co_3(CO)_8(Ph_2PCH_2POPh_2)],\ 6, \qquad [6]$$

The crystal structure of **5** shows that two Co-Co edges are bridged by dppm to form a five-membered ring in an envelope conformation.[30] Related trinuclear clusters, $[(\mu_3\text{-CR})Co_3(CO)_8(\mu\text{-dppm})]$, $[(\mu_3\text{-CR})Co_3(CO)_5(\mu\text{-dppm})_2]$ and $[(\mu_3\text{-CR})Co_3(CO)_x(\mu\text{-dppm})]$ ($x = 5 - 6$) have also been prepared and characterized.[31] It should be mentioned that complex **5** shows catalytic activity for hydroformylation of 1-pentene at 80 bar and 110°C with a H_2-Co radio of 1 : 1.[30]

Some cobalt carbonyl complexes containing rigid ligands such as $CF_3C{\equiv}CCF_3$ or $R'C{\equiv}CR$ (R, R' = H, Ph) can also react with dppm to produce Co-dppm-CO complexes as equations **[7]** and **[8]** show, in which the fluxional process is stopped at room temperature (see section 3.c).[33,34,35]

$$\begin{aligned}&[Co_2(\mu\text{-}CF_3C{\equiv}CCF_3)(CO)_6] + L \longrightarrow [Co_2(\mu\text{-}CF_3C{\equiv}CCF_3)(CO)_5(\eta^1\text{-}L)] +\\ &\qquad [Co_2(\mu\text{-}CF_3C{\equiv}CCF_3)(CO)_4(\mu\text{-}L)] \qquad [7]\\ &\qquad (L = \text{dppm, dppe})\end{aligned}$$

$$Co_2(\mu\text{-}RC{\equiv}CR)(CO)_6] + \text{dppm} \xrightarrow{\text{toluene}} [Co_2(\mu\text{-}RC{\equiv}CR)(CO)_2(\mu\text{-dppm})_2] \qquad [8]$$

Phosphine displacement is another common route to prepare Co-dppm-CO complexes.[36] Some typical reactions are shown in equations **[9]** and **[10]**.

$$\mathrm{Co(CO)_2Cl(PPh_3)_2} + \mathrm{L} \xrightarrow{\mathrm{TiClO_4}} \mathrm{[Co(CO)(\eta^2\text{-}L)_2]ClO_4} \qquad [9]$$

(L = dppm, dppe)

$$\mathrm{CpCo(CO)_2} \text{ or } \mathrm{CpCo(PMe_3)_2} \xrightarrow{\mathrm{dppm}} \mathrm{CpCo(CO)(\eta^1\text{-}dppm)} + \mathrm{CpCo(\eta^2\text{-}dppm)} \qquad [10]$$

From the foregoing discussion, it is clear that the most widely used routes to metal-CO-phosphine complexes are from reactions between cobalt carbonyls, or their derivatives, and phosphines. Since many metal carbonyls are air sensitive, volatile, extremely toxic and in some cases not readily available, it is not always convenient to use them directly. Over the past several years, the Holah-Hughes research group has aimed at developing a new method for the synthesis of a variety of metal-CO-phosphine complexes using $NaBH_4$ or $NaBH_3CN$ as reducing agents in the presence of a phosphine and CO. For example, by suitably adjusting experimental conditions, at least six products have been obtained from the reaction of Co^{II} with $NaBH_4$ in the presence of dppm in a CO atmosphere. Three of them now have been fully characterized as the ion pair $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$,[37] **7**, $[Co_2(\mu\text{-dppm})_2(CO)_4]$,[38] **8**, and $[Co_2(CO)_2(\mu\text{-CO})_2(\mu\text{-dppm})_2]$,[38] **9**. Complexes **8** and **9** are in equilibrium in solution although pure **8** can be obtained by crystallization from CH_2Cl_2 while pure **9** is obtained from **8** by stirring with EtOH. At room temperature, the equilibrium (equation [11]) lies to the left.[39] At lower temperatures, the equilibrium shifts in favour of the carbonyl bridged isomer.[39]

$$Co_2(CO)_4(\mu\text{-dppm})_2 \rightleftharpoons Co_2(CO)_2(\mu\text{-CO})_2(\mu\text{-dppm})_2 \qquad [11]$$

The remaining three characterized products, which include phosphido-bridged and metallaborane complexes, will be discussed in later sections.

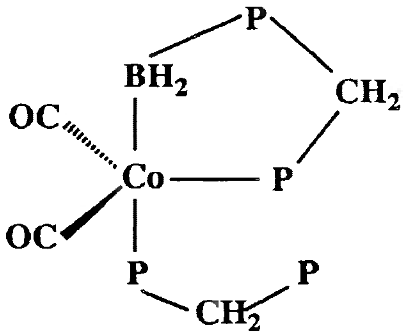
Other groups have also carried out similar direct reductions of CoX_2 (X = Cl, Br) with $NaBH_4$ under CO in the presence of phosphines and PR_4X (R = Ph-, $PhCH_2$-).[40] For example, with PPh_3 the following reaction occurs.

$$CoX_2 + NaBH_4 + PR_4X + CO + PPh_3 \longrightarrow PR_4[CoX_2(CO)_2(PPh_3)] \qquad [12]$$

3. Co-dppm-CO-BH_X Complexes

Transition metal complexes containing $M\text{-}BH_2$ units have proved to be elusive, despite intensive research in transition metal-borane chemistry.[41] The first such complex $[(CO)_4CoBH_2.THF]$ has recently been characterized by Fehlner and co-workers using spectroscopic methods at low temperature.[42] The complex is unstable and decomposes rapidly at room temperature. However, one of the products formed in one step in very low yield in the Co^{II}/dppm/BH_4^-/CO reactions mentioned in the preceding section is $[Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm-}BH_2)]$, **10**.[43] The complex is air stable at room temperature. An X-ray structure of the complex shows a distorted trigonal-bipyramidal (TBP) cobalt centre with the monodentate dppm and the boron atom of BH_2 in the axial positions as shown in **Figure 1.**[43]

Figure 1. Structure of $Co(CO)_2(\eta^1$-dppm)(μ-dppm-BH_2)



(10)

The Co-BH_2 bond is presumably stabilized by bridging dppm. Since M-BH_2 complexes have great potential in a variety of catalytic reactions,[41] high yield synthetic routes to this system should be explored and this will be discussed further in the Results and Discussion section of this thesis.

II. NICKEL COMPLEXES WITH dppm AND CO

1. Ni-dppm Complexes

Ni^{II} halides react under controlled conditions with dppm to give the monomeric, four-coordinated chelate complexes $[NiX_2(\eta^2\text{-dppm})]$.[44] The complex $[NiI_2(\eta^2\text{-dppm})]$ can be converted into a five-coordinated iodo-bridged dimer $Ni_2(\mu\text{-}I)_2I_2(\eta^2\text{-dppm})_2$ in solution.[44] It is interesting that the chelating dppm ligand of $[NiCl_2(\eta^2\text{-dppm})]$ can be converted into a monodentate ligand as illustrated by the equation **[13]**.[44]

$$[NiCl_2(\eta^2\text{-dppm})] + dppm \xrightarrow[\text{or } ClCH_2CH_2Cl]{\text{Heptane}} [NiCl_2(\eta^1\text{-dppm})_2] \quad [13]$$

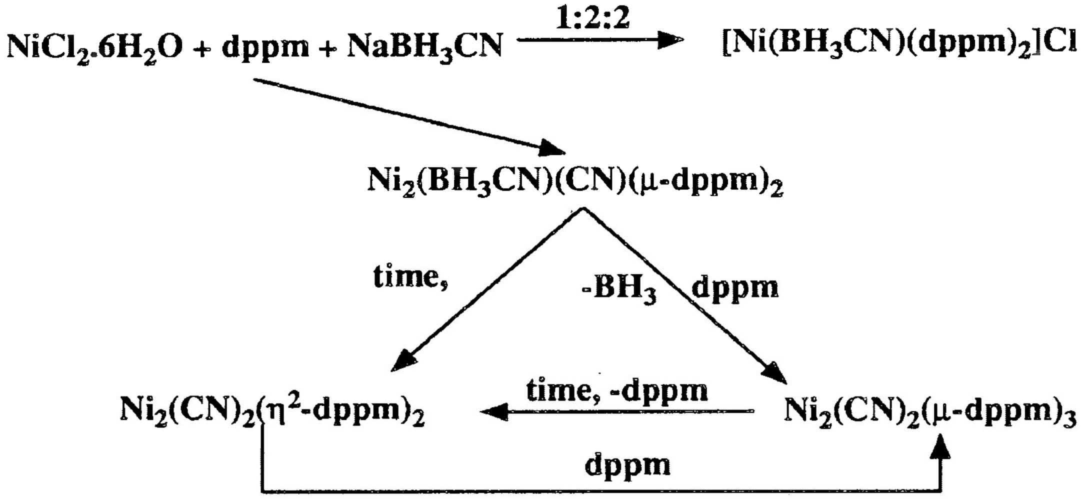
Ni^{II} compounds can be reduced by $NaBH_3CN$ in the presence of dppm to give Ni^{I}-dppm complexes. The most important aspect of this work is that the reduction is accompanied by cleavage of B-C bonds to produce Ni-CN-dppm complexes as shown in **Scheme 3**.[45]

It is worth mentioning here that other reducing reagents also have been explored. For example, the reaction of $[Ni_2(\mu\text{-CNMe})_3(\mu\text{-dppm})_2][(PF_6)_2]$ with sodium amalgam leads to the formation of the complex $[Ni_2(\mu\text{-CNMe})(CNMe)_2(\mu\text{-dppm})_2]$.[46,47,48] The structures of these compounds have been determined by X-ray crystallography and the M_2L_3 core has a cradle structure.[47,48]

This cradle type of complex, $[Ni_2(CNMe)_4(\mu\text{-dppm})_2][(PF_6)_2]$, has been shown to activate CO_2 to give two Ni containing complexes as outlined in **Scheme 4**.[49]

In other developments, a novel trinickel complex $[Ni_3(\mu_3\text{-CNMe})(\mu_3\text{-I})(CNMe)_2(\mu\text{-dppm})_2][I]$, has been synthesized recently as shown in equation **[14]**.[50]

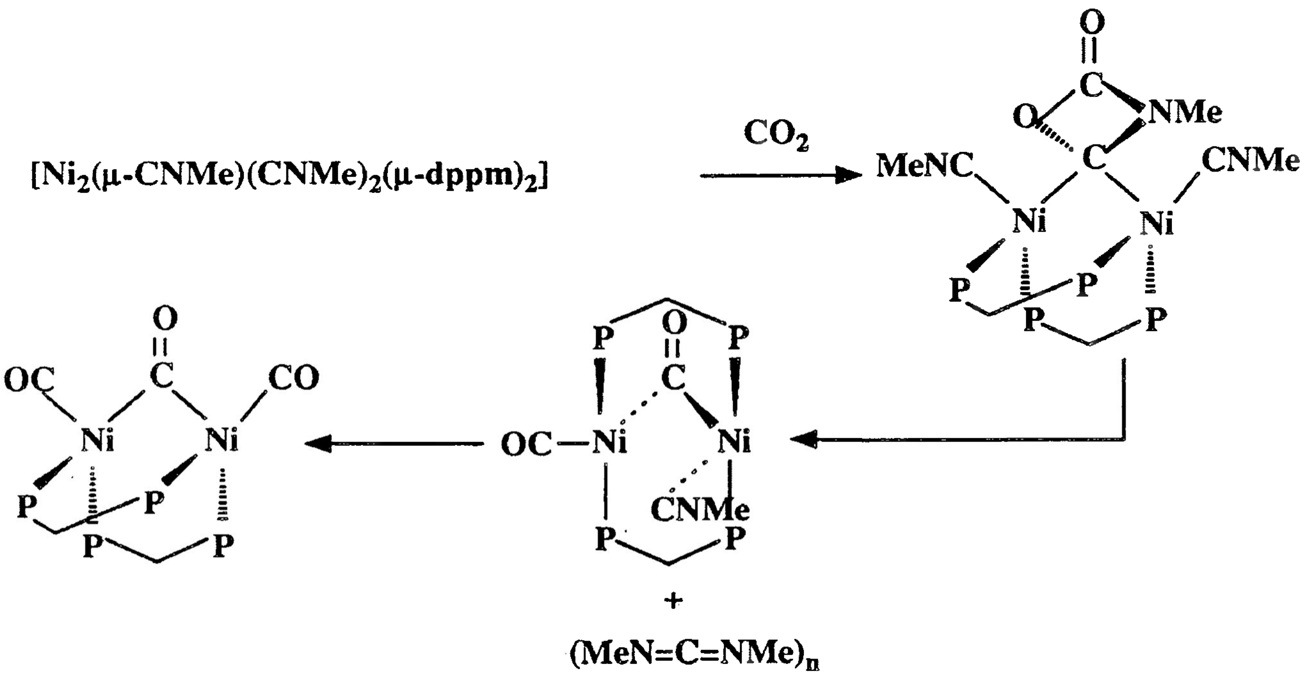
Scheme 3. Reactions of Ni^{II} with $NaBH_3CN$ and dppm



$$Ni_2(\mu_2\text{-CNMe})(CNMe)_2(\mu\text{-dppm})_2\ (11) + CH_2I_2 \xrightarrow{\text{Toluene/50°C}} [Ni_3(\mu_3\text{-CNMe})(\mu_3\text{-I})(CNMe)_2(\mu\text{-dppm})_2][I]\ (12) \qquad [14]$$

The ^{31}P NMR spectrum shows an AA'BB' spin system centred at $\delta = 0.5$ characteristic of an asymmetrically coordinated dppm in the complex. The crystal structure of the complex revealed the first example of symmetrically triply-bridging linear μ_3-η^1 isocyanide. The μ_3-η^1 mode of isocyanide binding was unprecedented in

Scheme 4. Reactions of $[Ni_2(\mu\text{-}CNMe)(CNMe)_2(\mu\text{-}dppm)]$ with CO_2



both cluster chemistry and on metal surfaces.[50] Iodide in the cluster appears to be essential to the stability of the cluster and other similar halide clusters are too unstable to obtain. For example, the reaction of complex **11** with CH_2Br_2 in toluene results in the precipitation of a intermediate which decomposes in all solvents.[50]

A unique example of a coordinatively unsaturated μ_3-η^1 CO-Ni cluster $[Ni_3(\mu_3\text{-}CO)(dmpm)_4][BH_3CN)_3]_2$ has also been prepared by Puddephatt et al..[51]

In an effort to further stabilize the trinickel core of

$[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(CNMe)_2(\mu\text{-}dppm)_2]^+$, an additional dppm was used to bridge the third side of the Ni_3 triangle as shown in equation **[15]**.[52]

$$\mathbf{[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(CNMe)_2(\mu\text{-}dppm)_2]^+ + dppm \xrightarrow[1:1]{Vacuum}}$$
$$\mathbf{[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(CNMe)_2(\mu\text{-}dppm)_3]^+ + 2CNMe \qquad [15]}$$

This work suggests that diphosphino ligands can be used to stabilize triangular Ni_3 clusters with unusual properties.

2. Ni-dppm-CO Complexes

The majority of nickel complexes containing both CO and dppm have been prepared either by the direct reaction of the metal carbonyl with dppm or by the action of CO with Ni-dppm complexes.[46,48] However, an alternative route (as outlined above in the case of cobalt complexes) that involves the reaction of CO-saturated solutions of Ni^{II} salts and phosphines, such as PPh_3 and $Ph_2P(CH_2)_nPPh_2$ (n = 1 - 6), with $NaBH_4$ or $NaBH_3CN$ under a variety of conditions has recently been reported.[53] This method avoids the use of metal carbonyls. In such reactions with dppm, a metal-CO-dppm complex containing monocoordinating ligands, $Ni(CO)_2(\eta^1\text{-}dppm)_2$ **13**, is first produced as shown in equation **[16]**. The complex is unstable and rapidly reacts further in the solution to give $Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ **14**, the structure of which is similar to that of **11**, as equation **[16]** shows.[53]

$$\mathbf{NiCl_2.6H_2O + dppm + CO + NaBH_4 \longrightarrow Ni(CO)_2(\eta^1\text{-}dppm)_2,\ 13,}$$

$$\mathbf{13 \longrightarrow Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2,\ 14,} \qquad [16]$$

III. PROPERTIES OF COBALT COMPLEXES WITH dppm AND CO

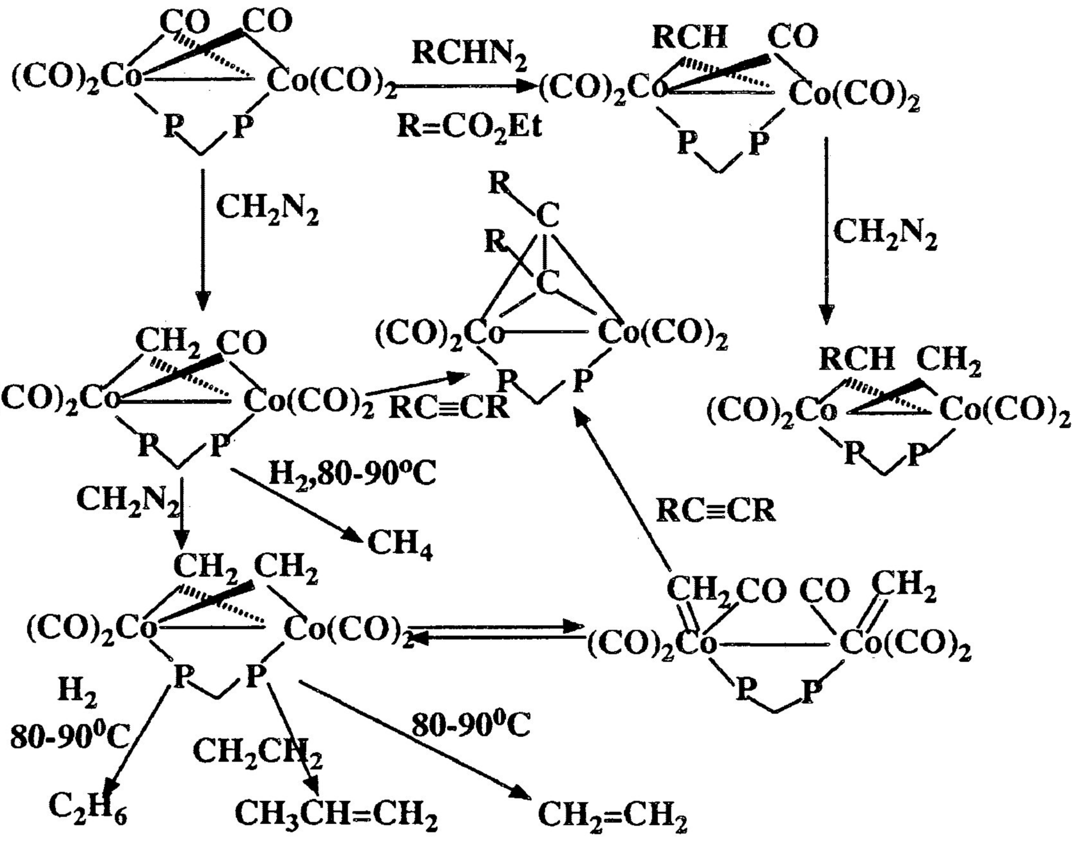
With the increase in the variety of Co-dppm-CO complexes known, related chemical, physical and catalytic properties have also been studied. In particular, cobalt complexes with CO and dppm ligands can undergo further reactions such as substitution by other ligands or redox reactions, as discussed in the following sections.[54,55]

1. Ligand Exchange Reactions

At room temperature, the μ-CO groups in the complex $Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-}dppm)$ **15** are easily displaced by μ-alkylidene groups.[55,56,57] This is the first case in which μ-alkylidene complexes have been prepared by direct displacement of a μ-CO group as shown in **Scheme 5**.[56]

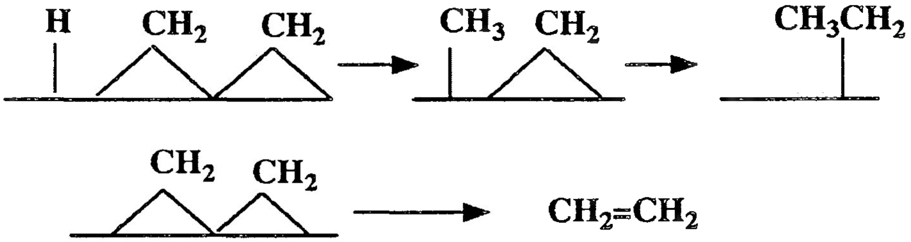
The di-(μ-methylene)cobalt complex can hydrogenolysized to give ethane and ethylene (see **Scheme 5**) and the reactions are significant as models (see **Scheme 6**) for proposed steps in the Fischer-Tropsch synthesis using transition metal catalysts.[55]

Scheme 5. Reactions of $Co(CO)_6$(dppm) with $RCHN_2$



Other similar complexes have also been prepared from reactions of $Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-dppm})$, **15**, with a variety of arenediazonium salts, $[p\text{-}XC_6H_4N_2]^+A^-$ ($X = NO_2$, F, H, CH_3, $CH(CH_3)_2$, OCH_3; $A^- = [BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$). The reaction proceed at 0°C to produce a series of air-stable, deep red-purple crystalline complexes as equation [17] shows.[58]

Scheme 6. Model for Fischer-Tropsch Synthesis



$$Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-dppm}) + \text{Arenediazonium salt} \longrightarrow$$

$$[Co_2(CO)_4(\mu\text{-}N_2C_6H_4\text{-4-Me})(\mu\text{-dppm})]X \qquad [17]$$

$$(X = BF_4^-, PF_6^-, SbF_6)$$

2. Redox Reactions

The redox properties of $[Co_2(CO)_3L_2]$ (L = **dppm** or **dmpm**), **16**, were studied by Lisic and his colleagues.[59] The studies show that **16** can be oxidized easily by I_2 and the oxidized products can be reduced by zinc back to the starting materials as equations [18] and [19] show.[59]

$$[Co_2(CO)_3L_2] + I_2 \longrightarrow [Co_2(CO)_3L_2I]I \qquad [18]$$

$$(L = \text{dppm, or dmpm})$$

$$[Co_2(CO)_3L_2]I + Zn \longrightarrow [Co_2(CO)_3L_2] \qquad [19]$$

$[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)_2(\mu\text{-}I)]I$ has an A frame structure with one CO occupying a bridging site.[59]

Normally, these lower oxidation state Co-dppm-CO complexes are easily oxidized by I_2, S and HBr.[38] Typical examples are given in equations **[20]**[38] and **[21]**[59]

$$[Co_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-dppm})_2],\ \mathbf{9},\ \text{or}\ [Co_2(CO)_4(\mu\text{-dppm})_2],\ \mathbf{8},\ + I_2 \longrightarrow [Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(\mu\text{-dppm})_2]I \qquad [20]$$

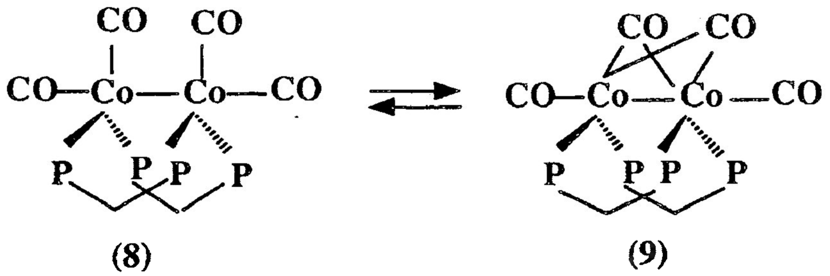
$$Co_2(CO)_6(\mu\text{-dppm}) + S_8 \longrightarrow Co_2(CO)_3(\mu\text{-dppm})_2(\mu\text{-}S) \qquad [21]$$

Oxidation of $Co_2(dppm)(CO)_4(\mu\text{-}CO)_2$ by iodine in THF gives $[(Co_2(\mu\text{-dppm})_2(CO)_4(\mu\text{-}CO)(\mu\text{-}I)]I$ in low yield. The yield of the complex is increased dramatically if an excess of dppm is added to the reaction mixture.[26]

Another interesting redox reaction involving only electron transfer from $[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]$ to $[Co_2(\mu\text{-}RC{\equiv}CR)(CO)_2(\mu\text{-dppm})_2]$ gives $[Co_2(\mu\text{-}RC{\equiv}CR)(CO)_2(\mu\text{-dppm})][PF_6]$ in yield of 73-79%.[54]

3. Equilibrium Between Bridged and Non-bridged Isomers

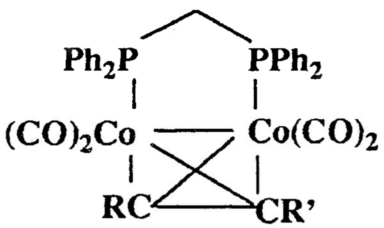
In solution, NMR studies have shown that $Co_2(CO)_4(\mu\text{-dppm})_2$ exists as an equilibrium between carbonyl bridged and non-bridged isomers and the process is summarized in equation [22].[39]



[22]

The cobalt dimer $Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-dppm})$ and the tetramer $Co_4(CO)_5(\mu\text{-}CO)_3(\mu\text{-dppm})_2$ also undergo rapid bridge-terminal CO exchange in solution.[25] This exchange is fast even at temperatures down to -60°C. However, this fluxional process can be stopped when a rigid alkynyl group is introduced into a Co-dppm dimeric system, such as complex **17** as **Figure 2** shows.[33]

Figure 2. Structure of $Co_2(CO)_4(dppm)(RC{\equiv}CR')$, 17



R=R'=H, Ph;

R=H, R'=Ph;

4. Pyrolysis

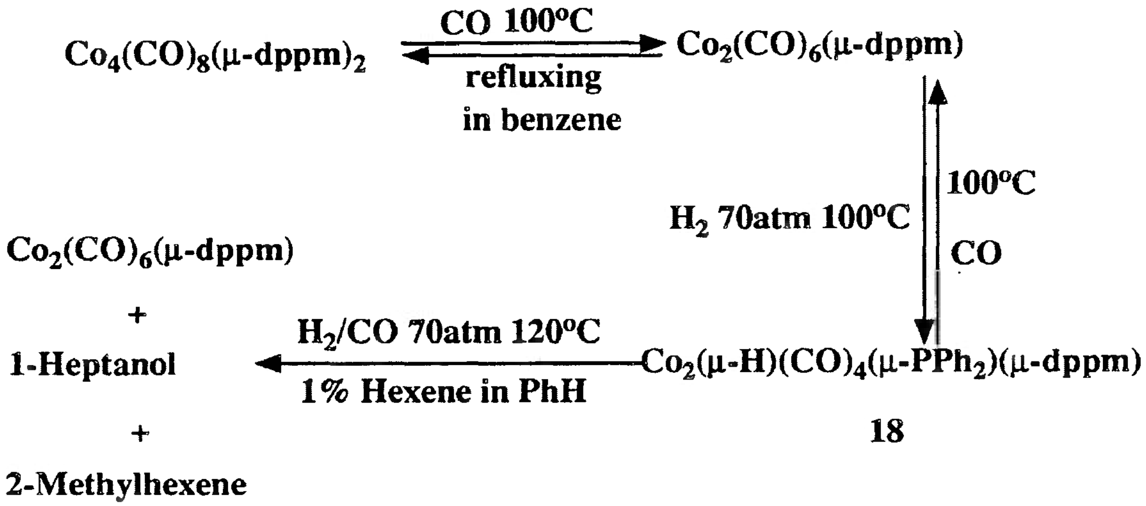
Pyrolysis of $Co_2(CO)_6(\mu\text{-dppm})$ gives a black crystalline complex identified as the tetramer $Co_4(CO)_8(\mu\text{-dppm})_2$ which is formed either in the autoclave or in refluxing benzene. The reaction appears to be a general synthetic route to the substituted tetranuclear cluster.[19]

5. Cleavage Reactions

The reaction of $Co_2(CO)_6(\mu\text{-dppm})$ with molecular hydrogen has been investigated with the goal of synthesizing phosphine substituted hydridocobalt carbonyl complexes. The reaction occurs at moderate pressure (75 atm) and results in cleavage of the dppm ligand to yield $Co_2(\mu\text{-H})(CO)_4(\mu\text{-PPh}_2)(\mu\text{-dppm})$, **18.**[26] The same compound, **18,** can also be synthesized directly from $Co_2(CO)_6(\mu\text{-dppm})$ and Ph_2PH as **Scheme 7** shows[26] and also catalyzes the reactions of 1-hexene with H_2/CO to give 2-methylhexene and 1-heptanol (**Scheme 7**).

From reactions of Co^{II} and Ni^{II} salts with $NaBH_4$ or $NaBH_3CN$ in the presence of dppm and CO, a variety of M-dppm-CO complexes (M = Ni, Co) can be synthesized as mentioned earlier in this chapter. In addition to these, other products can be obtained by adjusting the rate of addition of $NaBH_4$. For example, If the addition of $NaBH_4$ to the Co^{II}/dppm/CO system is carried out during 1 min. or less, a very rapid P-C bond cleavage in dppm occurs[60] at or below room temperature, leading to the formation of

Scheme 7. Dppm Cleavage Reactions



18, in 33% yield. The complex **18** may also be prepared by refluxing $Co_2(CO)_4(\mu\text{-dppm})_2$ in toluene under H_2.[60] A similar complex $[Ni_2(CO)_2(\mu\text{-dppm})_2(\mu\text{-PPh}_2)]Cl$ can also be obtained when a Co^{II}-dppm mixture is treated first with $NaBH_4$, then $NiCl_2$ is added, and finally, CO is passed.[60] These are the mildest reaction conditions yet to be reported for cleavage and the reaction provides a very simple and fast route for the synthesis of phosphido-bridged systems directly from transition metal salts.

IV. USES OF COBALT AND NICKEL COMPLEXES CONTAINING dppm AND CO

The uses of these cobalt and nickel complexes have been studied, especially in catalytic systems. Here, an important aspect is the control of the reactivity of the metal centre. Since the presence of two metal atoms may facilitate multi-electron redox reactions, binuclear complexes provide better control of the reactivity of these systems. Complexes of CoI_2 with bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$ (n = 1 - 6), can catalyze efficiently the homologation of methanol to ethanol. Ethanol selectivities as high as 89% have been achieved by using $Ph_2P(CH_2)_nPPh_2$ (n = 6) as the ligand.[61] In another useful reaction, the $Co_2(CO)_8$-$Ph_2P(CH_2)_nPPh_2$ (n = 2) system can catalyze the hydrocarbonylation of ethylene with CO and water to produce diethylketone with a selectivity of 99.1%.[62] Similarly, the $Co_2(CO)_8$-diphosphine system catalyzes effectively the hydroformylation of allyl acetate and allyl formate. The activity decreases in the order of $Ph_2P(CH_2)_nPPh_2$ (n = 2) > cis-$Ph_2PCH{=}CHPPh_2$ > trans-$Ph_2PCH{=}CHPPh_2$ > none > $Ph_2PCH_2PPh_2$ > PPh_3.[63]

The catalytic mechanism also has been studied.[35,56,57,64] For example, the work of Roy et. al. showed that pyrolysis of $[Co_2(\mu\text{-}R)(\mu\text{-}R')(CO)_4(\mu\text{-dppm}))]$ (R = CH, CHMe, CHCOOEt; R' = CO, CH_2, CHMe, CHCOOEt, SO_2) resulted in coupling of μ-R groups with CO to form ketones and therefore this step may occur during the Fischer-Tropsch syntheses catalyzed by cobalt compounds.[56,57]

It has been shown that hydridocobalt derivatives are probable intermediates in the hydrogenation of olefins and dienes.[65] In this connection, Alper and his colleagues have used a hydridocobalt species produced from HBF_4 and $Co_2(CO)_8$ to catalyze reaction [23] and they have obtained high yields of 2-ethylnaphthalene.[65]

$$\text{2-Vinylnaphthalene} + \text{p-Me}(CH_2)_{11}C_6H_4SO_3Na \xrightarrow{HBF_4/Co_2(CO)_8} \text{2-ethylnaphthalene (68\%)} \qquad [23]$$

If dppm is added into the above reaction system, it can further promote the reaction.[65]

These studies represent only a brief survey of the catalytic activity shown by dppm complexes. It is too early to tell whether the demonstrated abilities of dppm to bridge metals and to stabilize compounds containing unusual bonding modes of small molecules like carbon monoxide or alkynes will form the basis for useful catalysts.

V. HETEROMETALLIC COMPLEXES OF COBALT AND NICKEL WITH OTHER TRANSITION METALS

A novel method of changing reactivities of these catalytic systems is by having two different metal atoms in the same molecule, resulting in a different electron population on the two metal atoms in the same complex thus causing variable reactivities. The importance of such systems has been recognized only recently and is evident from the synthesis of a large number of such compounds in recent years.[3,4]

There are normally four synthetic approaches to these heterometallic systems. In the following section we will discuss these methods and see examples.

1. Heterobimetallic Cobalt with Other Transition Metals

a. Use of η^1-dppm Metal Complexes

Some of the M^I and M^0 carbonyl complexes containing η^1-dppm formed in the reactions described in the foregoing discussion can react with other metal complexes to form bimetallic complexes. There is now considerable interest in using this method to prepare bimetallic systems.[3] For example, the first heterometallic Pd-Co cluster $Pd_2Co_2(CO)_7(\mu\text{-dppm})_2$ has been prepared from the reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ or $PdCl_2(\eta^1\text{-dppm})_2$ and $[Co(CO)_4]^-$ and its structure was established by X-ray diffraction.[66] Other approaches to bimetallics are discussed below.

b. Use of $Co_2(CO)_8$ or $Na[Co(CO)_4]$

Mixed-metal clusters are of particular interest because of the dppm-assisted metal-metal bond formation as a precursor for a heterogeneous carbonylation catalyst.[67,68] For example, this kind of catalyst can selectively transform o-nitrophenol into benzoxazol-2-one.[69,70]

$Co_2(CO)_8$ or $Na[Co(CO)_4]$ are often used to react with other metal dppm complexes to form bi- or mixed metal nuclear clusters.[71] For example, the reaction of $Na[Co(CO)_4]$ with $Pd_2Cl_2(\mu\text{-dppm})_2$ affords a deep green Pd_2Co_2 core cluster in high yield.[71] Similarly, the reaction of $Na[Co(CO)_4]$ with $PdPtCl_2(\mu\text{-dppm})_2$ gives a deep blue green mixed-metal $PdPtCo_2$ core cluster.[71] The total reaction is illustrated in **Scheme 8.**

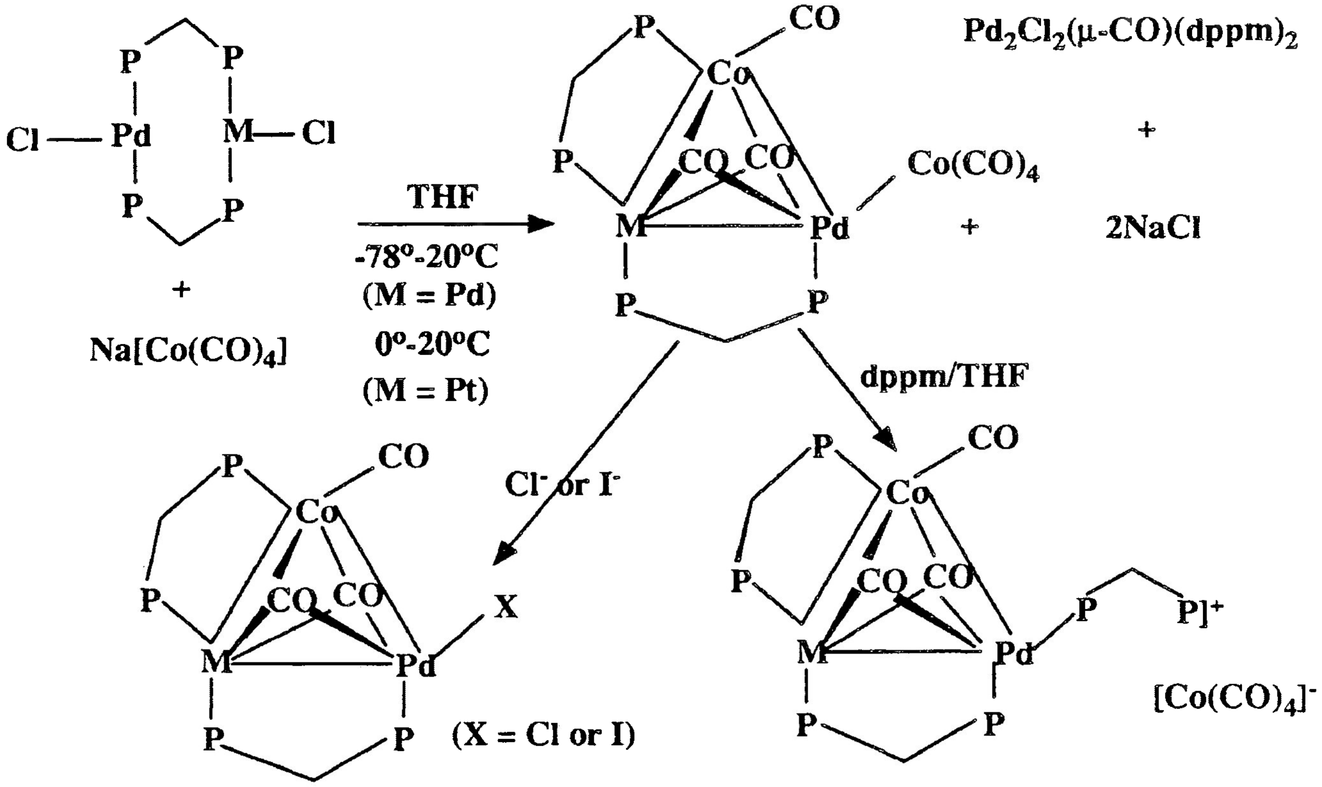
The M-Co unit bridged by dppm produced from a Pd-M unit bridged by dppm illustrates the mobility of dppm, i.e. the lability of the Pd-P bond is greater than expected. $Pt(dppm)Cl_2$ can react with $Na[Co(CO)_4]$ to give a heterotrinuclear cluster (**Figure 3**) without dppm transfer.[73]

These clusters also exhibit different electrochemical characteristics. Thus, in DMSO, $Pd_2Co_2(CO)_7(\mu\text{-dppm})_2$, $Pd_2CoI(CO)_3(\mu\text{-dppm})_2$ and $[Pd_2Co(CO)_3(\mu\text{-dppm})_2PR_3]PF_6$ clusters undergo two distinct quasi-reversible 1-electron reduction steps whereas the corresponding tetra- and tri-nuclear clusters such as $PtPdCo_2(CO)_7(\mu\text{-dppm})_2$, $PtPdCoI(CO)_3(\mu\text{-dppm})_2$ and $[PtPdCo(CO)_3(\mu\text{-dppm})_2PR_3]PF_6$, undergo a single quasi-reversible 2-electron reduction.[74,75]

The carbyne-tungsten complex $[W{\equiv}C(p\text{-}MeC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$ reacts readily with $Co_2(CO)_8$ in pentane at room temperature with evolution of CO and formation of the complex $[Co_2W(\mu_3\text{-}CC_6H_4Me)(CO)_6(L)(L')(\eta^5\text{-}C_5H_5)$, **19**.[69,72,76] The reactions and structures of these complexes are illustrated in **Scheme 9.**

Following a similar route, Co-Fe clusters also can be obtained from reactions **[24]**

Scheme 8. Preparation of Co-Pd-M Core Clusters



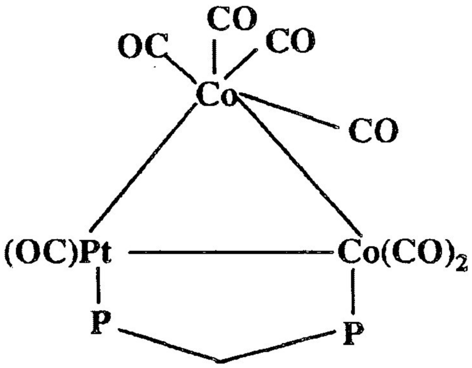
and [25].[69,76]

$$Na[Co(CO)_4] + [Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)]PF_6 \longrightarrow (22) \qquad [24]$$

$$(R{=}Me, Ph)$$

$$(22) + dppm \longrightarrow (23) \qquad [25]$$

Figure 3. Structure of $Co_2Pt(CO)_7(dppm)$



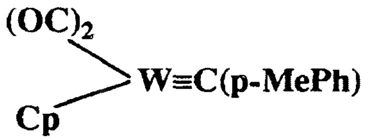
The structures of 22 and 23 are illustrated in **Figure 4**.

c. Ligand Replacement Reactions

The bi- or mixed metallic system can be easily obtained from the ligand replacement reactions of bi- or mixed metal-carbonyl clusters with dppm. The following reactions[78] [26] and [27] illustrate this method.

$$(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3 + dppm \xrightarrow[\text{Reflux}]{\text{THF}}$$

Scheme 9. Reactions of $W(CO)_2(Cp)(CPh\text{-}4\text{-}Me)$ with $Co_2(CO)_8$

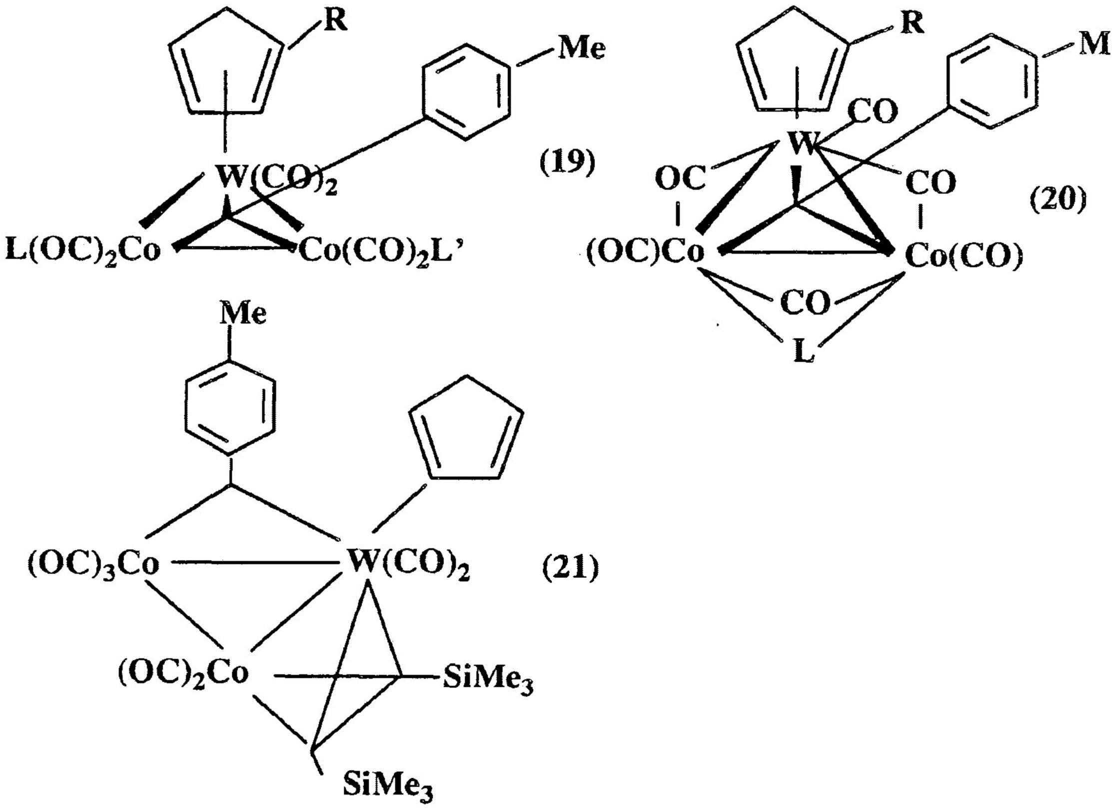


$$(OC)_2(Cp)W{\equiv}C(p\text{-}MePh) + Co_2(CO)_8 \xrightarrow{r.t} (19)\ (L = L' = CO)$$

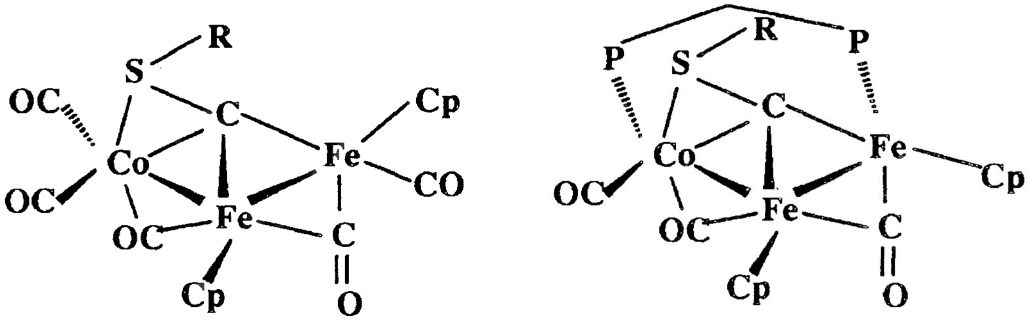
$$(19) + L \text{ and } L' \longrightarrow (19)\ (L' = PhPMe_2;\ L = dppm)$$

$$(19) + L \longrightarrow (20)\ (L = dppm;\ PhPMe_2)$$

$$(19) + Me_3SiC{\equiv}CSiMe_3 \longrightarrow (21)$$

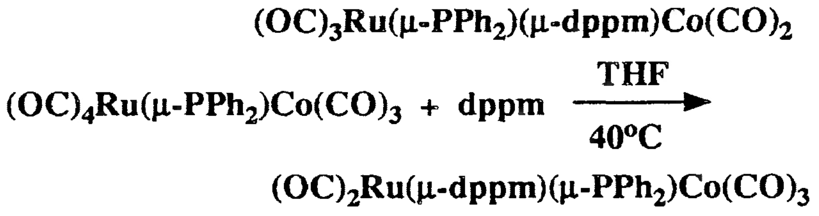


(19) (20) (21)



(22) (23)

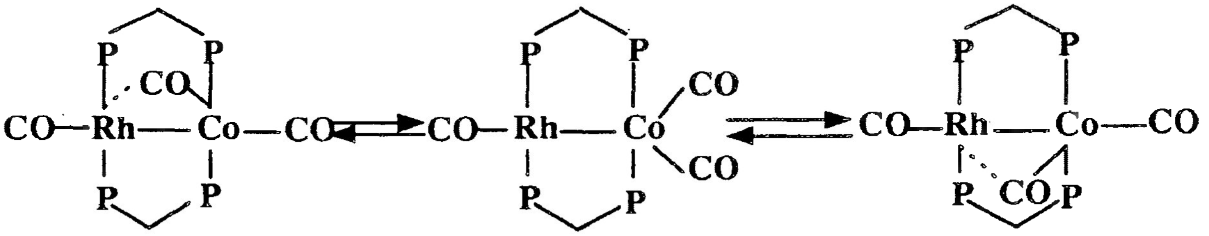
Figure 4. Structures of $Fe_2Co(CO)_5(Cp)_2(CSR)$ and $Fe_2Co(CO)_3(Cp)_2(CSR)(dppm)$



$$\begin{array}{ll} & (OC)_3Ru(\mu\text{-}PPh_2)(\mu\text{-dppm})Co(CO)_2 \quad [26] \\ (OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3 + \text{dppm} \xrightarrow[40^{\circ}C]{THF} & \\ & (OC)_2Ru(\mu\text{-dppm})(\mu\text{-}PPh_2)Co(CO)_3 \quad [27] \end{array}$$

d. Direct Reduction of Metal Salts in The Presence of dppm and CO

Mixtures of metal salts can be directly reduced by $NaBH_4$, $NaBH_3CN$ or other reducing reagents in the presence of dppm and CO to form bimetallic systems. For example, when $NaBH_4$ is added to a solution of $RhCl_3.xH_2O$, $CoCl_2.6H_2O$ and dppm under CO, slow addition of $NaBH_4$ gives the homobimetallic complex $[Rh_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ whereas fast addition gives the heterobimetallic complex, $[RhCo(CO)_3(\mu\text{-}dppm)_2]$ in good yield.[79] The complex is fluxional in the sense that the two carbonyls attached to the cobalt atom are in equilibrium in solution as equation [28] shows but in the solid state, one carbonyl group is semi-bridging.[79]

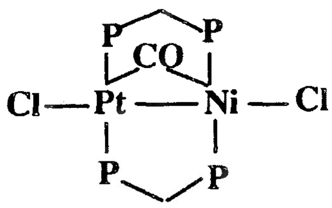


[28]

2. Heterobimetallic Nickel and Other Transition Metals Complexes

The first isolated heterometallic dppm complex of nickel appears to be the binuclear $CpNi(\mu\text{-}SPh)(\mu\text{-}dppm)Mo(CO)_4$ and $CpNi(\mu\text{-}dppm)(\mu\text{-}CN)Mo(CO)_4$ which does not contain a metal-metal bond.[80] There is considerable interest at present in using complexes containing monodentate dppm as precursors to prepare such bimetallic systems and there is obvious potential for the use of $Ni(CO)_2(\eta^1\text{-}dppm)_2$. Indeed this compound reacts very rapidly with $PtCl_2(COD)$, $NiCl_2.6H_2O$, $Rh_2Cl_2(CO)_4$, and $Mo(CO)_5(THF)$ in CH_2Cl_2 and a variety of bimetallic complexes have been isolated. For example, $[PtNiCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ has been obtained and its crystal structure shows that both the Ni and Pt atoms are each bonded to a terminal chlorine atom as **Figure 5** shows.[81]

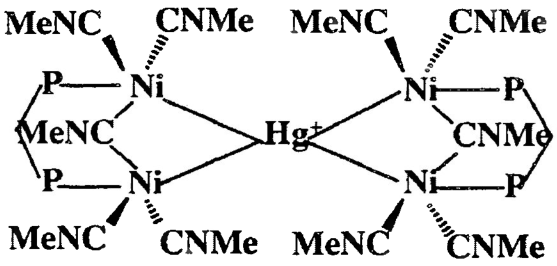
Figure 5. Structure of $PtNiCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$



Kubiak's group[82,83,84] has used the cradle nickel complex, $Ni_2(\mu\text{-}CNMe)(CNMe)_2(\mu\text{-}dppm)_2$, **11**, as a starting material and several heterometallic complexes have been synthezed and characterized. Thus, compound **11** reacts with $HgCl_2$ in a 1 : 1 ratio in THF at 25°C to give an extraordinary metallation product $\{[Ni_2(\mu\text{-}CNMe)(CNMe)_4(\mu\text{-}dppm)\}_2Hg][NiCl_4]$. The same complex can also be obtained from the direct reaction of $Ni(CNMe)_4$, dppm and $HgCl_2$ (5 : 2 : 2) in THF.[82] The structure of the complex is illustrated in **Figure 6.**[82]

Compound **11** also reacts with $[Pd(CNMe)_4]^{2+}$ to give a linear trinuclear Ni-Pd-Ni complex, $[Ni_2Pd(CNMe)_6(\mu\text{-}dppm)_2]^{2+}$.[83] The compound can lose MeNC to produce a Pd-Ni dimer the structure of which is still uncertain. These reactions are shown in **Scheme 10.**[66]

Figure 6. Structure of The Cation $[Ni_4Hg(CNMe)_{10}(dppm)]_2^+$



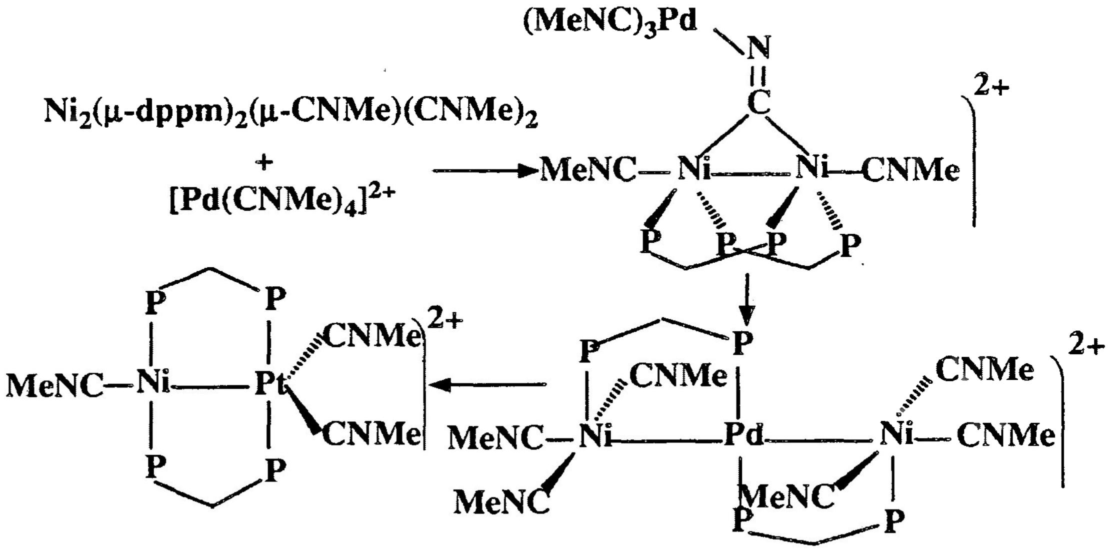
The strongly bonded Ni-Pt heterobimetallic red complex $[NiPt(\mu\text{-}CNMe)(CNMe)(\mu\text{-}dppm)_2Cl]Cl$, can be formed from reaction of **11** with $Pt(dppm)Cl_2$ in THF.[84]

Finally, treatment of $(Ph_3P)_2AuCl$ with **11** in THF at room temperature gives an orange precipitate $[NiAu(CNMe)_2(\mu\text{-}dppm)_2]Cl$.[85] Since treatment of the (dimethylamino)carbyne compound, $[Ni_2(\mu\text{-}CNMe_2)(CNMe)_2(\mu\text{-}dppm)_2]I$, with $Au(PPh_3)Cl$ did not afford a similar heterometallic complex, the initial interaction of the μ-CNMe nitrogen atom lone pair with the gold fragment $Au(PPh_3)^+$ may be a key step in the formation of $[NiAu(CNMe)_2(\mu\text{-}dppm)_2]Cl$.[67]

VI. Cu^I COMPLEXES WITH PHOSPHINE, CO AND OTHER LIGANDS

Interest in organocopper chemistry has grown considerably over the last 30 years

Scheme 10. Reactions of $Ni_2(CNMe)_3(dppm)_2$ with $[Pd(CNMe)_4]^{2+}$



when organocopper complexes were found to be useful reagents in organic synthesis and to play an important role in the active sites of copper proteins.[86] The first organocopper compound was isolated from the reaction of Cu^I with PhMgBr in diethyl ether in 1923.[86] Since then, a large number of copper complexes have been prepared and characterized.

Normally the Cu^+ ion is unstable but it can be stabilized effectively when solvated by MeCN and CuX($X = Cl^-, Br^-, I^-$) also have relatively high solubilities in MeCN compared with negligible solubilities in water. In MeCN, Cu^I is more stable than Cu^{II}

and the latter is a comparatively powerful oxidizing agent. The tetrahedral ion $[Cu(MeCN)_4]^+$ can be isolated as a salt with large anions such as ClO_4^- or PF_6^-.[87] It is used extensively as a precursor for preparing other Cu^I complexes.

The Cu^I ion can also coordinate with cyanide , carboxylates, triflate (trifluoromethanesulfonate), alkoxides, dialkylamides, phosphines and carbonyl etc. in mononuclear species, binuclear species (Cu_2), tetrameric (Cu_4) species and other polynuclear structural species. There are also some Cu^I complexes with bridging chloride, pyrazole and pyrazolyborate.[86] Cu^I, but not Cu^{II} can form a variety of compounds with Cu-C bonds from interactions between CuX with RLi or Grignard reagents and can be stabilized by phosphine ligands.[86]

^1H, ^{13}C and ^{31}P NMR spectroscopy have proved to be useful tools for the characterization of Cu^I complexes. In addition, the recent advent of multinuclear magnetic resonance instruments enables one to observe ^{63}Cu NMR. ^{63}Cu NMR provides a technique to follow the complexation of copper and to observe directly metal-ligand bonding.[88] An MeCN solution of $[Cu(MeCN)_4]PF_6$ is normally used as external reference ($\delta = 400$ ppm) in such studies.[88] It is well known that a nucleus of spin higher that 1/2 often gives broad resonance lines due to the quadrupole relaxation mechanism which depends on the coordination environment of the metal centre.[89] Fortunately, most Cu^I complexes are tetrahedral and many of them give a relatively sharp resonance line.[91] On the other hand two- or three-coordinate Cu^I complexes give quite broad resonance lines because of the low symmetry around the copper centre which leads to an increase of the quadrupole relaxation rate.[91] Normally, a large excess of ligand is utilized in an attempt to force the formation of the four-coordinate Cu^I complex (CuL_4). When tetrahedral CuL_4 complexes, for example those of pyridines and nitriles, are diluted with acetone, the resonance lines of the Cu^I species undergo line broadening. This fact reveals the presence of equilibria between CuL_4 and other complexes of lower symmetry. Hence there is a clear relationship between line broadening and the nature of the Cu^I complexes in solution.[91]

1. Cu^I Complexes with CO Ligands

There is considerable interest in the fixation of CO by Cu^I which is very important in the area of metal promoted CO reductions.[87] For example, much research work, directed towards improving our understanding of the conversion of CO/H_2 mixtures to methanol catalyzed by oxides of copper and zinc, has been carried out.[92] However, it is difficult to study the chemical environment of a Cu^I active site in the binding of carbon monoxide and other small molecules because of its high kinetic lability and its tendency to disproportionate to Cu^{II} and Cu^0.[91] Ligands with S and P donor atoms are excellent for preventing this disproportionation, although Cu^I complexes with these ligands can no longer bind CO or O_2.[87] Cu^I species bound to -OR or amino groups are much more reactive toward CO though disproportionation to Cu^{II} and Cu^0 can still occur.[93,94]

Since the formation of Cu^I carbonyls is implicated in the low pressure scavenging of CO and conversion of CO/H_2 gas mixture to methanol,[95] much effort has been directed towards the synthesis of stable CO-Cu complexes. The first reported thermally stable copper carbonyl complex, $[Cu(OBu^t)(CO)]_4$, is prepared by carbonylation of $[Cu(OBu^t)]_4$.[95,96] The structure of the complex was found to be tetrameric with a cubic Cu_4O_4 core.[97] Also, on passing a stream of CO through a suspension of $[Bu^tOCu]_4$ in benzene, a thermally stable pale yellow solid identified as $[Bu^tOCuCO]_4$ is produced.[98]

Hydrogenolysis of the Cu-OBu^t bond is a quite versatile synthetic method for the production of copper phosphine polymeric hydrides as equation **29** shows.[90]

$$\tfrac{1}{4}(\mathbf{CuO\text{-}Bu^t})_4 + \mathbf{L} + \mathbf{H_2} \xrightarrow{\mathbf{THF}} \mathbf{1/n(HCuL)_n + Bu^tOH} \qquad [29]$$

$$\mathbf{n = 6, 8;\ L = P(NMe_2)_3,\ \tfrac{1}{2}dppp.}$$

Since it is possible that hydrides are involved as intermediates in the conversion of CO/H_2 mixtures to methanol catalyzed by oxides of copper and zinc, the chemistry of these polyhydrides may provide more understanding of these processes.

A significant objective in Cu^I chemistry is the synthesis of a complex having a vacant coordination site available on the metal. These properties are a general prerequisite for the coordination and activation of small molecules like CO and O_2. For example, reactions of CuX (X = Cl, I, $PhCO_2$) with BEN (BEN = $PhCH{=}NCH_2CH_2N{=}CHPh$) in a 1 : 1 molar ratio in THF leads, via a mononuclear solvated species **24**, to a complex **25** containing the intact [Cu-X] unit as shown in Scheme **11**. If the reaction is carried out under CO in the presence of p-MeC_6H_4NC, the solvent molecule, S, in the intermediate species **24** is replaced by either CO or p-MeC_6H_4NC. Further reaction with BEN gives the first bridging carbonyl containing complex in Cu^I chemistry.[93,94]

Cu^I in methanol absorbs CO at room temperature in the presence of en giving a colorless solution. Depending on the Cu^I/en molar ratio and the anion present, the following thermally stable Cu^I carbonyls have been isolated as crystals.[100]

$[Cu(en)_2(CO)_2]I$ (ν_{CO}(Nujol) 2060cm^{-1})

$[Cu_2(en)_2(CO)_2]I_2$ (ν_{CO}(Nujol) 2062cm^{-1})

$[Cu_2(en)_3(CO)_2]BPh_4$ (ν_{CO}(Nujol) 2078cm^{-1})

Solutions of CuCl in HCl can also absorb CO yielding a white solid.[101] The process has been recognized as the most satisfactory for reversible fixation of CO under mild conditions. An investigation of the stoichiometry of the white solid by manometric methods indicated that the white solid is anhydrous, with the empirical formula Cu(CO)Cl.[102] Cu(CO)Cl has been considered to be a useful precursor for the synthesis of other organometallic complexes of Cu^I with CO ligand and for the preparation of structural models of possible intermediates in Cu^I promoted carbonylation. Recently, the structure of the white solid was fully characterized by X-ray crystallography.[103] It has a chloride-bridged layer structure in which the Cu^I is approximately tetrahedrally coordinated as **Figure 7** shows.

The relatively long Cu-C distance, short C-O distance and high ν(CO) in Cu(CO)Cl

Scheme 11. Reactions of CuX with BEN and CO

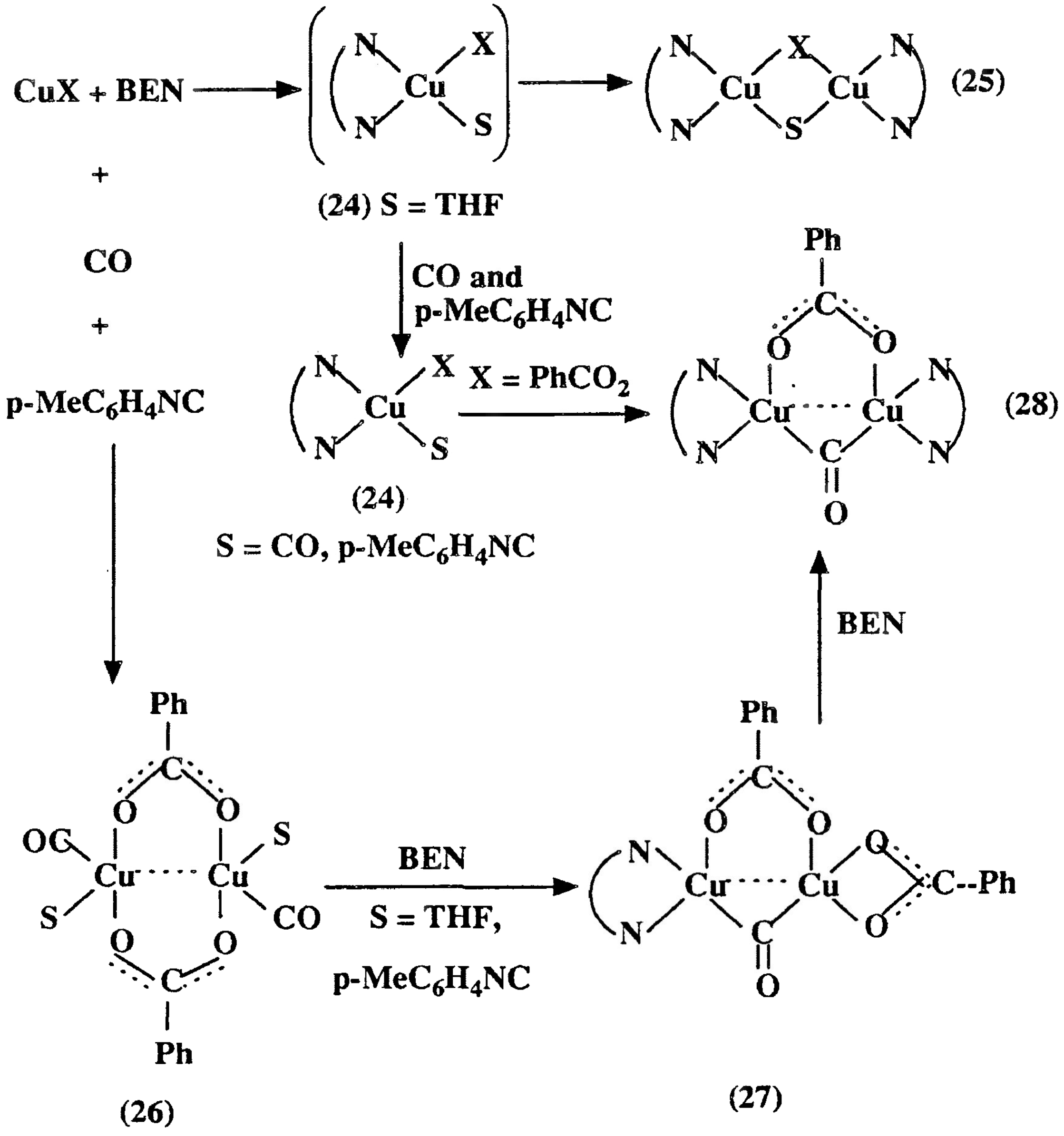
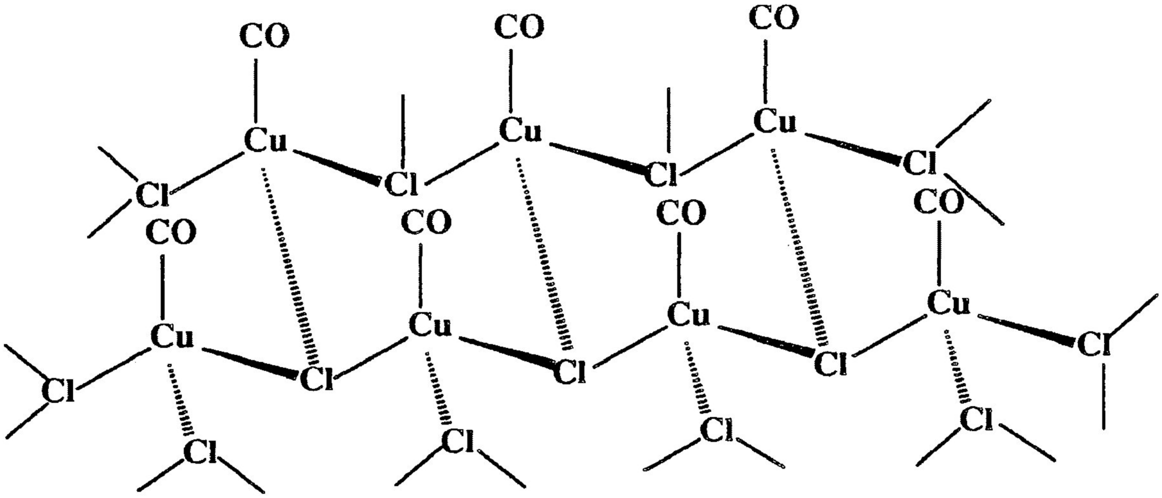


Figure 7. Three-dimensional View of Structure of Cu(CO)Cl



suggest a low d_π-p_π contribution to the metal-carbonyl bond. The compound undergoes rapid decarbonylation even at temperatures below 0°C in contrast to $[CuCO(OBu^t)]_4$.[103]

2. Cu^I Complexes with Both CO and Phosphine Ligands

There appear to be few Cu^I complexes with both phosphine and CO as ligands. Actually, CO ligands in Cu^I complexes are easily substituted by phosphines as shown below.[104]

$$\mathbf{CuCl + Na(2\text{-}MeQuin) + CO \longrightarrow [Cu(2\text{-}MeQuin)(CO)]_4 \xrightarrow{dppm} Cu_2(2\text{-}MeQuin)_2(\mu\text{-}dppm)} \qquad \mathbf{[30]}$$

3. Cu^{I} Complexes Containing Phosphine Ligands without CO

The chemistry of Cu^{I} with phosphines has been extensively studied and some Cu^{I}-phosphine complexes, such as $CuR(PPh_3)_2$, $(CuR)_2(dppe)$ (R = Me, Et, n-Pr, i-Bu, CH_2CN, $CH(CN)_2$, Ph), $Cu_3(Ph_2PCHPPh_2)_3$, and $[Cu(C{\equiv}CR)(L)]_4$ (L = dppm, dppe) have been prepared.[105] The structures of these compounds have been determined by IR, ^1H and ^{31}P NMR spectroscopy and X-ray diffraction.[105]

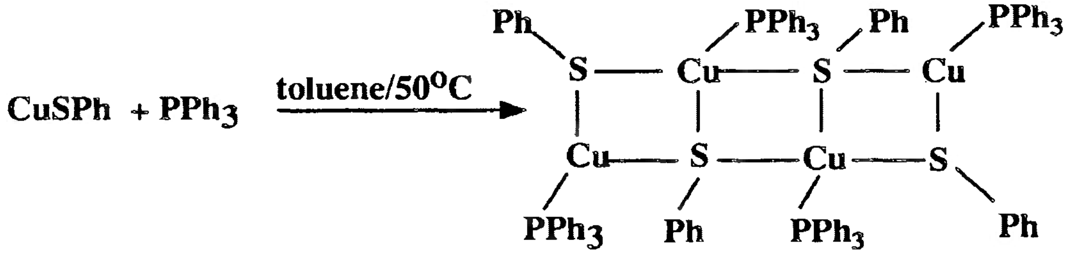
Most Cu^{I} complexes with phosphine ligands can be prepared directly from the reactions of Cu^{I} salts and phosphines at higher temperatures[106,107] as illustrated below.

$$\mathbf{CuBr + L \xrightarrow[\text{refluxing in Benzene}]{1:1} [CuBrL]_4,\ 29} \qquad \mathbf{[31]}$$

$$\mathbf{L = PBu_3^{t},\ P(C_6H_2Me_3)_3}$$

The tetrameric structure of compound **29** (L = PBu_3^{t}) with nearly ideal T_d symmetry for the Cu_4Br_4 core has been established.[108] With L = $P(C_6H_2Me_3)_3$, reaction **[31]** gives a two coordinate Cu^{I} phosphine halide, $CuBrP(C_6H_2Me_3)_3$, because of the large steric effects of $P(C_6H_2Me_3)_3$.[106]

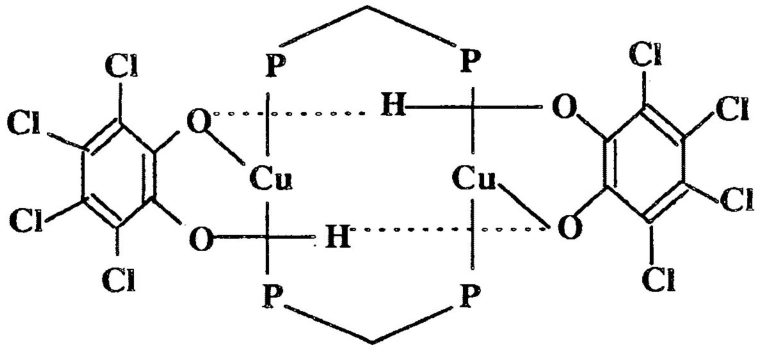
Very pale yellow crystals of $[Cu_4(SPh)_4(PPh_3)_4]$ are readily obtained by treatment of CuSPh with 1 equivalent of PPh_3 in toluene.[109] The complex possesses a "step" structure in which two copper atoms are trigonally coordinated and two are pseudotetrahedrally coordinated as the following equation shows.[109]



[32]

Electrochemical methods are often used to synthesize Cu^I complexes with phosphine ligands. One of the advantages of direct electrochemical synthesis is that the formation of lower oxidation state species from a metallic electrode is often favoured in non-aqueous solutions.[110] The electrochemical oxidation of copper anodes in a MeCN solution of diphenylphosphine, gives $Cu(PPh_2)$.[111] Similarly, copper anodes in an MeCN solution of dppm and either RSH or $HPPh_2$ gives $[(CuSR)_2dppm]$ and $Cu_4(PPh_2)_4(dppm)_2$ respectively.[105] In the presence of $R(OH)_2(R(OH)_2$, tetrachloro-1,2-dihydroxybenzene, 2,2'-dihydroxybiphenyl) and L (L = PPh_3, dppm), the electrochemical oxidation of copper in acetonitrile solution gives Cu^I species in which the copper atoms are ligated by $[R(O)OH]^-$ as shown in **Figure 8**.[110] The unusual stability of the compound may arise from intramolecular O-H---O hydrogen bonds.

Figure 8. Structure of $Cu_2[OC_6Cl_4(OH)_2](\mu\text{-dppm})_2$



Ligand exchange reactions also can be used to synthesize Cu^I-phosphine complexes.[112,113] Several complexes prepared by this method are shown below.[113]

$$\mathbf{Cu(Phen)_2X + L \xrightarrow{r.t} [Cu(Phen)L]X} \qquad \mathbf{[33]}$$

$$\mathbf{X = PF_6, NO_3; L = PPh_3, Ph_2P(CH_2)_nPPh_2\ (n = 1\text{-}3).}$$

The salts $Cu(MeCN)_4X$ ($X = ClO_4, BF_4$) react with equimolar amounts of dppm in CH_2Cl_2 at room temperature to give air stable white solid compounds $[Cu_2(\mu\text{-dppm})_2(MeCN)_n]_2X_2$ ($n = 2$ or 4).[114] ^1H and ^{31}P NMR spectra show that these complexes probably undergo ligand dissociation in solution as the equation [34] shows.[114]

$$[Cu_2(\mu\text{-}dppm)_2(MeCN)_4]_2X_2 \rightleftharpoons [Cu_2(\mu\text{-}dppm)_2(MeCN)_{4-x}]_2X_2 + xMeCN \quad [34]$$

The related compounds, $[Cu_2(\mu\text{-}dppm)_3]X_2$, can also be obtained from similar reactions in which $Cu(MeCN)_4X$ ($X = ClO_4, BF_4$) and dppm are heated together in acetone.[114] The relationship between these complexes and those mentioned above is shown in equation [35].

$$[Cu_2(\mu\text{-}dppm)_3][BF_4]_2 + 4MeCN \rightleftharpoons dppm + [Cu_2(\mu\text{-}dppm)_2(MeCN)_4][BF_4]_2 \quad [35]$$

Similar reactions were also studied by Ho and Bau who obtained a different product as equation [36] shows.[115]

$$[Cu(MeCN)_4]BF_4 + dppm \xrightarrow{r.t} [Cu_3(\mu_3\text{-}OH)(\mu\text{-}dppm)_3][BF_4]_2 \quad [36]$$

The structure of this compound consists of a triangular array of copper atoms with dppm bridging each edge of the triangle and a triply bridging OH group. The μ_3-hydroxy ligand presumably resulting from the deprotonation of water in $Cu(BF_4)_2.xH_2O$, the precursor to $[Cu(MeCN)_4][BF_4]$. In this case, the

$[Cu_3(\mu_3\text{-}OH)(\mu\text{-}dppm)_3]^{2+}$ dication consists of unusual three-coordinate 16-electron copper atoms.[115]

Dppm can react directly with organocopper compounds to give a variety of complexes.[116,117,113] For example[116]

$$\text{o-,m-,p-MePhCu} + CS_2 + \text{dppm} \xrightarrow[N_2]{\text{Toluene}} [Cu_4(\mu_2\text{-dppm})_4(\mu_4\text{-}CS_3)_2] + [(MePhCS_2)Cu(dppm)]_2 \quad [37]$$

However, in other situations, similar reactions between organocopper(I) compounds and dppm in toluene may cause the cleavage of dppm as equation [38] shows.[118]

$$(Cu_5mes_5) + \text{dppm} \xrightarrow{\text{r.t}} Cu_3(Ph_2PCHPPh_2)_3.MePh \qquad [38]$$

It is very interesting to note that organocopper compounds do not normally react with CO_2 but in the presence of phosphines such as Ph_3P, dppm and dppe, insertion reactions can occur as shown in equations [39]-[41].[119]

$$RCu + CO_2 + Ph_3P \xrightarrow{\text{r.t}} RCO_2Cu(PPh_3)_2 \qquad [39]$$

$$RCu + CO_2 + \text{dppe} \xrightarrow{\text{r.t}} (RCO_2Cu)_2(\text{dppe})_3 \qquad [40]$$

$$\mathrm{RCu + CO_2 + dppm \xrightarrow{r.t} (RCO_2Cu)_2(dppm) + [RCO_2Cu(dppm)]_2} \quad [41]$$

The function of the phosphine ligands is still not clear, but these insertion reactions could have very great potential in organic synthesis.

4. Heterobimetallic Cu^I Complexes

Using $Na[Co(CO)]_4$ as a starting material, several heterometallic Cu^I complexes have been synthesized as shown in equations [42][90] **and** [43] [120].

$$\mathrm{Na[Co(CO)]_4 + CuCl \longrightarrow [CuCo(CO)_4]_4 + [CuCo(CO)_4]_n} \quad [42]$$

$$\mathrm{L_2CuCl + [Co(CO)_4]^- \text{ or } [Co(CO)_3PR_3]^- \longrightarrow L_2CuCo(CO)_4 \text{ or } (R_3P)_2CuCo(CO_3)_3} \quad [43]$$

$$\mathrm{L = Ph_3P, MePPh_2, PBu_3; L_2 = Ph_2P(CH_2)_nPPh_2\ (n = 1, 2, 4)}$$

The existence of an infinite metal atom chain in some of these carbonyl heterometallic complexes, $[CuCo(CO)_4]_n$, was established by a single crystal investigation.[99,120] For example, the Cu-Co chain, $[CuCo(CO)_4]_n$, is constructed from a slightly bent backbone of copper atoms in which every two Cu atoms are bridged by a $Co(CO)_4$ unit to form Cu-Co bonds in a zig-zag chain.[90] Clearly, there is no Cu-CO bond but only $(CO)_4Co$-Cu-$Co(CO)_4$ polymeric chains.[120] In contrast, the heterobimetallic complex, $(Ph_3P)_3CuV(CO)_6$ only contains separated $[(Ph_3P)_3Cu]^+$ and $[V(CO)_6]^-$ ions.[121,122]

As discussed below, many other heterobimetallic compounds of copper containing phosphines and CO ligands have been studied. Normally, these complexes do not contain bridging CO or a direct link between Cu and CO. For example, treatment of $[Ir(CO)(dppm)_2]Cl$ with CuC≡CPh in boiling acetone gives a red complex $[IrCu(CO)(\mu\text{-}dppm)_2(C{\equiv}CPh)]Cl$.[123] Low temperature ^{31}P NMR spectra show an AA'BB' pattern consistent with dppm ligands bridging two different metal atoms. Single crystal X-ray diffraction confirms that the metal-metal bond is bridged by dppm ligands and that the CO and Cl ligands are respectively terminally bonded to Ir and Cu.[123]

In addition, other example are obtained from reactions of various Fe carbonyl complexes with $[MI(PPh_3)]$ (M = Ag, Cu, Au) which, in THF, lead to trinuclear clusters as shown in equations **[44]** and **[45]**.[124]

$$\mathbf{[NEt_4]_2[Fe_2(CO)_6(\mu\text{-}CO)_2] + [CuI(PPh_3)] \longrightarrow}$$
$$\mathbf{[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}Cu(PPh_3)\}]\ (30) + NEt_4I \qquad [44]}$$

$$\mathbf{[NEt_4]_2[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)] + [MI(PPh_3)] \longrightarrow}$$
$$\mathbf{[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}M(PPh_3)\}]\ (31) + NEt_4I \qquad [45]}$$

Compound **30** is air sensitive and thermally unstable and attempts to synthesize the analogous silver derivative have been unsuccesful due to decomposition in solution even at -40°C.[124] In constrast, compounds **31** are air stable species. The molecular structure of **31** (M = Cu) shows that the basic skeleton consists of an Fe_2Cu triangle. CO and PPh_2 ligands bridge the iron atoms.[124]

There are several examples in which Cu^I, Ag^I or Au^I groupsact as bridging units. For example[125]

$$\mathbf{Ru_3(\mu\text{-}dppm)_2(CO)_8 + A \longrightarrow Ru_3(\mu\text{-}dppm)_2(CO)_8(\mu\text{-}A)} \qquad [46]$$

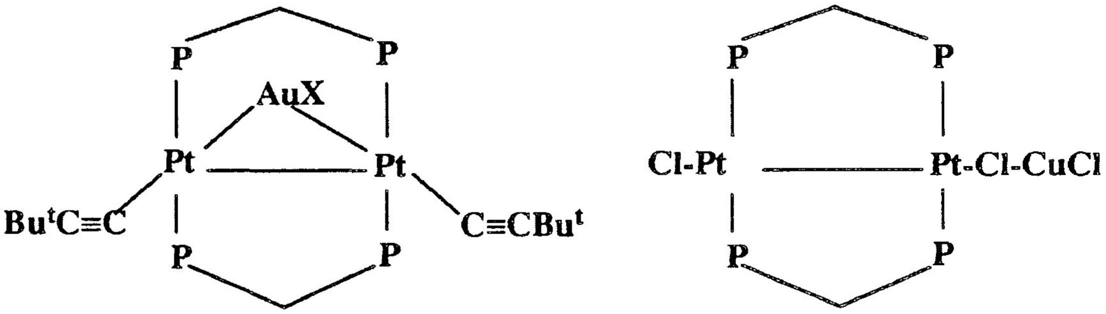
$$\mathbf{A = AgO_2CCF_3,\ Hg(O_2CCF_3)_2,\ Cu(NCMe)_4BF_4}$$

However, there are reactions in which CuCl or AuX behave differently. Both of them can react with $Pt_2Cl_2(\mu\text{-dppm})_2$ to give quite different products. The structures of these products are shown in **Figure 9** .[126]

$Cp_2Rh_2(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-MX})$ (M = Cu, Ag; X = Cl, I, CF_3CO_2) were prepared by treating $[Cp_2Rh_2(\mu\text{-CO})(\mu\text{-dppm})]$ with MX. The structures of the complexes were determined by X-ray diffraction and show that the three metal-atoms form a triangular cluster in a A frame arrangement.[127]

The Ru-Rh-dppm hydride cluster **32** can also interact with CuCl to form an unstable adduct which quickly converts into a Ru-Cu bimetallic compound as shown in **Scheme 12.**[128] The same Ru-Cu hydride product can also be obtained directly from reaction of the CuCl with the Ru hydride-dppm complex in toluene at 80°C.[128] Several other Ru-Cu complexes can also be obtained from the reactions of $RuH_2(dppm)_2$ with

Figure 9. Structure of Pt-Au and Pt-Cu Adducts



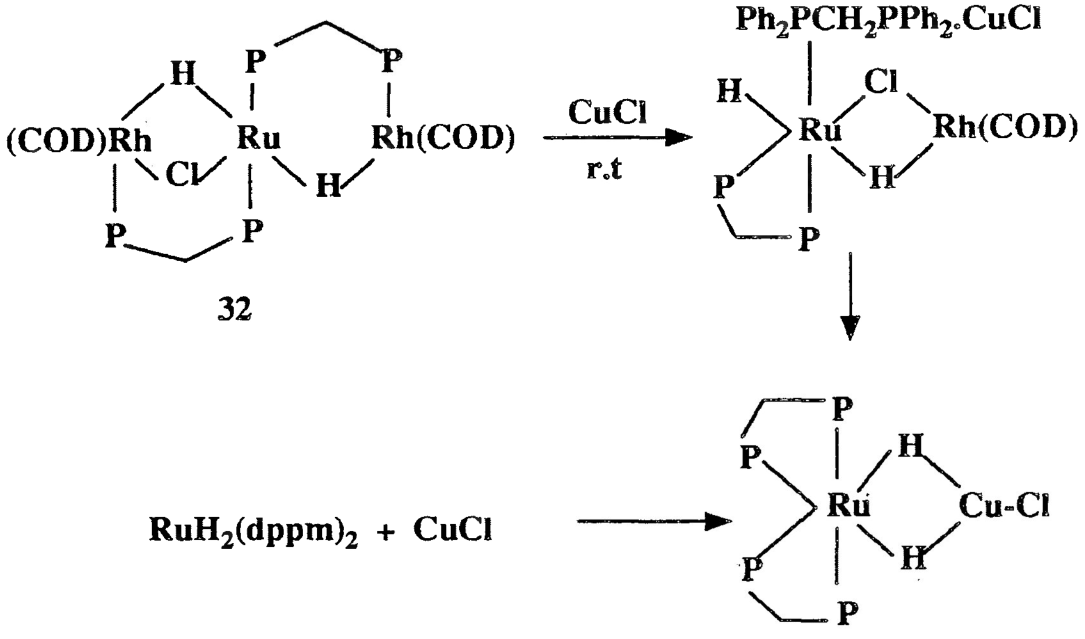
X = Cl, I

$Cu(MeCN)_4BF_4$ as shown in **Scheme 13.**[129]

Some heterometallic Cu^I complexes have bridging or semibridging CO groups such as $(tmed)Cu(\mu\text{-}CO)_2Mo(CO)(\eta^5\text{-}C_5H_5)$ and $[(tmed)Cu(\mu\text{-}CO)Co(CO)_3]$.[130] Their X-ray structures show that these complexes have longer Cu-CO and shorter OC-Co distances.[130]

In other situations, Cu^I, Ag^I and Au^I are found to induce ring opening reactions or the cleavage of metal-metal bonds and several heterobimetallic complexes have been prepared.[128-132] For example, on treatment of fac- or mer-$M(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ (M = Cr, Mo, W) with Cu^I, Ag^I or Au^I compounds, ring opening occurs to give heterobimetallic complexes as shown in equation **47.**[110]

Scheme 12. Formation of Ru-Cu Adduct

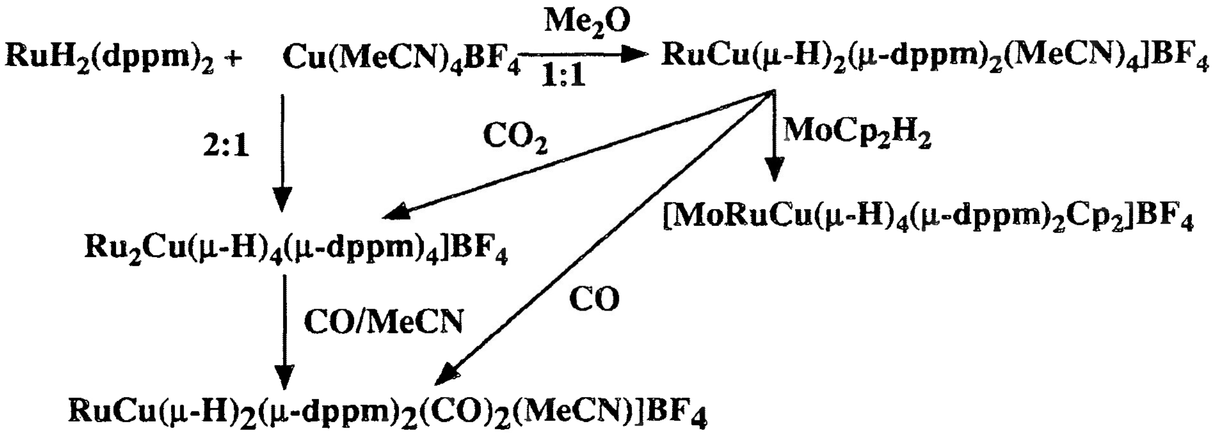


$$\text{mer-M(CO)}_3(\eta^1\text{-dppm})(\eta^2\text{-dppm}) + \text{CuX} \longrightarrow$$
$$\text{M(CO)}_2(\mu\text{-CO})(\mu\text{-dppm})_2(\mu\text{-X})\text{Cu} \qquad [47]$$

The molecular structure of this product (M = W) shows that the two metal centers, W-Cu, are almost symmetrically bridged by chlorine and semi-bridged by CO.[130]

Cu^I compounds can combine not only with transition metals but also with main group metals to give heterobimetallic complexes as shown in equation [48].[133]

Scheme 13. Reactions of $RuH_2(dppm)_2$ with $Cu(MeCN)_4BF_4$

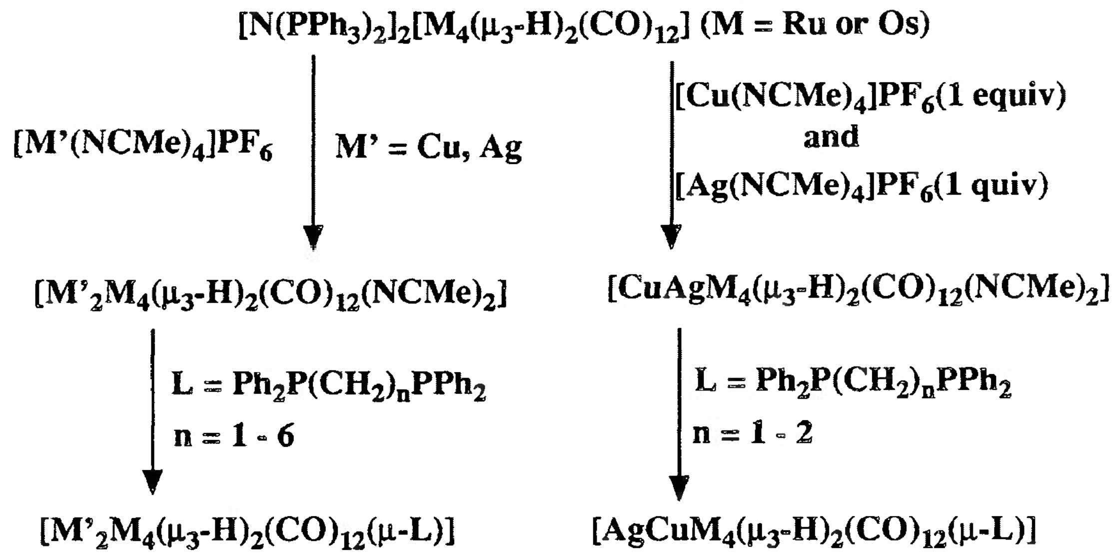


$$[CuX]_2(\mu\text{-}L)_3 + Ph_3SnLi \longrightarrow [CuSnPh_3]_2(\mu\text{-}L) \qquad [48]$$

$$L = Ph_2P(CH_2)_nPPh_2 \ (n = 3 - 4)$$

A wide variety of mixed metal cluster complexes containing one or two copper and/or silver atoms ligated by phosphines can be synthesized in very good yield in two steps.[134] First a Ru or Os cluster is treated with one or two equivalents of $[M(MeCN)_4]PF_6$ (M = Cu, Ag) and this is followed by a ligand exchange reaction in which the desired phosphine is exchanged with the labile MeCN on the unstable intermediate species as shown in **Scheme 14.**[134]

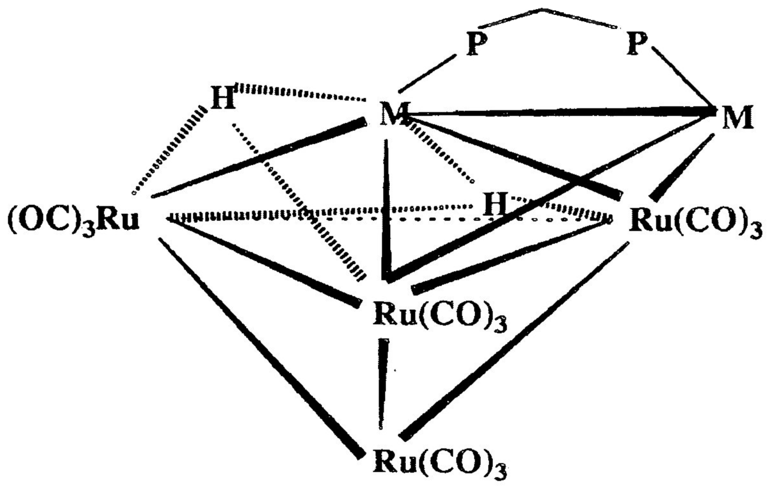
Scheme 14. Synthesis of $M_4M'_2$ Clusters



Similarly, treatment of a CH_2Cl_2 solution of $[N(PPh_3)_2]_2[Ru_4(\mu_3\text{-}H)_2(CO)_{12}]$ with two equivalents of $[M'(MeCN)_4]PF_6$ (M' = Cu, Ag or Au) at -30°C and with the subsequent addition of one equivalent of a bidentate phosphine, L (L = $Ph_2P(CH_2)_nPPh_2$, n = 1 - 6), affords dark red cluster compounds, $[M_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}L)(CO)_{12}]$.[134,135] The structure of the compounds is shown in **Figure 10**.[122,136]

If two equivalents of the complexes $[MX(PPh_3)]_4$ (M = Cu, Ag, Au; X = Cl, I) are

Figure 10. Structure of $M_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}dppm)(CO)_{12}$



added to a THF solution of $K_2[Ru_3(\mu_3\text{-}S)(CO)_9]$ in the presence of HPF_6, a mixture of clusters, $[MRu_3(\mu_3\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)]PF_6$, $[MRu_3(\mu_3\text{-}H)(\mu_3\text{-}S)(CO)_8(PPh_3)_2]$ and $[M_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)]$ are obtained.[121] The mixture can be readily separated by column chromatography on Florisil or alumina.[121]

5. Cu^I Hydroborate Complexes

Although the reducing abilities of BH_4^-, BH_3CN^- and $BH_2(CN)_2^-$ vary widely, all three species are able to coordinate with a variety of metals to form covalent complexes such as $M(BH_4)_n$.[96] The transition metal complexes of BH_4^-, BH_3CN^- and $BH_2(CN)_2^-$ can be stabilized by tertiary phosphines. Cu^I can form this kind of complex, such as $L_2Cu(BH_4)$, $LCu(BH_4)$, $L_3Cu(BH_3CN)$, $[L_2Cu(BH_3CN)]_2$, $L_2CuBH_2(CN)_2$, $L_3CuBH_2(CN)_2$ and $Cu(BH_3CN)(Diphos)_{1.5}$ ($L = PPh_3$, PPh_2Me, Diphos).[137,138] Studies on these hydroborate complexes indicate that the BH_4^- group is bonded to Cu^I either via a double hydrogen bridged structure, or via a simple Cu-H-B bond[139], while BH_3CN^- and $BH_2(CH)_2^-$ are invariably locked to Cu by the N atoms.[137] IR spectra have been successfully used to distinquish not only between η^1-BH_4 and η^2-BH_4 but also to establish the Cu-N bond absorption.[139]

VII. Ag^I COMPLEXES WITH dppm

Ag^I-phosphine complexes have been the subject of intense interest for many years. A variety of stoichiometries and structures are known for complexes of Ag^I with dppm, its derivatives and some related phosphines. The Ag^I-dppm complexes normally have been reported in terms of the Ag-dppm ratio of starting material which correspond to its final molecular framework.

1. Ag : dppm = 2 : 1 Complexes

Dinuclear complexes, $(Ph_2PCHRPPh_2)(AgO_2CR')_2$ (R = H or Me; R' = Me, Et, i-Pr and Ph) were synthesized from the direct reaction between AgO_2CR' and

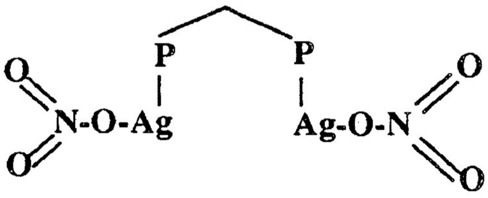
$Ph_2PCHRPPh_2$ in 2 : 1 ratio as shown in equation **[49]**.[141]

$$\mathbf{Ph_2PCHRPPh_2 + 2AgO_2CR' \longrightarrow (\mu\text{-}Ph_2PCHRPPh_2)(AgO_2CR')_2} \qquad [49]$$

The bridging bidentate nature of the ligands has been demonstrated using ^1H and ^{31}P NMR spectroscopy.[141]

The ligands L (L = dppm, dppe, dppp and Vpp) react with silver nitrate in a 1 : 2 molar ratio to produce $[Ag_2L](NO_3)_2$ complexes. These compounds are effectively non-conductors in nitromethane solution, (Λ_M values of ≤ 6 Ohm^{-1} cm^2 M), ruling out ionic structures and suggesting a coordinate structure as **Figure 11** shows.[142]

Figure 11. Structure of $Ag_2(\mu\text{-dppm})(NO_3)_2$

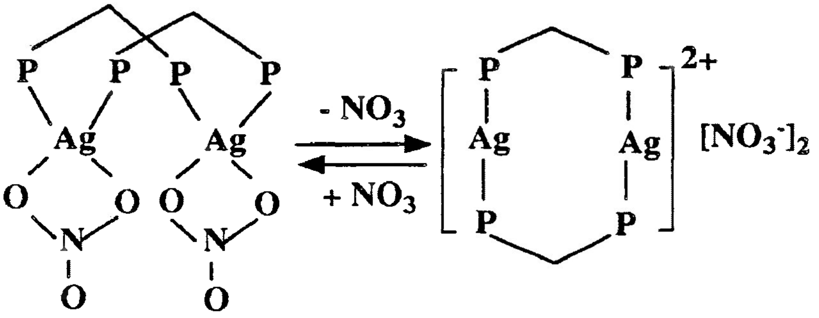


2. Ag : dppm = 2 : 2 Complexes

The complexes $[Ag_2(\mu\text{-}Ph_2PCHRPPh_2)_2](NO_3)_2$ (R = H, Me) can be directly synthesized from silver salts and dppm in 1 : 1 ratios as equation [50] shows.[143]

$$2AgNO_3 + 2Ph_2PCHRPPh_2 \xrightarrow{MeOH} [Ag_2(\mu\text{-}Ph_2PCHRPPh_2)_2](NO_3)_2 \quad [50]$$

NMR and X-ray structural studies show that the dppm ligands bridge the two silver atoms in these complexes.[143] The ^1H and ^{31}P NMR spectra indicate that $[Ag_2(\mu\text{-}Ph_2PCHRPPh_2)_2](NO_3)_2$ undergoes dissociation in solution to give the non-folded dicationic species with the dppm bound trans to one another as equation [51] shows.[143]

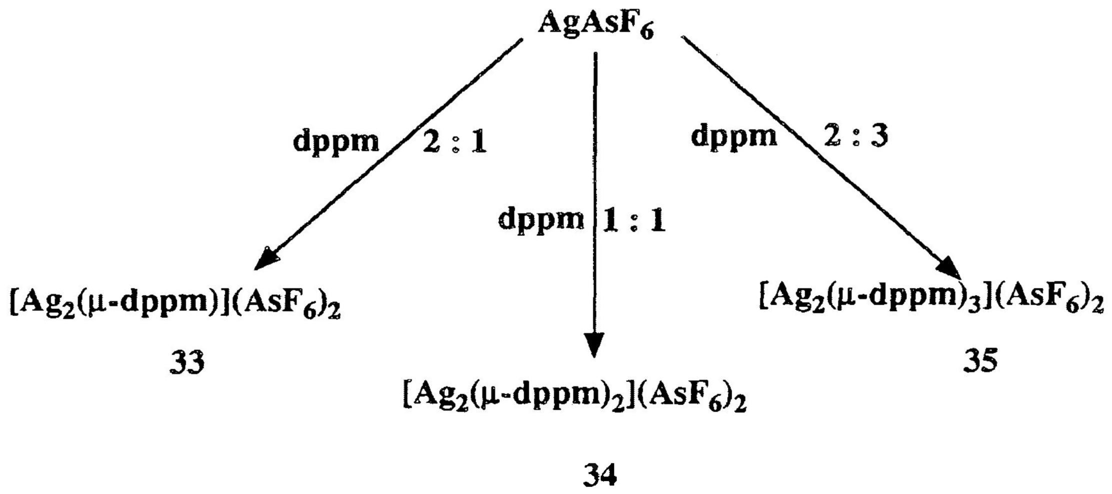


[51]

3. Ag : dppm = 2 : 3 Complexes

The synthesis of dppm-Ag complexes seems to be dependent on the reactant stoichiometries. Thus, detailed study on the reaction of $AgAsF_6$ and dppm shows that the product formed depends upon the Ag/dppm ratio of starting materials. When $AgAsF_6$ and dppm are mixed in a 1 : 0.5 ratio in $MeNO_2$ or Me_2CO, ^{31}P NMR spectra show that $[Ag_2(\mu\text{-dppm})]^{2+}$ is formed quantitatively. When the Ag:dppm ratio is changed to 1 : 1 in the reaction, $[Ag_2(\mu\text{-dppm})_2]^{2+}$ appears as the major product. If the reaction between $AgAsF_6$ and dppm is carried out in a 1 : 1.5 ratio, $[Ag_2(dppm)_3](AsF_6)_2$ is produced in good yield as **Scheme 15** shows.[144]

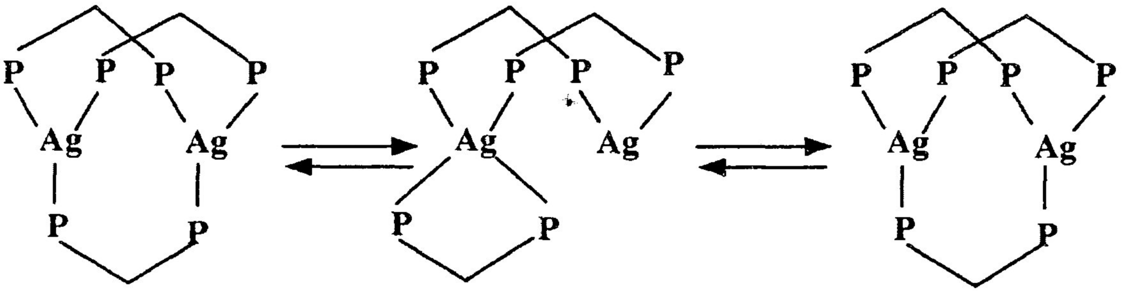
Scheme 15. Reactions of $AgAsF_6$ with dppm



When the amount of dppm is further increased, no new products were obtained.[144] At ambient temperature, only one broadened signal is observed in the ^{31}P NMR spectrum of 35, indicating intermolecular ligand exchange.[145] The ^{31}P NMR spectrum of the mixture of $[^{107}Ag_2(\mu\text{-dppm})_3](AsF_6)_2$ and $[^{107}Ag_2(\mu\text{-dmpm})_3](AsF_6)_2$ at ambient temperature also shows the formation of the mixed ligand binuclear cations, $[^{107}Ag_2(\mu\text{-dppm})_{3-x}(\mu\text{-dmpm})_x](AsF_6)_2]^{2+}$ (x = 1 or 2) as shown in equation [52].[145,146]

$$\begin{gathered}[Ag_2(\mu\text{-dppm})_3](AsF_6)_2 + [Ag_2(\mu\text{-dmpm})_3](AsF_6)_2 \rightleftharpoons \\ [Ag_2(\mu\text{-dppm})_{3-x}(\mu\text{-dmpm})_x](AsF_6)_2] \qquad [52]\end{gathered}$$

The ^{31}P NMR spectrum of $[^{107}Ag_2(\mu\text{-dppm})_3](AsF_6)_2$ provides evidence for an intramolecular exchange process which involves "end-over-end" exchange of bridging dppm. Variable-temperature NMR studies revealed that the Ag-P bonds are kinetically stable on the NMR time scale below 233K. At ambient temperature there is intramolecular ligand exchange. The inter-metal exchange of the phosphorus atoms of the dppm ligands occurs as equation [53] shows.[145]



[53]

4. Ag : dppm = 3 : 3 Complexes

A novel $[Ag_3(\mu_2\text{-dppm})_3(\mu_3\text{-Br})_2]^+$ species is synthesized from the reaction of AgBr and dppm in 1 : 1 ratio as shown in equation **[54]**.[147]

$$\mathbf{3AgBr + 3dppm \longrightarrow [Ag_3(\mu\text{-dppm})_3(\mu_3\text{-Br})_2]Br} \quad \mathbf{[54]}$$

X-ray analysis of the 3 : 3 compound revealed that the two Br atoms are each bound to all three Ag atoms and another Br atom is present as an isolated ion. Each dppm bridges two Ag atoms in a trimeric arrangment as the structural formula, $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-Br})_2]Br$, shows.[147] The complex $[(dppm)(AgO_3SMe)]_3$ also has a trimeric structure in $CHCl_3$.[148]

5. Ag : dppm = 4 : 4 Complexes

Metathesis of $[Ag_2(\mu\text{-Ph}_2PCHRPPh_2)_2](NO_3)_2$ (R = H and Me) with an excess of $K[PF_6]$ gives a tetranuclear complex $[Ag_4(\mu\text{-Ph}_2PCHRPPh_2)_4(NO_3)_2][PF_6]_2$ as shown in equation **[55]**.[143]

$$\mathbf{[Ag_2(\mu\text{-Ph}_2PCHRPPh_2)_2][NO_3]_2 + KPF_6 \xrightarrow{MeOH} [Ag_4(\mu\text{-Ph}_2PCHRPPh_2)_4(NO_3)_2][PF_6]_2} \quad \mathbf{[55]}$$

An X-ray structural study showed that the 4 : 4 cation $[Ag_2(\mu\text{-dppm})_2]_2(NO_3)_2(PF_6)_2$ consists of two equivalent $Ag(\mu\text{-dppm})_2Ag$ subunits.[143]

6. Ag : dppm = 1 : 2 Complexes

The reaction of AgO_3SMe with dppm produces a monomeric species **36** in $CHCl_3$ as shown in equation **[56]**.

$$\mathbf{AgO_3SMe + 2dppm \longrightarrow [(AgO_3Me)(dppm)_2],\ 36 \quad [56]}$$

Its structure is still uncertain.[148]

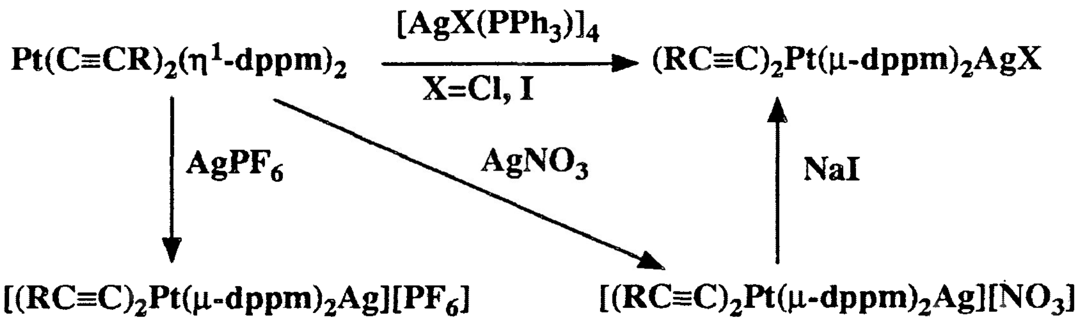
7. Heterometallic Binuclear Complexes

Dppm is an excellent ligand for grouping two metal centres together to form eight membered ring complexes, such as $M(\mu\text{-dppm})_2Ag$ (M = Hg, Cu, Ru, Pt, Cr, Mo, W, etc.). Many other complexes containing the skeleton $M(\mu\text{-dppm})Ag$ also have been described.[145]

A series of heterobimetallic complexes $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2MX_n]$ (M = Hg, Cu, Ag, Au, Cr, Mo, W; X=Cl, Br, $MeCO_2$) generated from Pt^{II} acetylides containing monodentate dppm and MX_n have been reported.[149] When different Ag^I compounds were used as starting materials, several ionic and neutral complexes were obtained.

(see **Scheme 16**)

Scheme 16. Synthesis of Pt-Ag Complexes



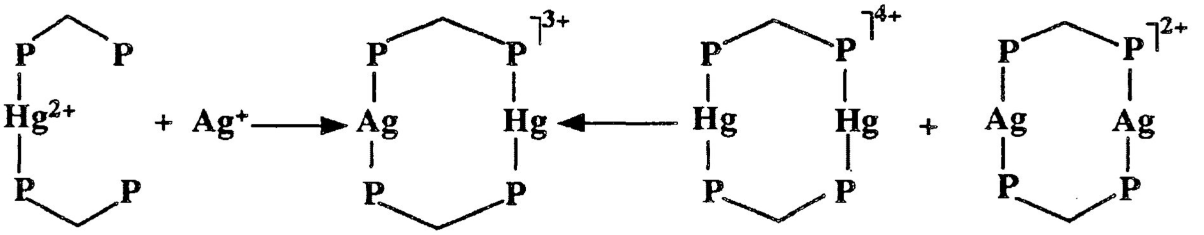
The $^1H\text{-}\{^{31}P\}$ resonance for the CH_2 protons of dppm in the NMR spectrum of $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$ appears as a singlet with ^{195}Pt satellites at room temperature. At -80°C in CD_2Cl_2 the singlet becomes very broad but still does not resolve indicating that there are fluxional processes which equilibrate the CH_2 protons.[131]

The interaction between Pt and Ag in $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$ is not very strong. If the complex is treated with $Rh_2Cl_2(CO)_4$, Ag is replaced by Rh to give $[ClPt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CR)Rh(CO)][AgCl_2]$.[93]

The $Ag^I\text{-}Pt^{II}$ complexes, $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$, also can be prepared from a one-pot reaction in acetone at 0°C as equation **[57]** shows.[149]

$$\mathbf{Pt(\eta^1\text{-}dppm)_2Cl_2 + AgO_2CMe + PhC{\equiv}CH \longrightarrow}$$
$$\mathbf{[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]} \qquad [57]$$

The reaction of $Hg(\eta^1\text{-dppm})_2(O_3SCF_3)$ and AgO_3SCF_3 leads to heterobimetallacyclic complexes in high yield according to equation **[58]**. The mixed-metal compound is also accessible from the rearrangment of the respective homobimetallic mercury and silver rings.[150]



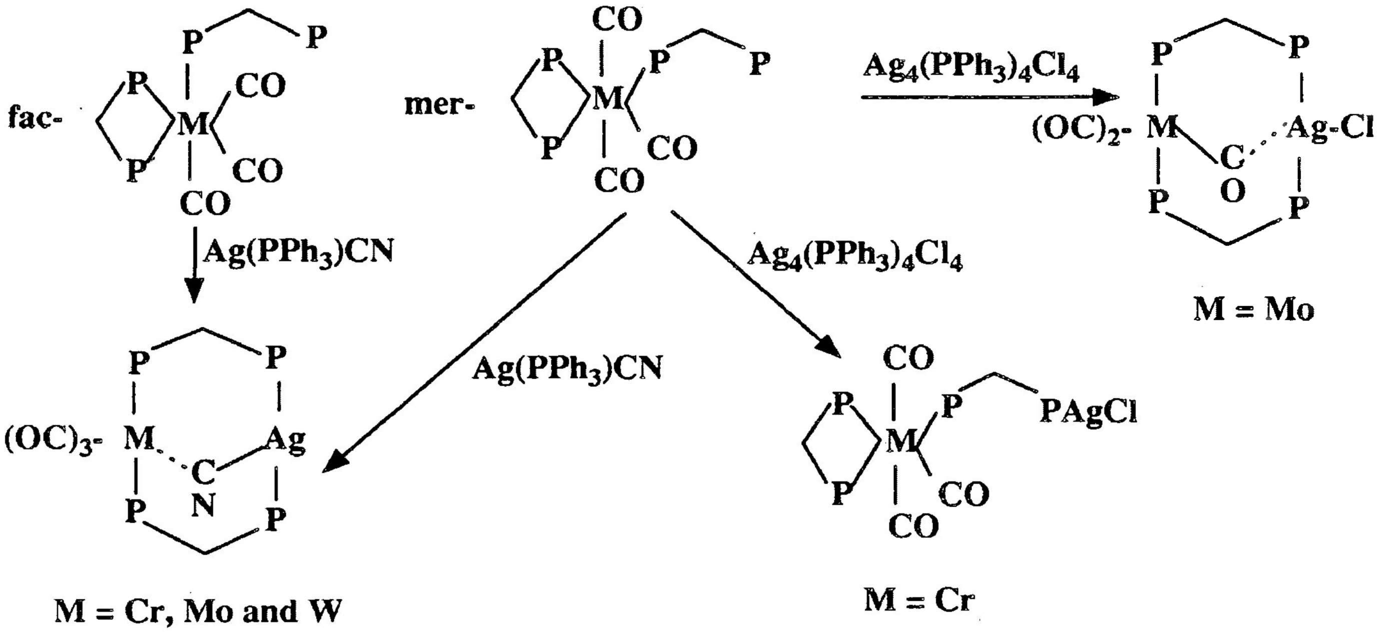
[58]

Alternatively, this Hg^{II}-Ag^{I} complex, $[AgHg(\mu\text{-dppm})_2]^{3+}$, also can be synthesized directly from equivalent amounts of $Hg(SbF_6)_2$ and $AgSbF_6$ in $MeNO_2$ in the presence of two equivalents of dppm.[144]

Treatment of fac- or mer-$[M(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$ with $Ag(PPh_3)(CN)$ gives stable yellow heterobimetallic complexes of the type $[M(CO)_3(\mu\text{-dppm})_2AgCl]$ (M = Cr, Mo, W). Only mer-$[M(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$ reacts $[Ag_4Cl_4(PPh_3)_4]$, to give an unstable heterometallic dimer $[M(CO)_3(\eta^2\text{-dppm})(\mu\text{-dppm})AgCl]$ (M = Cr) (see **Scheme 17**). In contrast, redox reactions occur on treatment of either fac- or mer-

$[M(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$ (M = Cr, Mo or W) with $AgNO_3$.[130]

Scheme 17. Reactions of $M(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ with Ag^I Salts



There is considerable interest in mixed-metal cluster complexes containing CO and dppm. However, reports of such species containing silver are still relatively rare.[151] The reactions shown in **Scheme 14** and already discussed provide a new, flexible synthetic procedure to prepare such $M_4M'_2$ core complexes (M = Ru, Os; M' =

Ag, Cu).[152]

The Ag(μ-dppm)Ag unit also has been established in the cluster $[Ag_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-dppm})(CO)_{12}]$ by X-ray crystalltography.[142]

A similar reaction in which Ag is introduced into a $[Ru_4(\mu_3\text{-}H)_3(CO)_{12}]^+$ cluster has been observed and is illustrated in equation **[59]**.[153]

$$\mathbf{[N(PPh_3)_2][Ru_4(\mu_3\text{-}H)_3(CO)_{12}] + M(NCMe)_4PF_6\ (M = Cu, Ag) \longrightarrow}$$

$$\mathbf{MRu_4(\mu_3\text{-}H)_3(CO)_{12}(NCMe) \xrightarrow{dppe} [MRu_4(\mu_3\text{-}H)_3(CO)_{12}(\mu\text{-}L)]} \quad [59]$$

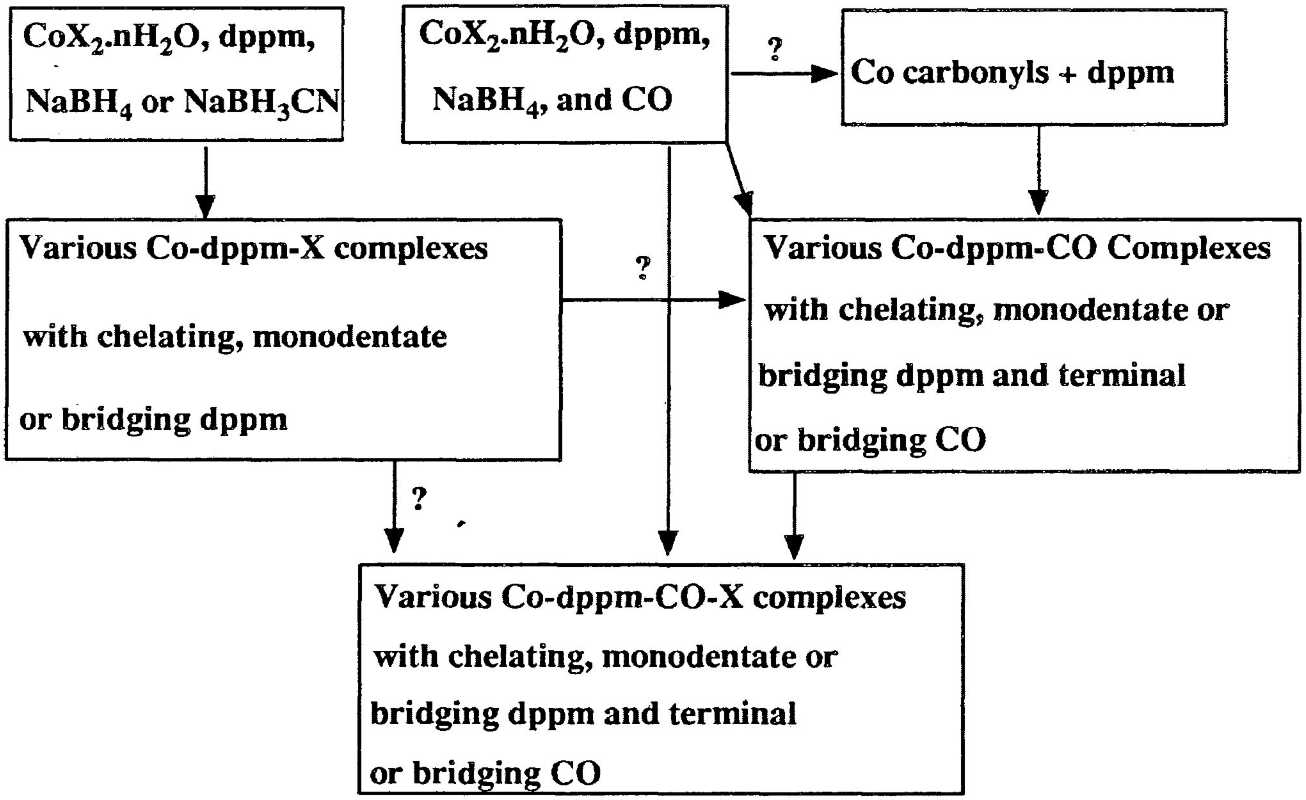
$^{109}Ag\{^1H\}$ INEPT NMR spectroscopy shows that only a single silver environment in these mixed metals complexes is visible at ambient temperature, thus directly confirming that compound, $[Ag_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-dppm})(CO)_{12}]$ is undergoing a fluxional process in solution.[153]

RESEARCH PROPOSAL

From the preceding introduction, it is clear that the most widely used route to metal-CO-phosphine complexes is the treatment of metal carbonyls with phosphines. A second relatively common route involves reactions of metal-phosphine complexes with CO. As mentioned earlier, since many metal carbonyls are air sensitive, volatile, extremely toxic and some of them are either not readily available or expensive, it is therefore not always convenient to use them directly. In the past several years, the Holah-Hughes group has been developing a new method for the synthesis of metal-CO-phosphine complexes with the metal in a variety of oxidation states. As has already been outlined, higher oxidation state metal salts can be reduced directly by using $NaBH_4$ or $NaBH_3CN$ in the presence of a phosphine and CO to give metal-phosphine-CO products. The exact nature of the products depend upon the reaction conditions.

The proposed research, based upon earlier work by the Holah-Hughes group is divided into three areas.

1. In the reactions of Co^{II} and Ni^{II} by $NaBH_4$ or $NaBH_3CN$ in the presence of dppm with or without CO, several complexes containing chelating, bridging, or monodentate dppm have been prepared. Their properties, such as oxidation, formation of heterometallic complexes, their structures and spectroscopy also have been studied extensively as already discussed. However, what has not yet been established are the reaction pathways whereby the various products are formed. Some known and possible interrelationships are shown below and these will be investigated further in this thesis.



2. $Ni(CO)_2(\eta^1\text{-dppm})_2$, **13**, possesses two free phosphorus atoms which can act as donors towards other metal atoms and such reactions should lead to the formation of heterometallic complexes. Although some of these complexes have been studied preliminarily (such as Ni-Pt, Ni-Pd, and Ni-Ni complexes, see early discussion) no d^{10}-d^{10} complexes have yet been obtained and this will be investigated further in this thesis.

3. $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm-}BH_2)]$, **11**, the first stable metallaborane complex has been prepared in very low yield as mentioned before. We propose to try and improve the yield and establish the mechanism by which, this interesting and important compound **11**, (see section I.3) is formed. This will be investigated in several ways.

a. We will reinvestigate the reaction which is known to give the borane complex by the route reported above by varying the reaction conditions such as time, temperature, molar ratios of reactants, rate of BH_4^- addition, etc..

b. Since several Co^I-dppm-CO complexes have already been isolated directly or indirectly from Co^{II}/dppm/ BH_4^-/CO reactions, we will be able to examine reactions between Co^I-dppm-CO compounds and both BH_3 and BH_4^- as possible new high-yield routes to **11**.

c. We will try to use the known compounds, $Co(CO)_3BH_2$[189] and $[BH_2(\eta^2\text{-dppm})]I$[190] as a starting material to synthesize the Co-BH_2 complex **11**.

If some of the routes are proven to be effective, it also may establish the pathway whereby **11** is formed and the procedure might be adaptable to the synthesis of other metallaboranes.

Numerical Codes to Identify Compounds in Experimental and Results & Discussion Sections

1. $CoX(\eta^1\text{-dppm})_3$ (X = Cl, 1a; X = Br, 1b)
2. $Co_2X_3(dppm)_2$ (X = Cl, 2a; X = Br, 2b)
3. $[CoH(dppm)_2X]X$ (X = Cl, 3a; X = Br, 3b)
4. $CoX(CO)_2(\eta^1\text{-dppm})_2$ (X = Cl, 4a; X = Br, 4b)
5. $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]X$ (X = Cl, 5a; X = Br, 5b; X = BPh_4, 5c; X = $Co(CO)_4$, 5d)
6. $[Co(CO)(\eta^2\text{-dppm})_2]X$ (X = Cl, 6a; X = Br, 6b; X = BPh_4, 6c; X = $Co(CO)_4$, 6d)
7. $[Co_2(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]Y.S$ (X = Y = Cl, no S, 7a; X = Y = Br, S = $4CH_2Cl_2$, 7b; X = Br, Y = BPh_4, no S, 7c)
8. $[Co(CO)_4(\eta^1\text{-dppm})]Br.C_6H_6$
9. $Co_2(CO)_4(\mu\text{-dppm})_2$
10. $Co_2(CO)_2(\mu\text{-CO})_2(\mu\text{-dppm})_2$
11. $Ni(CO)_2(\eta^1\text{-dppm})_2$
12. $[NiCu(CO)_2(\mu\text{-dppm})_2(MeCN)_2]X.S$ (X = ClO_4, S = $0.4CH_2Cl_2$, 12a; X = ClO_4, no S, 12b; X = BPh_4, no S, 12c; X = PF_6, no S, 12d)
13. $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$
14. $[Ag_2(\mu\text{-dppm})_3]X_2.S$ (X =NO_3, S = CH_2Cl_2, 14a; X = O_3SCF_3, no S, 14b; X = AsF_6, no S, 14c)
15. $[CoRh(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]Y$ (X = Y = Cl, 15a; X = Cl, Y = BPh_4, 15b)
16. $Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm-}BH_2)$
17. $Co_2(\mu\text{-CO})_2(CO)_4(\mu\text{-dppm})$
18. $[Co(CO)_3(\eta^1\text{-dppm})_2][Co(CO)_4]$

EXPERIMENTAL

Reagents and Solvents Dppm was obtained from Strem Chemicals Inc., and was used without further purification. $NaBH_4$ (Alfa) and $NaBH_3CN$ (Alfa) were stored under dry conditions. $NiCl_2.6H_2O$, $CoBr_2.xH_2O$, $CoCl_2.6H_2O$, $NaPF_6$, $BH_3.THF$, $AgNO_3$, $NaBPh_4$, $Co_2(CO)_8$ and all other chemicals were reagent grade and were used without further purification. The compounds $CoX(\eta^1\text{-dppm})_3$,[18] $Co_2X_3(dppm)_2$,[18] $[CoH(dppm)_2X]X$ (X = Cl, Br),[18] $Ni(CO)_2(\eta^1\text{-dppm})_2$,[53] $Ni_2(CO)_3(\mu\text{-dppm})_2$,[53] $Cu(MeCN)_4ClO_4$,[186] $[Rh(CO)Cl]_2$,[187] $Pt(COD)_2Cl_2$,[188] $Co(CO)_3BH_2$,[189] and $[H_2B(\eta^2\text{-dppm})]I$[190] were prepared as reported in the literature. All the solvents used were reagent grade and were degassed prior to use and storage under N_2 in a glovebox. Reactions involving $Co_2(CO)_8$ or $BH_3.THF$ require dry solvents. Therefore benzene, toluene and THF were dried by refluxing with CaH_2 and stored under N_2 in a glove box.

Physical Measurements Samples and reagents were protected from atmospheric oxidation during weighing and data collection. Microanalyses for C, H and N were acquired in our laboratories using a Control Equipment Corporation model 240XA analyzer using V_2O_5 as a combustion aid. Infrared spectra (Nujol mulls) were recorded on Beckman IR-4250 or Bruker IFS 66 (for FTIR) spectrophotometers. A Bruker AC-E 200 NMR spectrometer equipped with a variable temperature controller (BVT-1000S) was used to record ^1H, ^{13}C and ^{31}P spectra at 200 MHz, 50.3MHz and 81MHz respectively. Chemical shifts are reported as δ values with positive shifts downfield of Me_4Si for ^1H and ^{13}C and downfield of the signal of external 85% H_3PO_4 for ^{31}P spectra. For the ^{31}P spectra, frequency lock was provided either by a deuterated solvent or, in the cases of reaction mixtures in which deuterated solvents were not used, a coaxial D_2O insert. Molecular weights were determined by vapour pressure osmometry using a Wescor model 5500 instrument. Mass spectra were acquired using an Hitachi-Perkin-Elmer RMU-7 spectrometer. X-ray fluorescence spectra was measured by a Philips PW 1352 X-ray powder diffractometer. Scanning Electron Microscopy (SEM) Spectra were collected from a Hitachi 570 Energy Dispersive X-ray Microanalysis equipped with a Tracor Northern 5502 Energy Dispersive X-ray spectrometer.

Synthesis of the Compounds Syntheses were generally carried out in a 100mL, 2-necked flask either in a fume hood with CO passing followed by work-up in a N_2 filled glovebox, or directly in the glovebox. CO was passed into the reaction flask at an approximate rate of 30 bubbles per minute. In general, it was found to be easier to isolate pure products in good yield from reactions using $CoBr_2$ than from those from those in which $CoCl_2$ was used. The water content of commercial $CoBr_2.xH_2O$ is listed as 28% and implies a molecular formula $CoBr_2.4.7H_2O$. This was used in calculation of the amounts of cobalt in the following reactions. Small changes in the amounts of Co if $CoBr_2.6H_2O$ is used as the molecular formula can cause major changes in a reaction.

I. Reactions of $CoX(\eta^1\text{-dppm})_3$, 1; $Co_2X_3(dppm)_2$, 2; and $[CoH(\eta^2\text{-dppm})_2X]X$, 3, with CO or CO/$NaBH_4$

1. Reactions of $CoX(\eta^1\text{-dppm})_3$ with CO

$CoCl(CO)_2(\eta^1\text{-dppm})_2$ 4a: Carbon monoxide was passed into a solution of $CoCl(\eta^1\text{-dppm})_3$ (0.5g, 0.4 mmol) in benzene (20mL), with stirring, for 30 min.. The colour of the solution quickly turned from deep green to orange. To the resulting solution, hexane (20 mL) was added and the mixture was stored at 0°C for 48 h. The yellow-orange crystalline product which formed (a mixture of **5a** and **6a**, see Results and Discussion Section) was collected, washed with diethyl ether and hexane, and then dried under vacuum. The solid was then dissolved in benzene (20 mL) and the solution was heated to 50-60°C with CO passing until most of the solvent had evaporated. Peroxide-free diethyl ether (10 mL) was added to the viscous residue and the resulting yellow solid was collected by filtration, washed with diethyl ether and dried to give **4a** (0.25 g, 68%). Anal. Calcd for **4a** ($C_{52}H_{44}O_2ClP_4Co$): C, 67.95; H, 4.82. Found: C, 67.69; H, 5.07. IR: ν_{co} 1988(s), 1927(s), 1900(m) cm^{-1}. ^1H NMR ($CDCl_3$), δ 3.1 (m, vb, 4H, P-CH-P). $^{31}P\{^1H\}$ NMR (C_6D_6), simplified AA'XX' pattern, $\delta P_A = \delta P_{A'} =$ 54.8 (dd), $\delta P_X = \delta P_{X'} = -24.8$ (dd), J = 41.7 and J = 29.5 Hz.

$CoBr(CO)_2(\eta^1\text{-dppm})_2$ 4b: The corresponding yellow bromo compound **4b** was prepared from $CoBr(\eta^1\text{-dppm})_3$ by a virtually identical procedure (yield, 72%).

Anal. Calcd for **4b** ($C_{52}H_{44}O_2BrP_4Co$): C, 64.81; H, 4.60. Found: C, 65.07; H 5.14. IR: ν_{co} 1988(s), 1927(s), 1900(m) cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 3.1 (m, vb, 4H, P-CH_2-P). $^{31}P\{^1H\}$ NMR (C_6D_6), Simplified AA'XX' pattern, $\delta P_A = \delta P_{A'} = 51.2$ (dd), $\delta P_X = \delta P_{X'} = 24.8$ (dd), J = 42.0 and J = 29.4 Hz. Mol. Wt.: Calcd 963.65. Found 955.2 and 978.8.

[Co(CO)$_2$(η^1-dppm)(η^2-dppm)]Br **5b**: Treatment of CoBr(η^1-dppm)$_3$ (0.5 g, 0.39 mmol) in benzene (20 mL) with CO followed by addition of hexane (15 mL) and storage at O°C for 48 h in the manner outlined above yielded an orange crystalline mixture of **5b** and **6b**. This was dissolved in benzene (10 mL) under CO, hexane (10 mL) was added, and the solution heated to 70°C under CO. It was then cooled to toom temperature and allowed to stand for 8 h. Pure orange crystalline **5b** (0.13 g, 35%) was obtained. Anal. Calcd for **5b** ($C_{52}H_{44}O_2BrP_4Co$): C, 64.81; H, 4.60. Found: C, 64.95; H, 4.83. IR: ν_{co} 1990(s), 1925(s), 1898(sh) cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 2.2 (m, vb, 2H, η^2-P-C$\underline{H}_2$-P), 3.1 (m, vb, 2H, η^1-P-C$\underline{H}_2$-P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ambient temp., fluxional system) δ -3.44 (unresolved, η^2-$\underline{P}_A$-CH_2-$\underline{P}_B$), 50.35 (dt, Co-$\underline{P}_C$-CH_2-P_D), -28.66 (d, Co-P_C-CH_2-$\underline{P}_D$), $J_{AC} = J_{BC} = 24.5$, $J_{CD} = 50.1$ Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, -85°C), δ 12.6 (dd, $\underline{P}_A$), -21.0 (dd, $\underline{P}_B$), 49.3 (dt, $\underline{P}_C$), -31.6 (d, $\underline{P}_D$); $J_{AB} = 113.0$, $J_{AC} = 109.0$, $J_{BC} = 58.0$, $J_{CD} = 50.7$ Hz.

[Co(CO)$_2$(η^1-dppm)(η^2-dppm)]BPh$_4$ **5c:** The corresponding BPh_4^- salt 5c was prepared by a variation on the above method. A stirred solution of CoBr(η^1-dppm)$_3$ (0.5 g, 0.39 mmol) in benzene (20 mL) was treated with CO for 30 min and $NaBPh_4$ (0.2 g, 0.58 mmol) in tetrahydrofuran (2 mL) was added. The solution was allowed to stand at 0°C for 48 h under CO during which time red crystals (mainly **5c** with some **6c**) were deposited. These were collected and washed several times with diethyl ether followed by hexane. The crystals were then dissolved in a mixture of benzene (10 mL) and dichloromethane (10 mL) and heated to boiling under CO. The solution was cooled and allowed to stand at room temperature for 8 h after which the orange crystals of **5c** (0.2 g, 40%) were collected. Anal. Calcd for **5c** ($C_{76}H_{64}O_2P_4BCo$): C, 75.88, H, 5.36. Found: C, 75.68, H, 5.29. IR and NMR (^1H and ^{31}P) identical to those of **5b**. IR: ν_{CO} 1990(s), 1924(s), 1900(sh) cm^{-1}. ^1H NMR ($CDCl_3$), δ 2.2 (m, vb, 2H, η^2-P-C$\underline{H}_2$-P), 3.1 (m, vb, 2H, η^1-P-C$\underline{H}_2$-P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ambient temp., fluxional system), δ -3.5 (unresolved, η^2-$\underline{P}_A$-CH_2-$\underline{P}_B$), 50.2 (dt, Co-$\underline{P}_C$-CH_2-P_D), -28.1 (d, Co-P_C-CH_2-$\underline{P}_D$), $J_{AC} = J_{BC} = 25.9$Hz, $J_{CD} = 55.9$Hz.

The analogous complex **5a** (prepared from $CoCl_2$) was characterized only spectroscopically.

[Co(CO)(η^2-dppm)$_2$]X (X = Br, 6b; X = BPh$_4$, 6c): The initial steps in the syntheses of **6b** and **6c** are virtually identical to those recorded above for **5b** and **5c**. After the first filtration (removing mainly **5b** and **5c**) the filtrates were treated with additional hexane (10 mL) and the solutions were allowed to stand at 0°C for a further 48 h under N_2. The resulting red crystals of **6b** and **6c** obtained respectively in the two syntheses were washed with diethyl ether followed by hexane several times (for **6b**) or benzene followed by hexane (for **6c**). The two products were recrystallized (benzene/hexane 1 : 1 for **6b**, and benzene/dichloromethane 1 : 1 for **6c**) and were obtained in yields of 37% and 39% respectively. Anal. Calcd for **6b** ($C_{51}H_{44}OBrP_4Co$): C, 65.47; H, 4.74. Found: C, 65.17; H, 5.06. IR: υ_{CO} 1930(s) cm^{-1}. ^1H NMR ($CDCl_3$), δ 2.1 (m, vb, 4H, η^2-P-CH_2-P). ^{31}P-{^1H} NMR ($CDCl_3$), δ -6.78. Anal. Calcd for **6c** ($C_{75}H_{64}OBP_4Co$): C, 76.68; H, 5.49. Found: C, 76.51, H 5.25. IR: v_{co}1930(s) cm^{-1}. ^1H NMR ($CDCl_3$), δ 2.1 (m, vb, 4H, η^2-P-CH_2-P). ^{31}P{^1H} NMR ($CDCl_3$), δ -6.89 or ^{31}P{^1H} NMR (CD_2Cl_2), δ -6.1.

As with **5a, 6a** (prepared similarly from $CoCl_2$) was characterized only spectroscopically.

6b can also be prepared directly from the reaction of $CoBr_2.4.7H_2O$ and $NaBH_4$ in the presence of dppm under a CO atmosphere in high yield. $CoBr_2.4.7H_2O$ (0.91 g, 3mmol) in EtOH (20mL) was mixed with dppm (2.3 g, 6mmol) in toluene (20 mL). Then, $NaBH_4$ (0.10 g, 3mmol) in EtOH (20 mL) was added over a 30 min. period. The solution turned orange after stirring for another 30 min. and the resulting yellow-orange solid was filtered off, washed with benzene, EtOH and hexane sequentially and dried under vacuum. Yield 0.23g, 83%.

In a similar way, **6c** was obtained in 88% yield, if $NaBPh_4$ (0.1 g, 3mmol) in THF (2 mL) was added to the reaction solution immediately after addition of the $NaBH_4$.

6c was also obtained from the reaction of $[Co_2(\mu\text{-}Br)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]Br.4CH_2Cl_2$, **7b**, with dppm. **7b** (1 g, 0.68mmol) and dppm (0.52 g, 1.5mmol) were dissolved in CH_2Cl_2 (20 mL) and stirred for 30min. under a CO atmosphere. The brown solution slowly turned orange. Hexane (10 mL) was then added and a red crystals of **6c** (0.54 g) were obtained in 63% yield.

2. Reactions of $CoX(\eta^1\text{-dppm})_3$ with $CO/NaBH_4$

$[Co(CO)_4(\eta^1\text{-dppm})]Br.C_6H_6$ 8: $CoBr(\eta^1\text{-dppm})_3$ (1.3 g, 1 mmol) was dissolved in benzene (20 mL) and CO was passed (with stirring) for 5 min. A solution of $NaBH_4$ (0.04 g, 1 mmol) in ethanol (10 mL) was then added over a period of 10 min. after which the mixture was stirred for 1 h. The orange solution turned deep red. Most of the solvent was then removed by passage of a slow stream of N_2/CO and a red solid precipitated. This was removed by filtration, washed several times with peroxide-free ether and then hexane, and dried under reduced pressure to give pure **8** (0.16 g, 22%). Anal. Calcd for **8** ($C_{35}H_{28}O_4BrP_2Co$): C, 58.91; H, 3.93. Found: C, 59.03; H, 3.35. IR: ν_{co} 2000(s), 1950(s), 1920(s) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: 59.52 (d, Co-$\underline{P}$-CH_2-P), -25.96 (d, Co-P-CH_2-$\underline{P}$), J_{pp} 75.16 Hz. The presence of benzene was confirmed by mass spectrometry. MS : 79 (8%), 78 (100%).

Complex **8** can also be prepared (36% yield) by treating $CoBr(CO)_2(\eta^1\text{-dppm})_2$

4b with CO and $NaBH_4$ in a manner similar to that outlined above.

3. Reactions of $Co_2X_3(dppm)_2$ with CO or $CO/NaBH_4$

<u>**Reactions of $Co_2X_3(dppm)_2$ with CO**</u>: Treatment of a solution of pure $Co_2Br_3(dppm)_2$ (0.47 g, 0.42mmol) in ethanol/benzene (1 : 1, 20 mL) with CO produced a green solution with complex ^{31}P NMR spectra. Several ^{31}P NMR spectra were recorded under a variety of different conditions, as follows

i. $^{31}P\{^1H\}$ NMR (room temp., reaction solution), δ -6 (s), -3.5 (br) and +51.8 (br),

ii. $^{31}P\{^1H\}$ NMR (low temp. -68°C, reaction solution), δ -6 (s), 51.8(dt), 14.1(dd), -19.5(dd), -28(d),

iii. $^{31}P\{^1H\}$ NMR (room temp., reaction solution with addition of dppm), δ -6 (s), -3.5 (br) and +51.8 (br).

iv. $^{31}P\{^1H\}$ NMR (room temp., reaction solution with extra $CoBr_2$), δ -6 (s), -3.5 (br) and +51.8 (br).

v. $^{31}P\{^1H\}$ NMR (room temp., solution of pure **5b** and $CoBr_2.4.7H_2O$ in ethanol/benzene), δ -6 (s), -3.5 (br) and +51.8 (br).

The same spectra were also observed after the reaction of [Co(CO)(η^2-dppm)$_2$]Br (1 equiv) with CoBr$_2$.4.7H$_2$O (1 equiv) in EtOH/CH$_2$Cl$_2$ with CO passing.

Reactions of Co$_2$X$_3$(dppm)$_2$ with CO/NaBH$_4$: Co$_2$Cl$_3$(dppm)$_2$ (0.5 g, 0.5 mmol) in THF and NaBH$_4$ (0.04 g, 1 mmol) were mixed, saturated with CO and stirred for 1 h. The green solution slowly turned brown. Solution ^{31}P NMR spectra show peaks at δ 69.5, 52.2, 36.9 and -5.46. A discussion of the above reactions can be found in the Results and Discussion Section.

4. Reactions of [CoH(η^2-dppm)$_2$X]X with CO or CO/NaBH$_4$

[Co$_2$(μ-Br)(CO)$_2$(μ-CO)(μ-dppm)$_2$]Br.4CH$_2$Cl$_2$ 7b:
[CoH(η^2-dppm)$_2$Br]Br, **3b**, (0.55 g, 0.6 mmol) was suspended in ethanol/toluene (1 : 1) solution and NaBH$_4$ (0.07 g, 1.8 mmol) in EtOH (10 mL) was added. The yellow solution slowly turned brown. The solution, which was stirred for 1 h, produced a large amount of brown solid. This was filtered off, dissolved in CH$_2$Cl$_2$ and Et$_2$O was allowed to diffuse slowly into the solution. Needle-like brown crystals, **7b**, were obtained from the solution. Yield 46%. Anal. Calcd for **7b** (C$_{57}$H$_{52}$O$_3$Br$_2$P$_4$Co$_2$Cl$_8$): C, 46.53; H, 3.54. Found: C, 46.76; H, 3.87. IR: ν_{co} 1950(s), 1965(sh), 1910(s), 1815(s) cm^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$), δ 52.2 (s). The presence of CH$_2$Cl$_2$ was confirmed by mass spectrometry. MS: MS: 88(5%), 86(33%), 84(56%) and 49(100%).[192] The spectroscopic data are identical in all respects with those of an

authentic sample.[159]

$[Co_2(\mu\text{-}Br)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]BPh_4$ 7c: The corresponding BPh_4 compound was easily prepared from the metathetical reaction of **7b** with $NaBPh_4$. Thus, **7b** (1g, 0.7mmol) in CH_2Cl_2 (20 mL) and $NaBPh_4$ (0.3g, 0.75mmol) were mixed and stirred for 2 h. When hexane (20 mL) was added to the solution, a red solid was obtained. Yield 86%. The solid was purified by recrystallization from CH_2Cl_2 and hexane. Anal. Calcd for **7c** ($C_{77}H_{64}O_3BrP_4Co_2B$): C, 68.05; H, 4.75. Found: C, 68.15; H, 4.81. IR: ν_{co} 1950(s), 1965(sh), 1910(s), 1815(s) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 52.2 (s).

Conversion of $[Co_2(\mu\text{-}Br)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]Br.4CH_2Cl_2$, 7b, to $Co_2(CO)_4(\mu\text{-}dppm)_2$, 9: **7b** (0.5 g, 0.34 mmol) was suspended in benzene (15 mL) and saturated with CO. $NaBH_4$ (0.035 g, 0.9 mmol) was added and the solution was stirred for 4 h with CO passing. A deep green solid was obtained and characterized by IR and NMR spectroscopy which gave spectra identical with those of an authentic sample of **9**.[38]

II. Experiments to study the Mechanism of $CoBr_2/dppm/NaBH_4/CO$ Reactions

(A full account of this work can be found in the Results and Discussion Section)

III. Synthesis of Heterobimetallic Complexes

1. Reaction of $Ni(CO)_2(\eta^1\text{-dppm})_2$, 11, with $Cu(MeCN)_4ClO_4$

$[NiCu(CO)_2(\mu\text{-dppm})_2(MeCN)_2]ClO_4.0.4CH_2Cl_2$ 12a: $Ni(CO)_2(\eta^1\text{-dppm})_2$, **11**, (1 g, 1.13 mmol) in benzene (20 mL) and $Cu(MeCN)_4ClO_4$ (0.4 g, 1.2 mmol) in MeCN (20 mL) were mixed and stirred for 1 h with CO passing. During this period, the almost colorless solution turned yellow-green. After filtering, hexane (20 mL) and ethyl ether (20 mL) were added to the filtrate and the solution was set aside at 0°C for three days. A yellow-green crystalline product was obtained in 73.1% yield. Anal. Calcd for **12a** ($C_{56.4}H_{50.8}O_6N_2Cl_{1.8}P_4NiCu$, M = 1162.59): C, 58.27; H, 4.40; N, 2.41. Found: C, 58.39; H, 4.51; N, 2.19. The microanalysis data are consistent with scanning electron microscopy energy dispersive X-ray data which show Ni : Cu : P : Cl = 1 : 1 : 4 : 1.5. The presence of CH_2Cl_2 was confirmed by mass spectrometry and ^1H NMR. MS: 88(6%), 86(36%), 84(58%) and 49(100%).[192] IR: ν_{CO} 2000 (s); 1918 (s) cm^{-1}; $\nu(ClO_4)$ 1088(s, br) cm^{-1}; ν_{CN} 2275 (m) and 2318 cm^{-1}. ^1H NMR (CD_3COCD_3), δ 3.1 (m, br, P-$C\underline{H}_2$-P), 5.3(s, $C\underline{H}_2Cl_2$), 1.94(s, $C\underline{H}_3CN$).[181] $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ambient temp.), δ: AA'XX' pattern, 25.08, 24.60, 23.93, 23.50, 23.37, 22.43, 22.29, 21.86, 21.19, 20.71 (Ni-$\underline{P}$-CH_2-P); -11 (br), -13 (br) (Cu-$\underline{P}$-CH_2-P). The X portion (Cu-P) is poorly resolved. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, low temp. 202K), δ: 25.32, 24.85, 24.16, 23.71, 23.60, 22.70, 22.59, 22.14, 21.45, 20.99 (Ni-$\underline{P}$-CH_2-P); -12.44, -12.91, -13.61, -14.15, -15.08, -15.63, -16.32, -16.79 (Cu-$\underline{P}$-CH_2-P).

$[CuNi(CO)_2(\mu\text{-dppm})_2(MeCN)_2]ClO_4$ 12b: The non-solvated material was obtained by direct crystallization of the filtrate of the reaction solution when hexane (20 mL) was added. Anal. Calcd for **12b** ($C_{56}H_{50}O_6ClN_2P_4CuNi$): C, 59.60; H, 4.47; N, 2.48. Found: C, 59.64; H, 4.63, N, 2.20.

$[NiCu(CO)_2(\mu\text{-dppm})_2(MeCN)_2]X.CH_2Cl_2$ (X = BPh_4, 12c; X = PF_6, 12d): The corresponding BPh_4^- or PF_6^-salts can be readily prepared by metathesis reactions in which **12a** (1 g, 0.86 mmol) in CH_2Cl_2 (10 mL) and either $NaBPh_4$ (0.6 g, 1.8 mmol) in THF (2 mL) or $NaPF_6$ (0.3 g, 1.8mmol) are mixed and stirred for 2 h. Hexane was then added until the solutions became slightly cloudy. Ethyl ether was allowed to diffuse slowly into the solution, yielding yellow-green crystalline compounds. These may still contain some unreplaced ClO_4^-. The compounds were dissolved in CH_2Cl_2 and either $NaBPh_4$ (~0.6 g) or $NaPF_6$ (~0.3 g) dissolved in THF (2 mL) was added. Addition of hexane and ether diffusion as described above produced the pure crystalline compound **12c** or **12d**. Anal. Calcd for **12c** ($C_{81}H_{72}O_2BCl_2N_2P_4NiCu$, M.W. = 1433.337): C, 67.88; H, 5.06; N, 1.95. Found: C, 68.09; H, 4.97; N, 2.18. The presence of CH_2Cl_2 was confirmed by mass spectrometry. MS: 88(7%), 86(39%), 84(54%) and 49(100%).[192] IR: ν_{CO} 2000 (s); 1945 (s) cm^{-1}; ν_{CN} 2275 (m) and 2320 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ambient temp.), AA'XX' pattern, δ 25.70, 25.28, 24.39, 24.03, 23.52(d), 23.01(d), 22.56, 22.20, 21.65, 21.24 (Ni-$\underline{P}$-CH_2-P); -12.08, -12.55, -13.45, -13.92 (Cu-$\underline{P}$-CH_2-P). X portion is poorly resolved. Anal. Calcd for **12d** ($C_{57}H_{52}O_2Cl_2N_2P_5NiCu$, M.W. = 1145.077): C, 59.79; H, 4.58; N, 2.45. Found: C, 60.05; H, 4.76; N, 2.26. The presence of CH_2Cl_2 was confirmed by mass spectrometry. MS: 88(6%), 86(36%), 84(58%) and 49(100%).[192] IR: ν_{CO} 2020 (s); 1925 (s) cm^{-1} ν_{CN} 2275 (m) and 2320 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ambient temp.), AA'XX' pattern, δ 25.31, 24.82, 24.15, 23.72, 23.60, 22.65, 22.52, 22.09, 21.43, 20.95 (Ni-$\underline{P}$-CH_2-P); -12.04, -12.56, -13.47, -13.91 (Cu-$\underline{P}$-CH_2-P). The X portion (Cu-P) is poorly resolved.

2. Reaction of $NiCl_2$/dppm/$NaBH_3CN$/$CuCl_2$

[NiCu(CO)$_2$(μ-dppm)$_2$(BH$_3$CN)].CH$_2$Cl$_2$ 13: $NiCl_2.6H_2O$ (0.5 g, 2 mmol) in benzene (20 mL) and dppm (2.8 g, 7.3 mmol) in EtOH (20 mL) were mixed and stirred for 30min. with CO passing followed by the addition of $NaBH_3CN$ (0.5 g, 9.6 mmol) in EtOH (10 mL). Passage of CO and stirring were continued for a further 2h by which time the solution had become almost colourless. $CuCl_2.2H_2O$ (0.36 g, 2.1 mmol) in EtOH (10 mL) was then added with stirring for another 1 h and the solution turned to yellow-green. After filtering, a yellow-greenish solid 1.49 g was obtained in a yield of 66.2%. The solid was dissolved in CH_2Cl_2 and enough hexane was added to produce the first traces of cloudiness. Ethyl ether was allowed to diffuse slowly into the solution at room temperature producing a yellow-green crystalline compound. By repeating the same recrystallization procedure, well formed crystals were obtained. Anal. Calcd for **13** ($C_{54}H_{49}O_2BCl_2NP_4NiCu$, M.W. = 1071.849): C, 60.51; H, 4.61; N, 1.31. Found: C, 60.62; H, 4.57; N, 1.26. The microanalysis data is consistent with scanning electron microscopy energy dispersive X-ray data which show Ni : Cu : P : Cl = 1 : 1 : 4 : 2. The presence of CH_2Cl_2 was confirmed by mass spectrometry. MS: 88(6%), 86(36%), 84(58%) and 49(100%).[192] IR: ν_{CO} 2000 (s); 1958 (s) cm^{-1}; ν_{BH} 2320(s)cm^{-1}; ν_{CN} 2280 (sh); 2190 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ambient temp.), δ: AA'XX' pattern, 25.29, 24.86, 23.92, 23.40(d) J = 5.4Hz, 22.60(d) J = 5.9Hz, 22.08, 21.14, 20.72 (Ni-$\underline{P}$-CH_2-P); -16.23, -16.74, -17.56, -18.05 (Cu-$\underline{P}$-CH_2-P). The X portion (Cu-P) is poorly resolved.

Crystal Structure Determination for [NiCu(CO)$_2$(μ-dppm)$_2$(BH$_3$CN)].xCH$_2$Cl$_2$, 13: Methylene chloride solvated crystals (containing approximately 0.4CH_2Cl_2 for molecule of the complex) of **13** suitable for X-ray examination were obtained, as flat hexagonal plates elongated along one direction, by dissolving the crude product obtained from the synthetic procedure outlined earlier in CH_2Cl_2 followed by diffusing dry ethyl ether into the solution. A crystal with dimensions 0.10 x 0.20 x0.60 mm was chosen for diffraction. Data collection was carried out on a Enraf Nonius CAD 4 diffractometer using the θ/2θ scan mode. Preliminary crystal data are described in the Results & Discussion Section and structure refinement data are summarized in **Tables 2** and **3**. The atomic position parameters are given in **Table 4** and ORTEP drawings of [NiCu(CO)$_2$(μ-dppm)$_2$(BH$_3$CN)].xCH$_2$Cl$_2$, **13**, are given in **Figures 15** and **16**.

Metathesis Reactions of 13 with $NaBPh_4$ or $NaPF_6$: Metathesis reactions of the above compound **13** with an excess of either $NaBPh_4$ or $NaPF_6$ in MeCN produced a mixture of unreacted **13** and $[NiCu(CO)_2(\mu\text{-dppm})_2]X$ (X = either BPh_4,**12b** or PF_6, **12c**). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, **12b**), δ 25-21 (m, Ni-P-CH_2-P); -12.08, -12.55, -13.45, -13.92 and -15.19, -15.70, -16.52, -17.03 (Cu-P-CH_2-P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, **12c**), δ 25-21 (m, Ni-P-CH_2-P); -11.04, -11.46, -12.37, -12.87 and -13.55, -14,17, -14.72, -15.44, -16.01, -16.69, (Cu-P-CH_2-P).

Conversion of $[NiCu(CO)_2(\mu\text{-dppm})_2(MeCN)_2]ClO_4.0.4CH_2Cl_2$, 12a, to $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$, 13: Compound **12a** (0.25 g, mmol) was dissolved in toluene/MeCN (2 : 1, 15 mL) and CO was passed through the solution for 5 min. $NaBH_3CN$ (0.05 g, mmol) suspended in MeCN (5 mL) was then added quickly and the resulting yellowish solution was stirred for a further 1 h. A mixture of hexane and ethyl ether (1 : 1, 30 mL) was added to precipitate the crude product of **13** (0.06 g; yield, 86%). Pure **13** was obtained after recrystallizing the crude product from CH_2Cl_2 using the ethyl ether diffusion technique.

3. Reactions of $Ni(CO)_2(\eta^1\text{-dppm})_2$ with Ag^I Salts

$[Ag_2(\mu\text{-dppm})_3](NO_3)_2.CH_2Cl_2$ 14: Reactions between equivalent amounts of $Ni(CO)_2(\eta^1\text{-dppm})_2$ in benzene and either $AgNO_3$, $Ag(PPh_3)NO_3$ or $Ag(diphos)NO_3$ in MeCN, were studied at ambient temperature or lower temperature

(-10°C). Only **14** was obtained from the reactions. The presence of CH_2Cl_2 was confirmed by mass spectrometry. MS: 88(6%), 86(36%), 84(58%) and 49(100%).[192] Anal. Calcd for **14** ($C_{76}H_{68}O_6N_2P_6Cl_2Ag_2$, Mol. Wt. = 1577.874): C, 57.85; H, 4.34; N, 1.78. Found: C, 58.07, H; 4.82; N, 2.07. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ambient temp., NO_3), δ: 10.8 (t); 4.5 (t) $^1J_{Ag-P} = 510.7$Hz. $^3J_{Ag-p} = 18.25$Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 K, NO_3), see discussion section.

4. Reactions of CoX(η^1-dppm)$_3$, 3, CoX(CO)$_2$(η^1-dppm)$_2$, 4, [Co(CO)$_2$(η^1-dppm)(η^2-dppm)]X, 5, or [Co(CO)(η^2-dppm)$_2$]X, 6, with metal salts

Reactions of CoBr(η^1-dppm)$_3$ with $RhCl_3.3H_2O$: CoBr(η^1-dppm)$_3$ (0.45g, 0.36mmol) was dissolved in benzene (10 mL) and EtOH (10 mL) and then $RhCl_3.3H_2O$ (0.16 g, 0.76mmol) in EtOH (10 mL) was added with stirring. After 1 h, the yellow-green solution was filtered and the volume of solvent was reduced to half by evaporation under N_2. The remaining solution was kept in a refrigerator for two days and produced a greenish crystalline compound in 27% yield. Melting point: 270°C (decomposed). The product is difficult to dissolve in most organic solvents except DMSO. Anal. Found: C, 52.66; H, 3.89; Co, 0.67; P, 5.46. $^{31}P\{^1H\}$ NMR (DMSO): no signals observed. Scanning electron microscopy energy dispersive X-ray and X-ray fluorescence spectra indicate that there are Co, Rh, Br, Cl, and P present in the compound. Attempts to identify this complex were unsuccessful

$[CoRh(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]Cl$ **15a**: A mixture of $CoCl(CO)_2(\eta^1\text{-}dppm)_2$ **4a** (0.213 g, 2.3 mmol) in benzene (10 mL) and $Rh_2(CO)_4Cl_2$ (0.043 g, 0.11 mmol) in dichloromethane (5 mL) was stirred for 30 min. and then hexane (10 mL) was added to precipitate yellow-brown crystals of **15a** (0.1 g, 43%) which was identical in all respects with an authentic sample.[159]

The same product was also obtained from reaction of **6a** (0.13 g, 0.15mmol) in chloroform (5 mL) and benzene (10 mL) and $Rh_2(CO)_4Cl_2$ (0.03 g, 0.15mmol) in methylene chloride (10 mL) with CO passing (~60 bubbles/minute). The solution was stirred for 30 minutes, and then hexane (10 mL) was added to produce the yellow-brown crystalline complex. Yield 0.064g, 39.4%.

$[CoRh(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]BPh_4$ **15b**: The corresponding BPh_4 compound was prepared from $[Co(CO)(\eta^2\text{-}dppm)_2]BPh_4$, **6c**, by a virtually identical procedure in 34% yield. Anal. Calcd for **15b** ($C_{77}H_{64}O_3BClP_4CoRh$, M = 1369.344): C, 67.54 H, 4.71. Found: C, 67.80; H, 4.38. IR: ν_{CO} 1988(m), 1960(m), 1847(m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), A_2M_2X pattern, 49.7 (t, P-Co), 30.3 (dt, P-Rh), $^2J_{pp}$ = 39.2 Hz, $^1J_{RhP}$ = 104.0 Hz. Spectral data are identical to those of an authentic sample.[159]

Reactions of 4, 5 and 6 with $Cu(MeCN)_4ClO_4$: $[Co(CO)(\eta^2\text{-}dppm)_2]BPh_4$,

6c, (1.1g, 0.9mmol) was dissolved in methylene chloride and the solution was saturated with CO. A solution of Cu(MeCN)$_4$ClO$_4$ (0.3g, 0.9 mmol) in MeCN (10 mL) was added to the mixture and stirred for 1 h. ^{31}P{^{1}H} NMR (reaction solution): **a)** at r.t., δ 50.1 (t), J = 25.8Hz, -2.3 (br), -18.24 (br); **b)** at -85°C, δ 47.8(dt), J = 51.9 and 60.7; 12.3(t), J = 109 Hz; 121.3(dd,) J = 54.2, -22.8(d), J = 55.2. All attempts to isolate a heterobimetallic complex failed. Instead, work up of the solutions resulted in the formation of [Cu$_2$(μ-dppm)$_2$(MeCN)$_4$](ClO$_4$)$_2$ or recovery of starting material **6c**. Analogous reactions of **4** or **5** with Cu(MeCN)$_4$ClO$_4$ gave similar results. Other efforts to prepare bimetallic complexes will be discussed in the next chapter.

IV. Preliminary Studies on Routes to the Formation of Co-BH$_2$ Complexes

Time, Temperature and Ratio of Reactants: Reactions between Co^{II} and NaBH$_4$ in the presence of dppm and CO, which under certain conditions produce [Co(CO)$_2$(η^1-dppm)(μ-dppm-BH$_2$)], **16**, in very low yield,[43] have been studied by changing reaction times from 0.5 h to 24 h, reaction temperature from -20°C to refluxing in toluene/ethanol, and Co^{II}/NaBH$_4$ ratios from 1 : 1 to 1 : 6. No compound **16** was detected by solution ^{31}P{^{1}H} NMR spectroscopy.

Co$_2$(μ-CO)$_2$(CO)$_4$(μ-dppm) 17: Co$_2$(CO)$_4$(dppm)$_2$ (0.5 g, 0.5 mmol) in benzene (15 mL) and BH$_3$.THF (1 M, 0.5 mL, 0.5 mmol) were mixed under CO and stirred for 1 h. Hexane (10 mL) was added and a white solid (BH$_3$.dppm) was filtered off. Another portion of hexane (10 mL) was then added to the filtrate, and a red solid was precipitated. The solid was recrystallized from CH_2Cl_2-hexane, and shown to be pure **17** (0.1 g, 19% yield). Anal. Calcd. for **17** ($C_{31}H_{22}O_6P_2Co_2$): C, 55.55; H, 3.31; Found: C, 55.76; H, 3.20. IR: 2040 (s), 2000 (s), 1884 (vs), 1820 (m), 1795 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: 60.35 (s).

17 was also obtained in 10% yield from the direct reaction of a mixture of BH_3.THF (1M, THF solution), $NaBH_4$ in EtOH and $CoBr_2.4.7H_2O$ in EtOH in the presence of dppm and CO.

Reactions of $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$ (1.1 g, 1 mmol) in THF with BH_3.THF (1 M, 1 mL, 1 mmol) gave similar results. **17** (0.15 g) was obtained in 14% yield.

Reaction of Co^{II}/BH_3.dppm/ $NaBH_4$/CO: $CoBr_2.4.7H_2O$ (0.5 g, 1.65 mmol) in EtOH (20 mL), was added to a CO saturated mixture of dppm.BH_3 (2 g, 5 mmol) in THF (30 mL) and $NaBH_4$ (0.063 g, 1.65 mmol) in EtOH (10 mL) and stirred for 2 h. $^{31}P\{^1H\}$ NMR (reaction mixture) δ 37, -5.5, 52.2 and 60.3ppm. These signals are due to complexes **6d**, **7b**, **9** and **17** respectively.

Reactions of 4b, 5b and 6c with BH_3.THF: $CoBr(CO)_2(\eta^1\text{-dppm})_2$, **4b**, (0.9g, 0.9mmol) was dissolved in benzene (15 mL) and BH_3.THF (1 M, 2 mL, 2 mmol) was added under a CO atmosphere. The solution quickly turned green and a white solid precipitated. A ^{31}P NMR spectrum (of the remaining solution) showed peaks at δ 15 (br) and -27 (d) and 51.2 (dd), -24.8 (dd). The white solid was shown to be a mixture of H_3B.dppm.BH_3 and dppm.BH_3 by spiking the solution of the mixture with authentic samples.[191] The same products were also observed in the reactions of $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]Br$, **5b**, (0.75 g, 0.8 mmol) in benzene or $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$, **6c**, (0.86 g, 0.6 mmol) and BH_3.THF (1 M, 2 mL, 2 mmol).

Reaction of $[H_2B(\eta^2\text{-dppm})]I$ with the ion pair $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$ 6d: $[BH_2(\eta^2\text{-dppm})]I$ (0.25 g, 0.5 mmol) in THF (15 mL) and **6d** (0.5g, 0.5 mmol) in CH_2Cl_2 (20 mL) were mixed together. The $^{31}P\{^1H\}$ NMR spectrum (solution) had peaks at δ -5.5(s), 15 (br) -23(d) which showed the products to be mainly dppm.BH_3.

Similarly, $Co_2(CO)_8$ in benzene was stirred with either $[BH_2(\eta^2\text{-dppm})]I$ in THF or BH_3.dppm/H_3B.dppm.BH_3 in THF (both in a 1 : 4 ratio). $^{31}P\{^1H\}$ NMR (reaction solution of $Co_2(CO)_8$ and $[BH_2(\eta^2\text{-dppm})]I$): δ 15(br). $^{31}P\{^1H\}$ NMR (reaction solution of $Co_2(CO)_8$ and BH_3.dppm/H_3B.dppm.BH_3) δ 15 (br) -23(d).

Reaction of $Co(CO)_4BH_2$.THF with dppm: $Co_2(CO)_8$ (1 g, 2.9 mmol) was dissolved in pre-cooled THF (15 mL, -18°C). BH_3.THF (1 M, 5.8 mL, 5.8 mmol) was added with a syringe and the mixture was stirred for 5-6 h at -18°C under a nitrogen atmosphere. A solution of dppm (4.5 g, 11.5 mmol) in benzene (20 mL) was added quickly to the solution and the stirring continued for 1 h. The colour of the solution remained brown. The major product of the reaction was $[Co(CO)(\eta^1\text{-dppm})(\eta^2\text{-dppm})][Co(CO)_4]$, **5d**, ($^{31}P\{^1H\}$ NMR spectrum (solution): at 51.7 (dt) J = 24.41 and J = 56.89 Hz, -2.3 (br, s), -27 (d) J = 57Hz). Besides **5d**, some other products were present in the reaction solution as shown by the $^{31}P\{^1H\}$ NMR spectrum which showed additional peaks at δ 60.1 (s), 53 (s), 36.1 (s), -5.5 (s), -22 (s), 44.8 (d) J = 96.6, -25 (m) and 6.7 (br). Pure **5d** can also be easily separated from the reaction solution of $Co_2(CO)_8$ with dppm at low temperature (-20°C). Thus, $Co_2(CO)_8$ (0.5g, 1.5 mmol) was dissolved in toluene (15 mL) at -20°C and stirred with CO passing for 10 min.. Then, dppm (2.25g, 6 mmol) dissolved in pre-cooled toluene (15 mL, -20°C) was added and stirred with CO passing for another 2 h, keeping the temperature at -20°C. The volume of the brown coloured solution was reduced to 10 mL by evaporation most of toluene by a CO/N_2 stream. Hexane (15 mL, -20°C) was added to the solution which then produced an orange solid. Yield 54%. Anal. Calcd for toluene solvated of **5d** ($C_{58.5}H_{48}O_5P_4Co_4$): C, 59.01 ; H, 4.06. Found: C, 59.27 ; H, 3.84. IR: ν_{co} 2055(m) 2000(s), 1994(s), 1958(br, s), 1990(br, s), 1880(br s) cm^{-1}. ^1H NMR ($CDCl_3$), δ 2H, η^2-P-C$\underline{H}_2$-P), 2H, η^1-P-C$\underline{H}_2$-P). $^{31}P\{^1H\}$ NMR (C_6D_6, ambient temp., fluxional system) δ -2.3 (unresolved, η^2-$\underline{P}_A$-CH_2-$\underline{P}_B$), 51.7 (dt, Co-$\underline{P}_C$-CH_2-P_D), -27.0 (d, Co-P_C-CH_2-$\underline{P}_D$), $J_{AC} = J_{BC} = 24.4$, J_{CD} 56.9 Hz.

RESULTS AND DISCUSSION

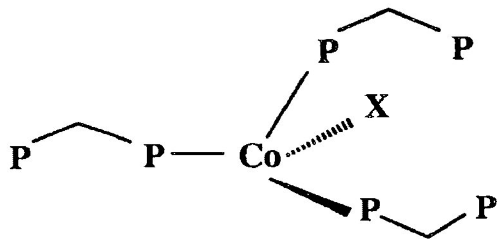
I. Reactions of Co-dppm complexes with CO or CO/$NaBH_4$

Reactions of Co^{II} salts with $NaBH_4$ or $NaBH_3$ CN in the presence of dppm have been shown to give a variety of products depending upon the reaction conditions.[18-20] These products include the tetrahedral Co^I species, $CoX(\eta^1\text{-dppm})_3$, **1**, (X = Cl, Br), the mixed oxidation state (Co^I-Co^{II}) system, $Co_2X_3(dppm)_2$, **2**, and Co^{III} complexes of the type of $[CoH(\eta^2\text{-dppm})X]^+$, **3**, (X = Cl, Br, I, and BH_3CN). These compounds have been structurally characterized by their NMR, IR, and magnetic properties and by elemental analyses. The structure of **1** was confirmed by X-ray diffraction analysis[18] while the structure of complex **2** was tentatively proposed according to its elemental analyses and magnetic properties but has not been fully established. More will be said about this later. All these compounds are formed from a simple one step experiment and their proposed structures are shown in **Figure 12.**

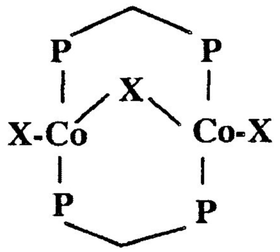
Since relatively few Co^I complexes containing the dppm ligand have been reported, the chemical properties of these products, especially their further reactions with CO or CO/$NaBH_4$, which may lead to a new route to Co-dppm-CO complexes, are worthy of attention. The following discussion explores this facet of Co/dppm chemistry. The numbering of the compounds follows the sequence given in Chapter 2 (Experimental Section).

It has been established[155] for some time that Co^{II}-phosphine complexes can form unstable Co^{II}-phosphine-carbonyl derivatives upon exposure to CO at room

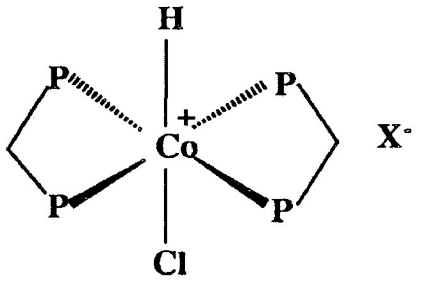
Figure 12. Structures of 1, 2 and 3



1 (X = Cl, Br)



2 (X = Cl, Br)



3 (X = Cl, Br, BH_3CN)

temperature. Further reactions of Co^{II}-phosphine-carbonyl derivatives can lead to slow reduction to Co^{I} by CO and to formation of the Co^{I} derivatives $CoX(CO)_2(PR_3)_2$ (X = I and CN).[154,155] The reaction under ambient conditions with CO can lead to the reversible formation of five-coordinate adducts $CoX(CO)_2(PR_3)_2$. Generally, however, the equilibrium

$$CoX_2(PR_3)_2 + CO \rightleftharpoons CoX_2(CO)(PR_3)_2 \tag*{[60]}$$

lies very far to the left[154] for bulkier, less basic, phosphines similar to dppm and the reduction process proceeds at a negligible rate for the case where X = Cl and PR_3 is a triaryl phosphine (see Table 1 on page 122).

If the reductions of $Co^{II}/dppm/BH_4^-$ are carried out in an atmosphere of CO, several Co-CO-dppm complexes in a variety of oxidation states can be formed with the nature of the major product being critically dependent upon the reaction conditions. These complexes include $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**, $Co_2(\mu\text{-CO})_2(CO)_2(\mu\text{-dppm})_2$, **10**, and $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **6d**. In these reactions leading ultimately to the formation[37,38] of $Co_2(CO)_4(\mu\text{-dppm})_2$, the exposure time of the Co^{II}-dppm mixture to CO is so brief (and the dppm is sufficiently bulky) that it is probable that some reduction of the phosphine-complexed Co^{II} by $NaBH_4$ occurs before significant interaction of CO with the metal center takes place. Accordingly, since the first products isolated from similar reactions in the absence of carbon monoxide are[18] the reduced species $Co_2X_3(dppm)_2$ and $CoX(\eta^1\text{-dppm})_3$ (X = Cl, Br) and since it is also well established[154,156] that CO interacts smoothly with Co^I-phosphine complexes, we have investigated the reactions of both of these products with CO in the absence and presence of $NaBH_4$. As a consequence, the mechanism of formation of the cobalt carbonyl complexes noted above has been established and several new Co-dppm-CO complexes have been synthesized.

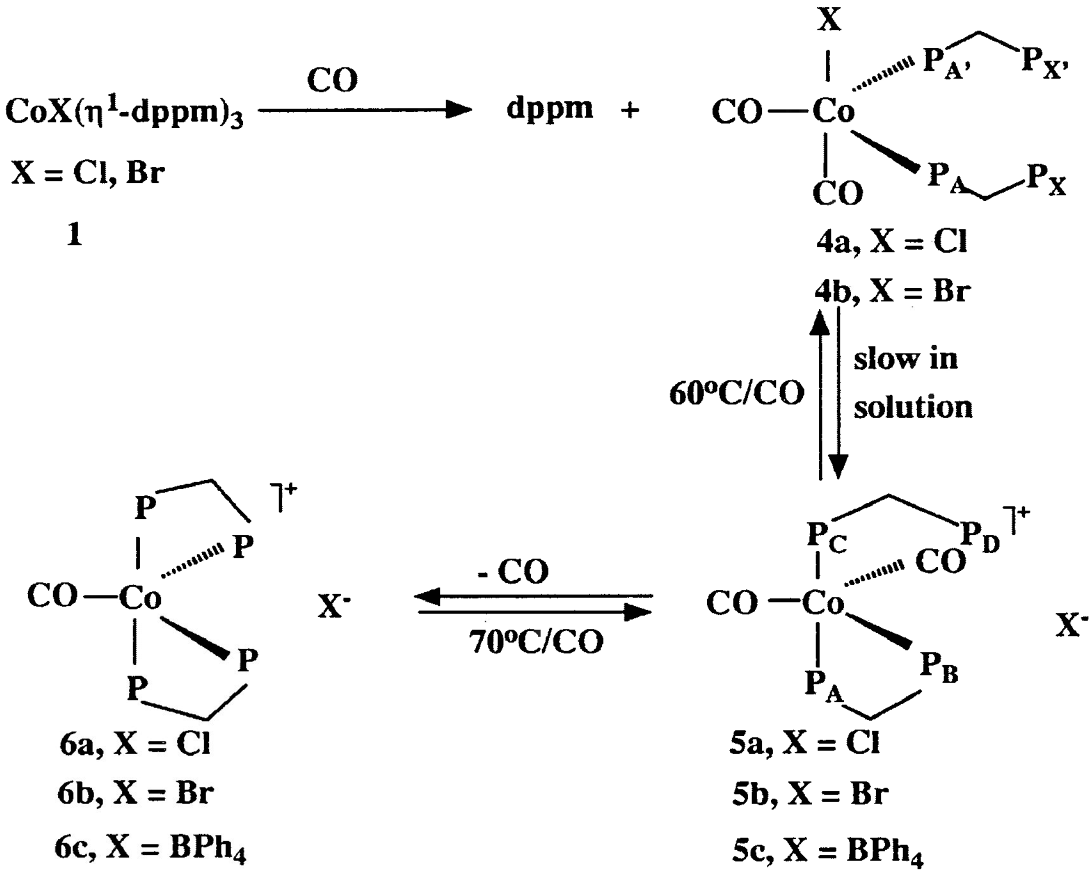
1. Reactions of $CoX(\eta^1\text{-dppm})_3$ with CO

Dealing first with $CoX(\eta^1\text{-dppm})_3$, **1** (X = Cl, **1a**; Br, **1b**), for which the structure

(X = Cl) has been established,[18] these can react rapidly and very cleanly with CO to give at least three products **4**, **5** and **6** (see **Scheme 18**) in sequence and in quantitative yields. All these complex types can be isolated in pure form and have been fully characterized (see Experimental Section and later discussion). The dppm, carbon monoxide and halogen ligands appear to compete for coordination sites in solution and the second and third steps in the reaction sequence can be reversed under certain conditions. Both the forward and reverse reactions are summarized in **Scheme 18.**

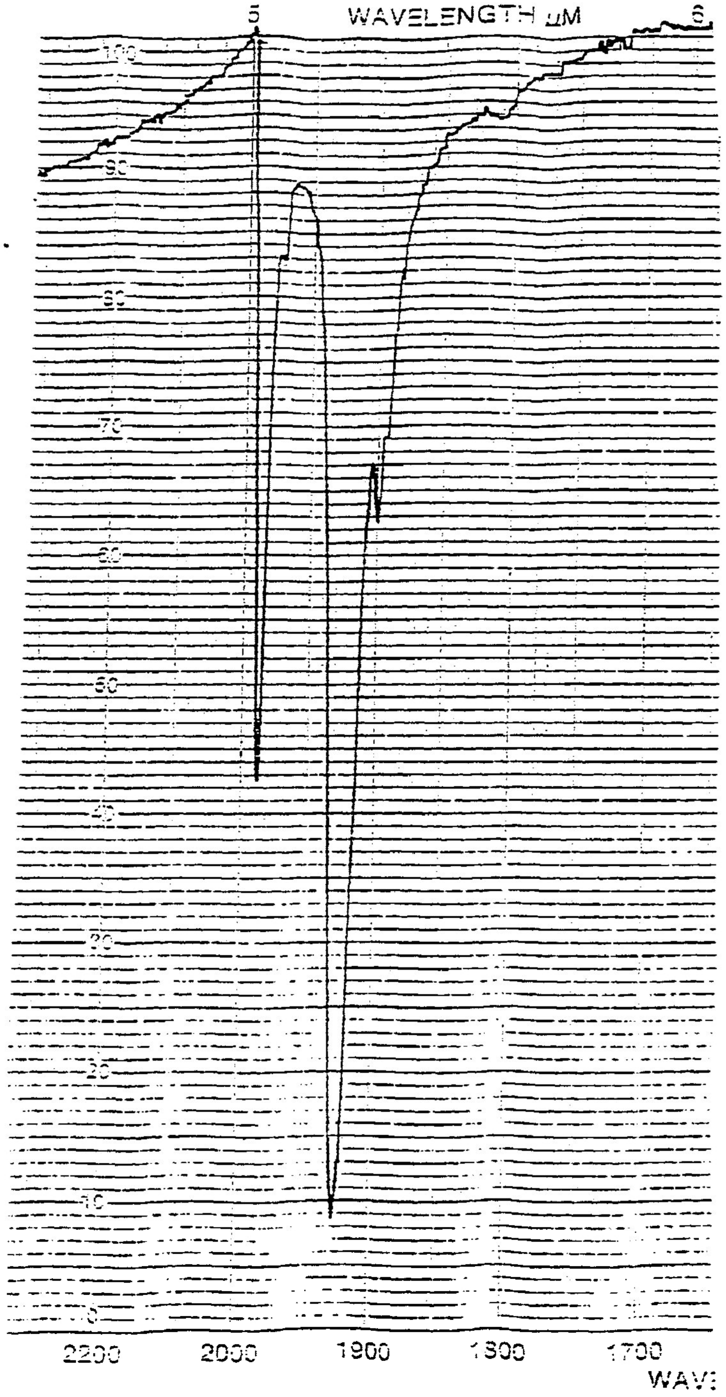
Thus, exposure of a benzene solution of the high-spin compounds $CoX(\eta^1\text{-dppm})_3$ to CO at ambient temperature and pressure leads to the very rapid formation of free dppm (as shown by the ^{31}P NMR spectrum of the reaction mixture) and the low-spin Co^I-dppm complexes, **4**, which, in the $^{31}P\{^1H\}$ NMR spectra, show a doublet of doublets for the coordinated P atoms centered on $\delta = 54.8$ppm (J = 41.7 and 29.5 Hz) coupled with a second doublet of doublets for the uncoordinated P atoms centered on $\delta = -24.8$ ppm. No other signals were observed in the spectra and the reactions therefore appear to be quantitative. Based on the fact that dppm is produced in these reactions, the complexes **1** seem to resemble in behaviour the simple Co^I-phosphine complexes of the type $CoX(PEt_3)_3$ (X = Cl, Br, NCS).[155] Thus, $CoX(PEt_3)_3$ are known to react with CO to give, initially, $CoX(CO)(PEt_3)_3$ and then $CoX(CO)_2(PEt_3)_2$. Complexes **4** could have the structure shown in **Scheme 18** or they could be the ionic species, $[Co(CO)_3(\eta^1\text{-dppm})_2]X$, although attempts to precipitate BPh_4^- salts were unsuccessful due to **4** converting easily into **5** and **6** under these conditions. However, a molecular weight determination on a pure sample of **4b** (see Experimental Section and later discussion) confirmed that this compound is indeed non-ionic. Only terminal CO

Scheme 18. Reactions of 1 with CO



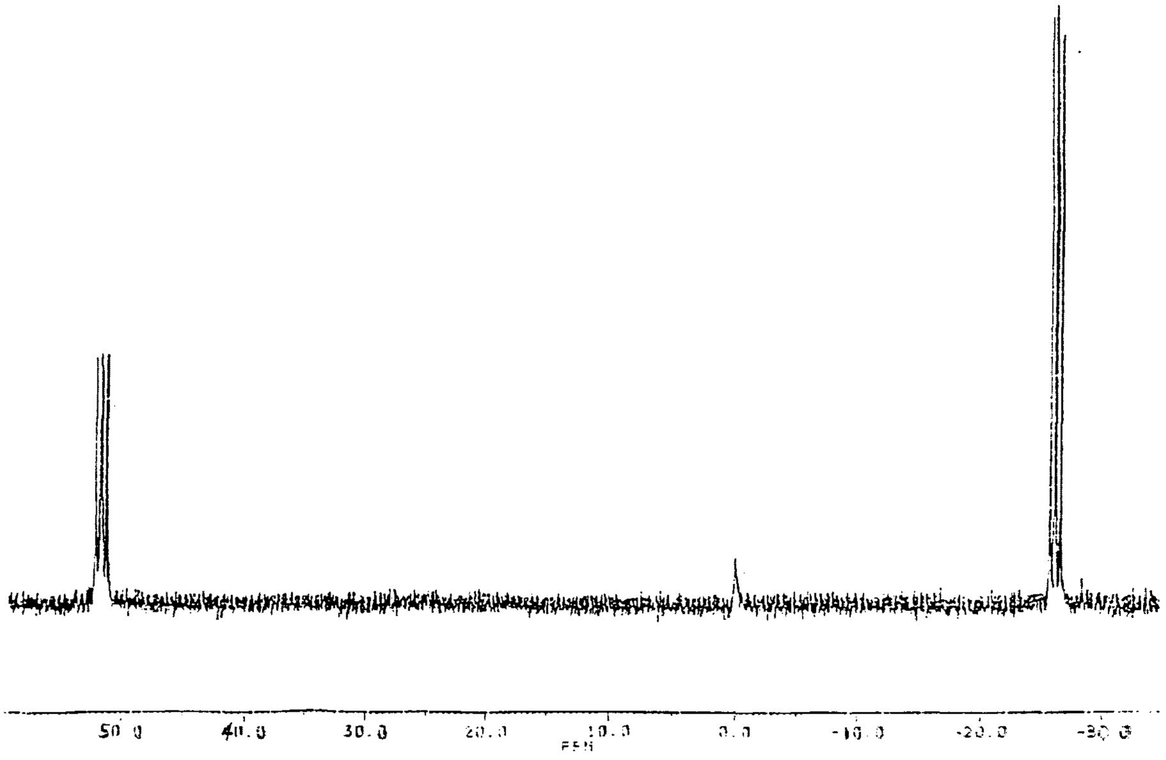
stretching frequencies at $1988cm^{-1}$, $1927cm^{-1}$ and $1900cm^{-1}$were observed in the IR spectra of 4 (see **Spectrum 1**). According to the proposed structure, the ^{31}P NMR spectra of 4, (see **Spectrum 2**) can be interpreted as a simplified AA'XX' spectrum of a probably fluxional five-coordinate system.

Spectrum 1. IR of 4b



Spectrum 2. $^{31}P\{^1H\}$ NMR of 4b in C_6D_6 at Room Temperature

(peak at δ = 0 is due to external reference H_3PO_4)



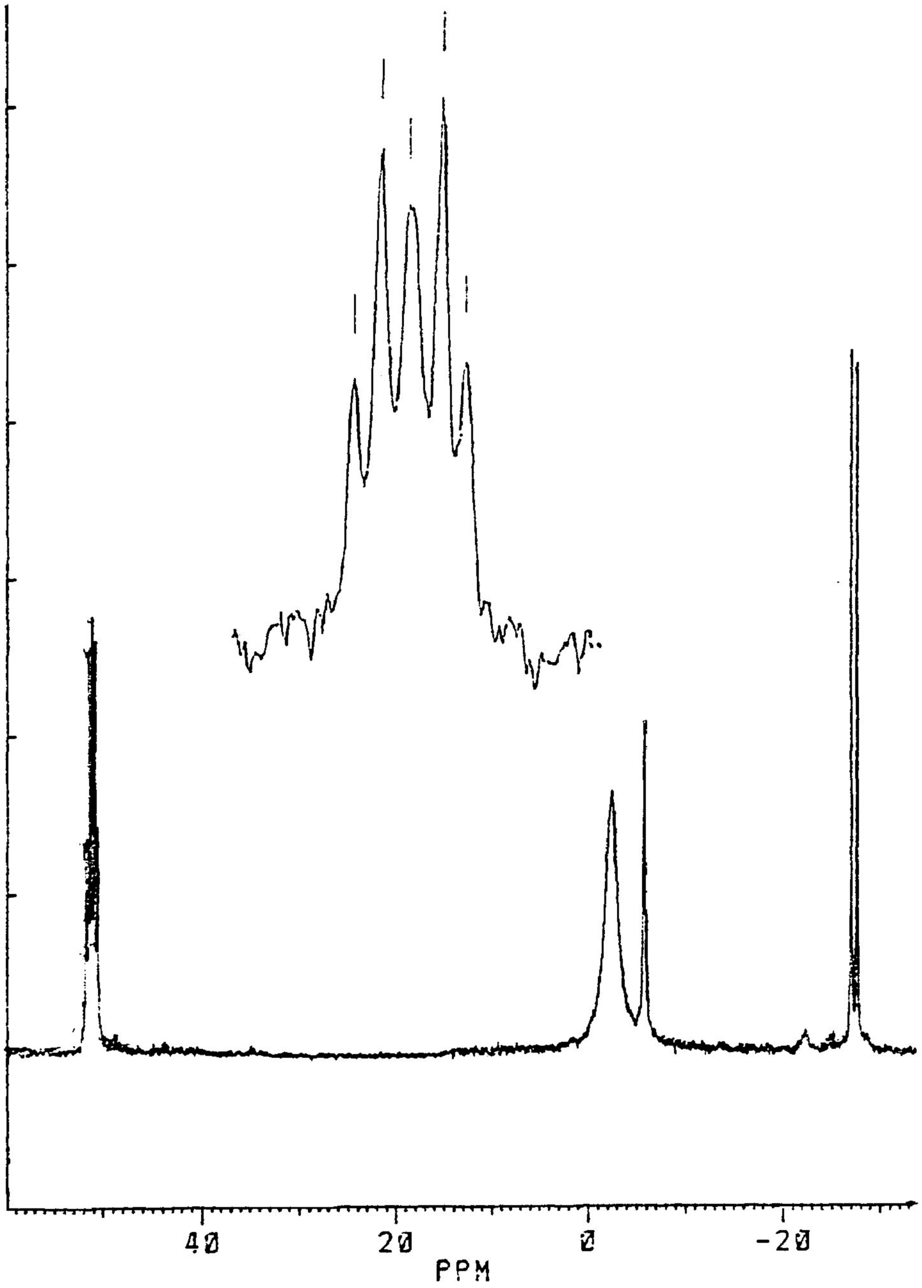
The products **4** cannot be isolated in the pure state directly from the forward reaction since attempts at crystallization under a variety of conditions lead to the formation of further reaction products (a mixture of **5** and **6**, see below). However, pure samples of **4** can be obtained from a less direct route (see later discussion).

Although **4** are stable in the solid state under a CO atmosphere, if reaction solutions containing **4** are allowed to stand, isomerizations to **5** occurs through displacement of X by one of the uncoordinated P atoms. The compounds **5** can be isolated in pure form by an indirect route also (see Experimental Section and later discussion). The complexes **5** show, in $CDCl_3$ at room temperature, ^{31}P spectra which are consistent with an A_2MX pattern arising from a fluxional five coordinate system. Thus , signals are observed at $\delta = -3.44$ (unresolved hump, P_A and P_B), 50.35 (doublet of doublets, J = 24.5 and 49.4 Hz, P_C), and -28.7 (doublet, J = 49.4 Hz, P_D) (see **Spectrum 3**). At -85°C in CD_2Cl_2, however, the fluxional process is slowed to the point that all P atoms and their couplings become clearly observable with P_A at $\delta = 12.6$, P_B at $\delta = -21.0$, P_C at $\delta = 49.3$ and P_D at $\delta = -31.6$ ($J_{AB} = 113.0$Hz, $J_{AC} = 109.0$Hz, $J_{BC} = 58.0$ Hz, $J_{CD} = 50.7$ Hz). A typical low temperature (-68°C) spectrum in $CDCl_3$ solution is shown in **Spectrum 4**.

The chemical shifts are slightly different from those measured in CD_2Cl_2. The single peak at δ -6 is due to **6b** which is formed from the unstable **5b** in solution. The assignments are made on the assumption that the geometry of **5** at low temperatures is as shown in **Scheme 18**.

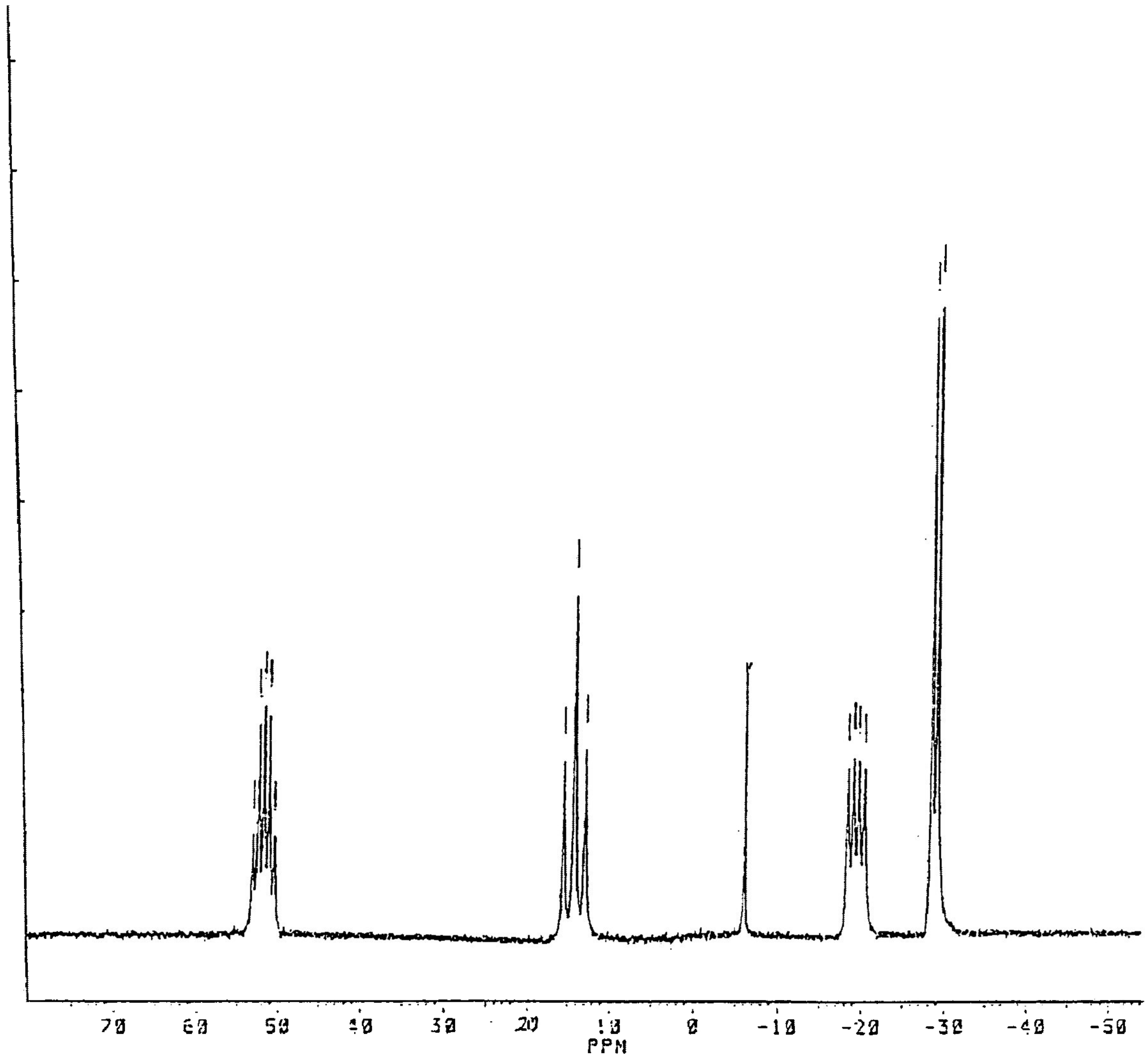
Spectrum 3. $^{31}P\{^1H\}$ NMR of **5b** in CD_2Cl_2 at room temperature

(peak at δ = -6 is due to **6b**)



Spectrum 4. $^{31}P\{^{1}H\}$ **NMR of 5b at -68°C in CDCl$_3$**

(peak at δ = -6 is due to the **6b**)



Thus, the chelated dppm would adopt the apical-equatorial arrangement to minimize strain and, while a value of J_{AC} of 109 Hz might seem to be low for a trans coupling, it is almost certainly much too high for the cis coupling which would be observed if the monocoordinated dppm were to adopt the equatorial arragement. It should be noted that the geometry shown is similar to that established[43] for $Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm-}BH_2)$, **16**.

As with the transformation **4** to **5** described above, solutions of **5** slowly give **6** ($\delta^{31}P$, -6.78 ppm in $CDCl_3$) by displacement of a CO ligand with the remaining uncoordinated P atom. Compounds **6** are easily isolated by crystallization as the Br^- or BPh_4^- salts. Therefore, possible routes to the cation of $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **6d**, (one of the products formed by direct Co^{II}/dppm/$NaBH_4$/CO reactions discussed[37] at the beginning of this section) previously also prepared[1572] by a phosphine ligand exchange reaction on $[CoX(CO)_2(R_3P)_2]$ in the presence of ClO_4^-, has been established from the formation of **6**.

In passing, it should be remarked that as noted elsewhere,[37] complex **6d** was originally formulated[38] as an isomer of $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**, and $Co_2(\mu\text{-CO})_2(CO)_2(\mu\text{-dppm})_2$, **10**, i.e., a complex of formula $Co_2(CO)_4(dppm)_2$. Its ^1H and $^{31}P\{^1H]$ NMR spectra are identical to those of **6a**, **6b** and **6c** except for the presence of ethanol signals in the ^1H spectrum. X-ray investigations[37] have shown that complex **6d** possesses one more CO ligand than **9** or **10** and has the ion-pair formulation used throughout this thesis.[37] The cation in **6d**, $[Co(CO)(\eta^2\text{-dppm})_2]^+$, has been shown to have the CO at an equatorial position,[37] and the cation in **6a**, **6b** and **6c** should be similar.

The complexes **6** are quite stable. Thus, the CO ligand in **6** cannot be further replaced by dppm in CH_2Cl_2. This can be explained in term of the small ligand CO being enclosed by four benzene rings on dppm and therefore the resulting steric hindrance prevents the CO ligand from being displaced.

As mentioned earlier, the pure complexes **4** and **5** are extremely difficult to isolate in pure form from the series of transformations outlined above. At best, mixtures of products are obtained. However, the process is reversible and it is by this route that pure **4** and **5** are obtained. Full details are given in the Experimental Section but the essentials of the process are that treatment of mixture of **5b** and **6b** or **5c** and **6c** in benzene/hexane with CO at 70°C followed by careful cooling and crystallization under CO produces pure crystalline **5b** or **5c**. A modification of this procedure produces **4a** or **4b**. The first step in this reverse process is clearly the displacement of one of the coordinated P atoms by CO (**6** → **5**). However, the second step is less straightforward since it is not a simple matter of X^- directly displacing a second coordinated P atom. If this were the case, the forward reaction **4** → **5** would be unlikely to occur under the conditions observed and the presence of CO would not be necessary for the reverse reaction. It seems probable then that in the transformation **5** → **4** under CO at ~60°C, the first step is displacement of coordinated P by CO to give the unstable species $[Co(CO)_3(\eta^1\text{-dppm})_2]X$ ($X = Cl$ or Br) which is quickly followed by displacement of a CO ligand by X^-. A species with the characteristics expected for $[Co(CO)_3(\eta^1\text{-dppm})_2]X$ ($X = [Co(CO)_4]$), which has a $^{31}P\{^1H\}$ NMR spectrum (benzene solution) of δ 57.41 (dd), -22.56 (dd), $^2J_{PP} = 27.3$ and 74 Hz, was observed in the direct reaction of $Co_2(CO)_8$ and dppm in benzene. This compound is very unstable and only exists in solution. All attempts to obtain this compound as a solid failed (see Section II.2 for full details) because it converts into $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})][Co(CO)_4]$, **5d**, and then $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**, quickly in the recrystallization processes. It should be noted, however, that no trace of a compound of this type has been detected in the conversion of **5** ⟶ **4**.

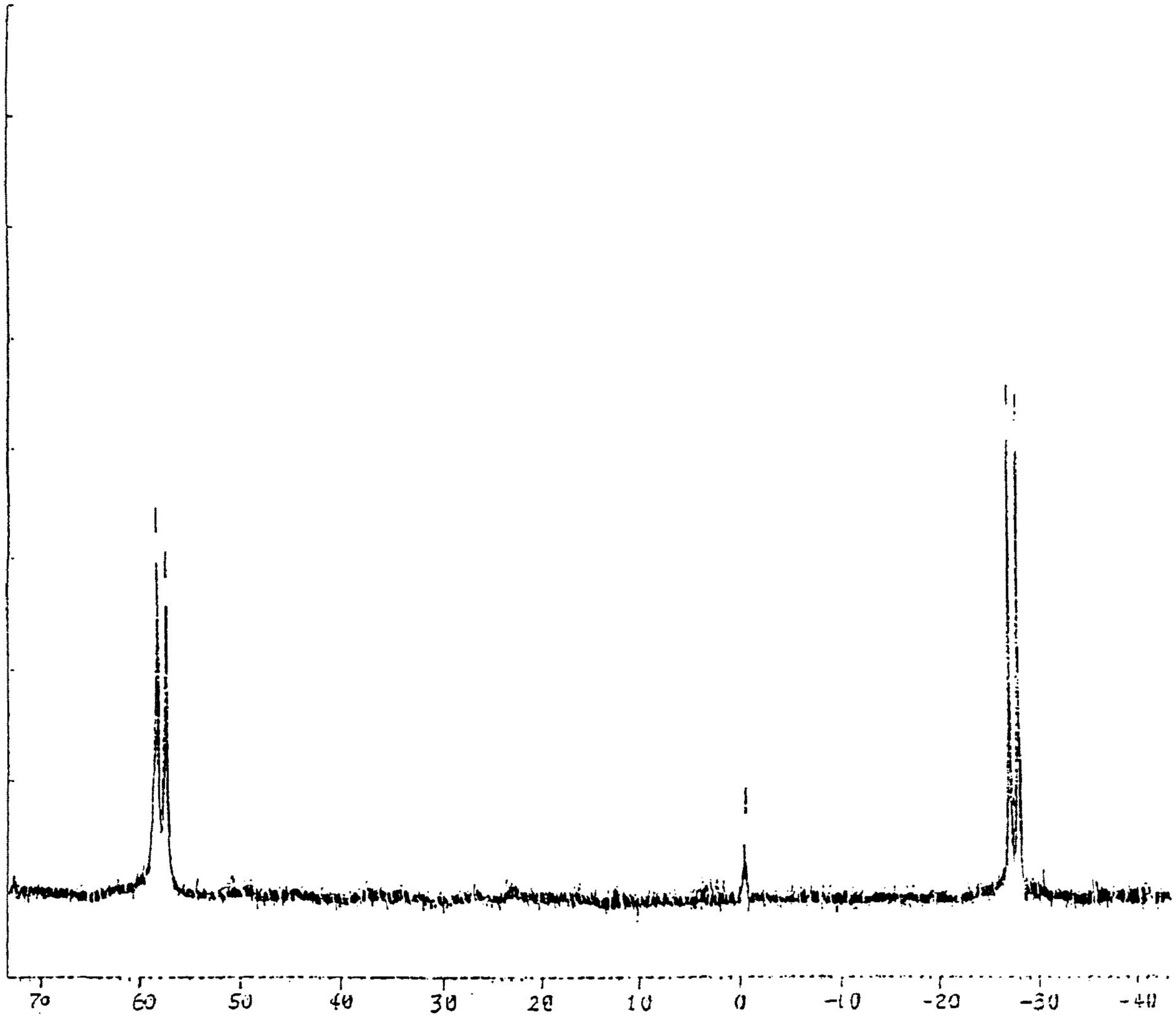
2. Reactions of $CoX(\eta^1\text{-dppm})_3$ with $CO/NaBH_4$

While it is clear from the foregoing discussion that $[Co(CO)(\eta^2\text{-dppm})_2]^+$ is readily formed in high yield in the reaction of $CoX(\eta^1\text{-dppm})_3$ with CO, there is no evidence for the formation of $[Co(CO)_4]^-$ in this reaction. It seemed probable then that, in the formation of **6d**, either $[Co(CO)_4]^-$ is formed as a result of the continued presence of $NaBH_4$ in the reaction mixture after $CoX(\eta^1\text{-dppm})_3$ has reacted with CO or an entirely different reaction pathway is followed.

The first of these possibilities initially seemed unlikely since treatment of a benzene solution of $CoBr(\eta^1\text{-dppm})_3$ under CO with ethanolic $NaBH_4$ (Co : BH_4^- ratio of 1 : 1) leads only to the formation of $[Co(CO)_4(\eta^1\text{-dppm})]Br.C_6H_6$, **8**, which is readily isolated in a pure state as a benzene solvate and which has been fully characterized (see Experimental Section). Similar results were obtained from the treatment of pure **4b** with $NaBH_4$. Only terminal CO stretching frequencies at ν_{co} 2000(s), 1950(s), 1920(s) cm^{-1} were observed in the IR spectrum of **8**. The $^{31}P\{^1H\}$ NMR spectrum of **8** shows a simple AB pattern with a large coupling constant (J_{PP} = 75.16Hz) (see **Spectrum 5**).

Spectrum 5. $^{31}P\{^1H\}$ **NMR of** $[Co(CO)_4(\eta^1\text{-dppm})]Br.C_6H_6$**, 8, in** CD_2Cl_2 **at Room Temperature**

(peak at $\delta = 0$ is due to external reference H_3PO_4)



The properties of this compound are quite different from those of the similar compounds $[Co(CO)_3L][Co(CO)]_4$,[25] which were only observed by IR spectroscopy and obtained from the reactions of $Co_2(CO)_8$ and L (L = dppm, dmpm, dpdm). When the more basic ligand dmpm was used, the $[Co(CO)_3L][Co(CO)_4]$ still slowly converts to the corresponding neutral dimer $[Co_6(CO)_6L]$, whereas compound **8** appears to be quite stable and can be isolated and characterized since cation-anion reaction cannot occur.

No further reduction of Co^I by $NaBH_4$ was observed when either $CoBr(\eta^1\text{-dppm})_3$, **1**, or $CoBr(CO)_2(\eta^1\text{-dppm})_2$, **4b**, was treated with $CO/NaBH_4$.

The steps involved in the transformations leading to **8**, which do not occur under CO in the absence of $NaBH_4$ have not been fully established. A possible reason for this lack of reactivity in the absence of $NaBH_4$ is that BH_3 released from decomposition of $NaBH_4$ can coordinate strongly with the uncoordinated P atoms in **4b** which weaken the Co-P bond and permits replacement by CO. This phenomenon also was observed in a study of the reaction of BH_3 with either $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**, or $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **5d**, (see Section **IV.3** of this chapter and Experimental Chapter). Similarly, reactions of $Ni(CO)_2(\eta^1\text{-dppm})_2$ (1 equiv) and $BH_3.THF$ (1 equiv) gives $Ni(CO)_3(\eta^1\text{-dppm})$[164] and $dppm.BH_3$. These examples provide evidence that coordination of BH_3 to the P atom of dppm at one end will lead to a decrease in the coordinating ability of the P atom attached to a metal. Therefore, this special property of BH_3 may provide a general and easy method to remove bis-phosphine ligands from metal-dppm complexes.

However, relating to the question of the possible formation of $[Co(CO)_4]^-$ in these reactions, when the molar ratios of CoBr(η^1-dppm)$_3$: NaBH$_4$ are increased from 1 : 1 to 1 : 2 - 4, the reactions of CoBr(η^1-dppm)$_3$ and ethanolic NaBH$_4$ in the presence of CO produced a solution containing (^{31}P{^{1}H} NMR spectrum) free dppm and the bis(borane) adduct H$_3$B.dppm.BH$_3$[161], as the only phosphorus-containing products. This same spectrum was obtained from reactions of CoX(CO)$_2$(η^1-dppm)$_2$ (1 equiv) (X = Br) in benzene and NaBH$_4$ (2.2 equiv) in EtOH with CO passing. Though the reasons for the disappearance of signals due to the P atoms coordinated to Co in the ^{31}P NMR spectra of these Co-dppm-CO system are not entirely clear, solution IR spectra indicate that there are peaks which could be absorptions due to [Co(CO)$_4$]$^-$ at 1890 and 2040 cm^{-1}.[26] No trace was found of Co$_2$(CO)$_8$ which should have a strong absorption at 2077 cm^{-1}.[184] It is possible that the Co^I species are further reduced by NaBH$_4$ under these conditions and that all the dppm ligands are replaced by CO. Therefore, these transformations are a possible route to the formation of [Co(CO)$_4$]$^-$ in **6d**, although,as will be seen shortly, another route is more likely.

3. Reactions of Co$_2$(dppm)$_2$X$_3$ with CO or CO/NaBH$_4$

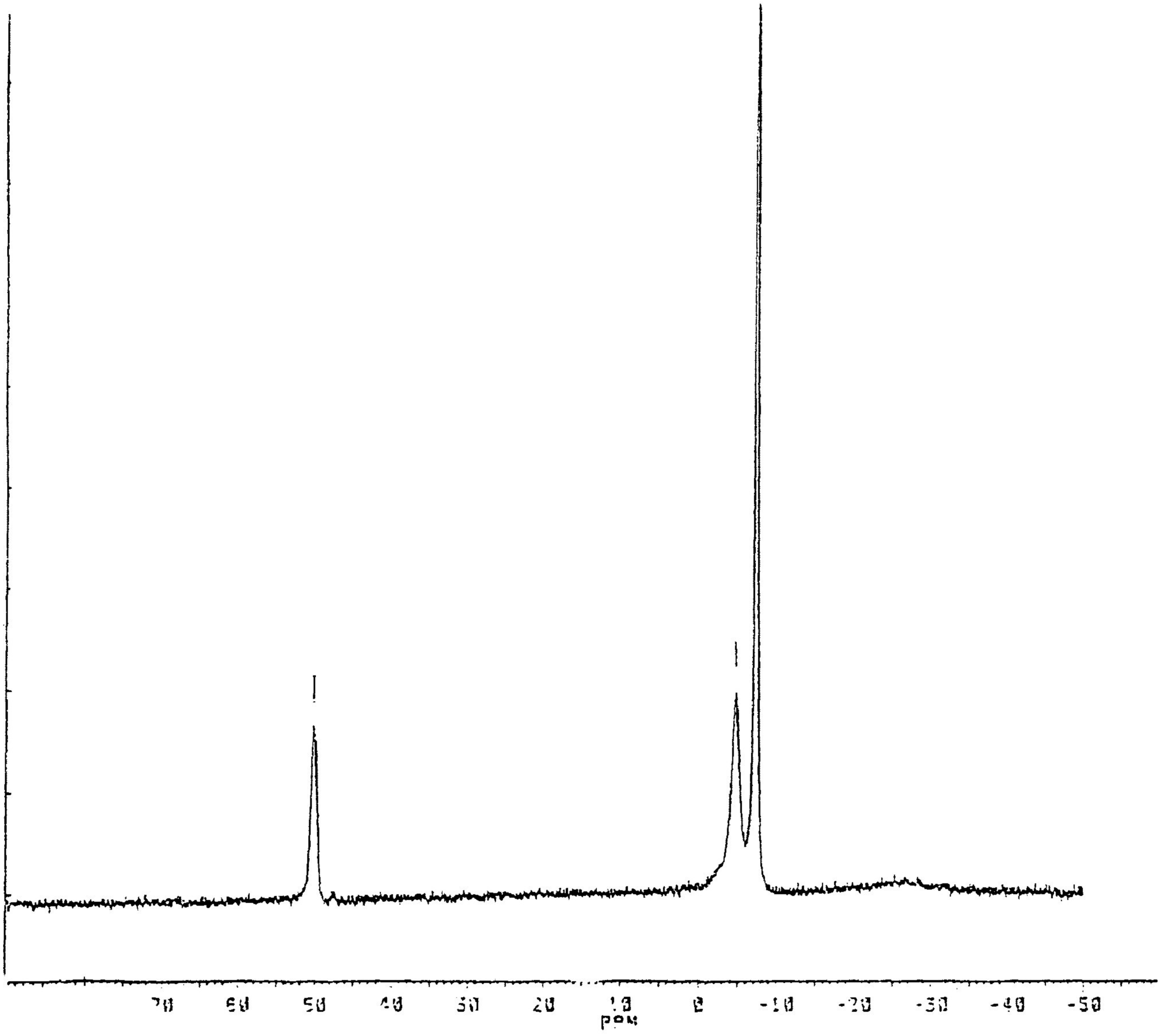
Since no confirmed evidence for the formation of [Co(CO)$_4$]$^-$ was found in the reactions of CoX(η^1-dppm)$_3$ with CO, the possibility that this anion is formed from the less well characterized[18] compounds Co$_2$X$_3$(dppm)$_2$, which are apparently precursors of CoX(η^1-dppm)$_3$ in the reduction of CoX$_2$/dppm mixtures with NaBH$_4$ in the absence of CO, was explored.

a. Reactions of $Co_2X_3(dppm)_2$ with CO

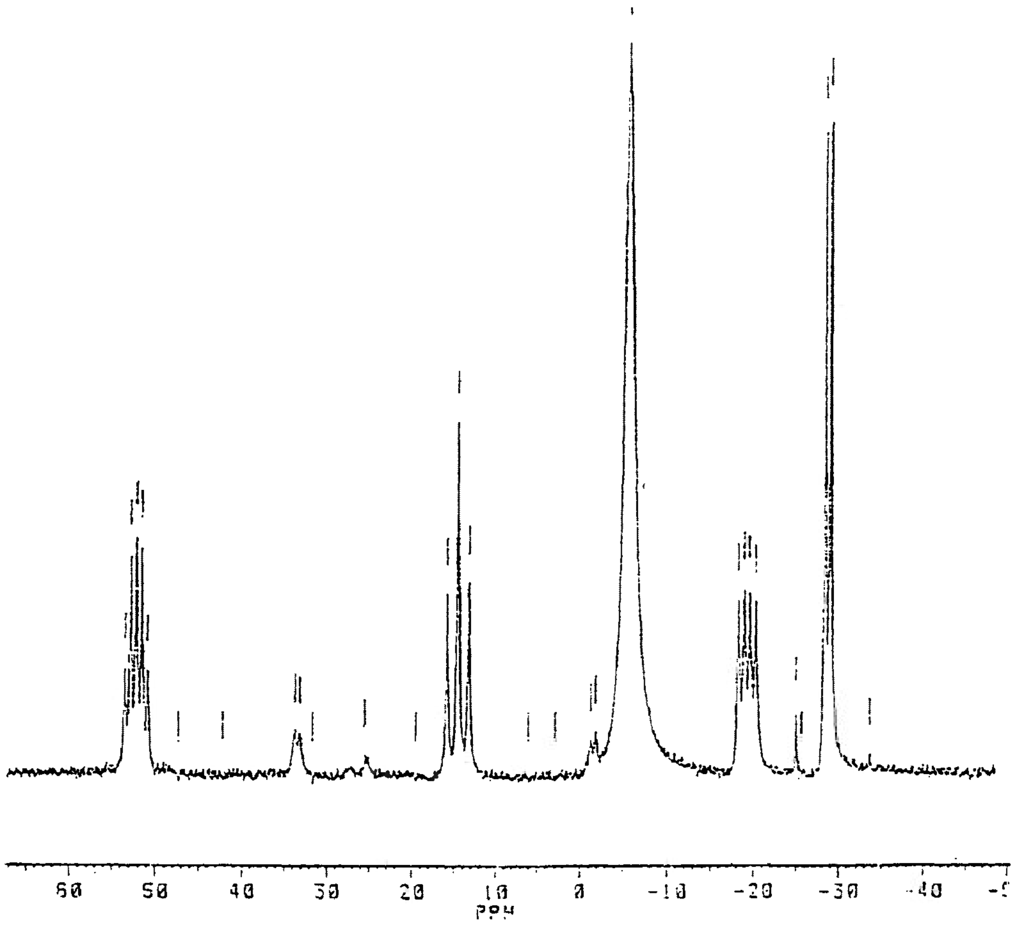
Treatment of pure $Co_2Cl_3(dppm)_2$ with CO in ethanol/benzene gives a solution which shows unexpected NMR properties. Thus, at room temperature, the spectrum shows a singlet at δ 6.0 due to the presence of **6a** and two broad and poorly-resolved humps at δ -3.5 and +51.8 (see **Spectrum 6**). However, as the temperature is reduced, a new doublet appears at around δ -28 and the signal at -3.5 disappears to be replaced by two new signals at δ -19.5 (doublet of doublets) and +14.1 (triplet) (see **Spectrum 7**). At -68°C, the spectrum is well resolved and virtually identical (apart from small chemical shift differences and the peak due to **6a**), with that of pure **5a** recorded under similar low-temperature conditions (see earlier discussion).

It appears then that the high-spin Co^I center in $Co_2X_3(dppm)_2$ reacts with CO to give, in addition to **6a**, the low-spin cation of **5** which, at room temperature, is weakly associated through the uncoordinated P atom with the unreacted high-spin Co^{II} center. As a result, the signal of this P atom is not observable because of the local paramagnetic environment which also causes considerable line broadening in the remainder of the spectrum. However, the rapid exchange between associated and non-associated **5** which apparently takes places at room temperature is slowed as the the temperature is decreased until the equilibrium (which favors the non-associated form of **5**) is frozen and the unperturbed spectrum of **5** is observed.

Spectrum 6. $^{31}P\{^1H\}$ NMR of $Co_2Br_3(dppm)_2/CO$ Ethanol/Benzene Solution at Room Temperature



Spectrum 7. $^{31}P\{^{1}H\}$ NMR of $Co_2Br_3(dppm)_2$/CO Ethanol/Benzene Solution at -68°C



These temperature dependent changes in the ^{31}P NMR are fully reversible and it is worth noting also that addition of small amounts of free dppm to the solution at room temperature causes no change in the NMR spectrum - i.e., no signal for free dppm is observed presumably because of the effect of the Co^{II} species (see **Spectrum 8a**).

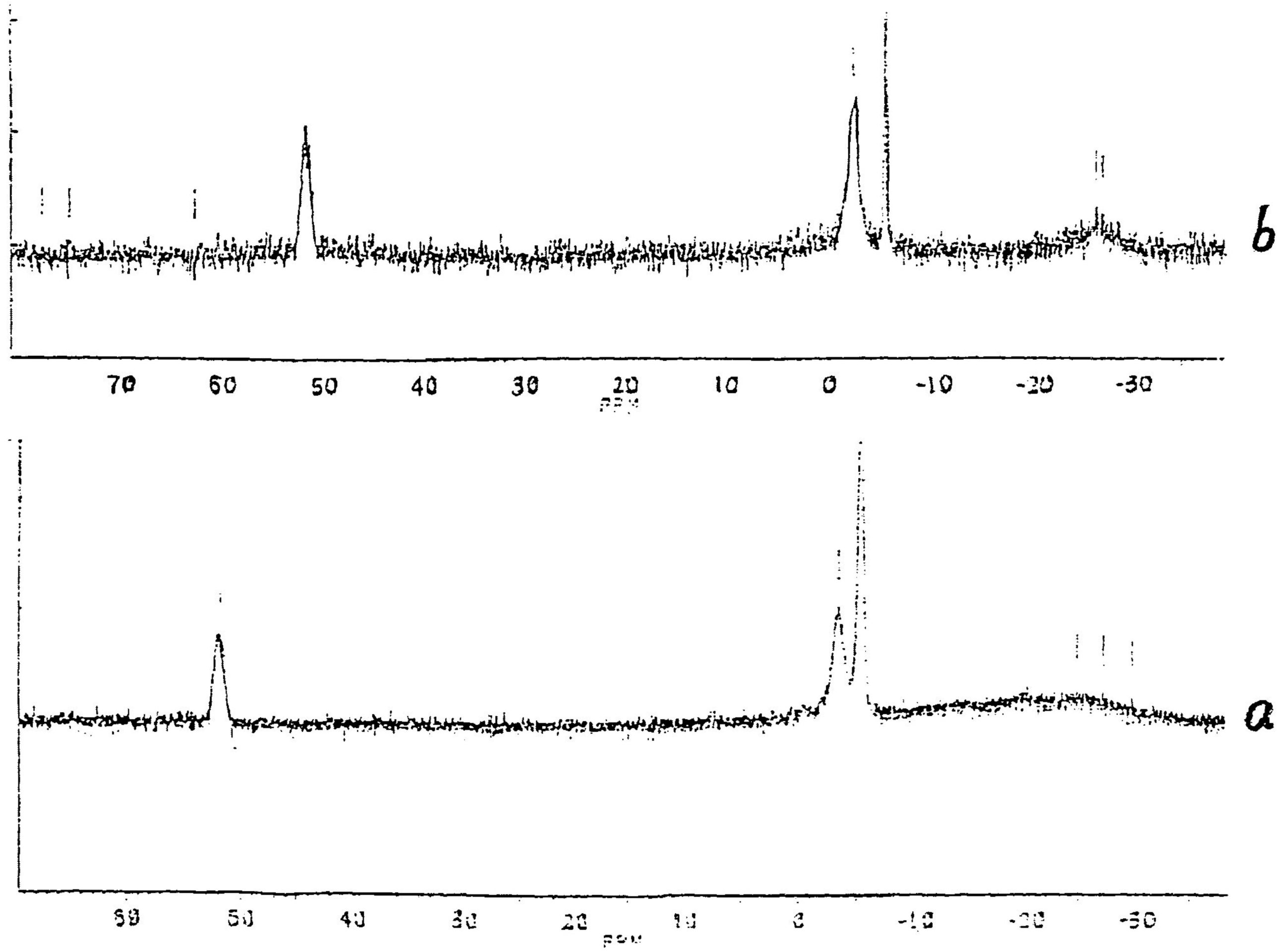
That this interpretation is correct was shown by treating a solution of pure **5b** in ethanol/benzene with an equimolar amount of $CoBr_2.xH_2O$. The resulting mixture possessed a ^{31}P spectrum identical (**Spectrum 8b**) with that of the mixture produced by direct treatment of $Co_2X_3(dppm)_2$ with CO in ethanol/benzene discussed above.

The reaction solution of $[Co(CO)(\eta^2\text{-dppm})_2]Br$, **6b**, (1 equiv) and $CoBr_2.xH_2O$ (1 equiv) under CO gives the same $^{31}P\{^1H\}$ NMR spectrum as mentioned above. Apparently, addition of Co^{II} leads to opening of the four membered ring of **6b**.

b. Reactions of $Co_2X_3(dppm)_2$ with $CO/NaBH_4$

Of even more interest is the fact that further treatment of the reaction solution of $Co_2Br_3(dppm)_2/CO$ with $NaBH_4$ (in a $Co/NaBH_4$ ratio of 2 : 1) results in the reduction of the Co^{II} center to Co^I and the formation of the known[159] $[Co_2(\mu\text{-Br})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]Br$, **7b** (as ascertained by ^{31}P NMR examination of the reaction mixture and "spiking" the mixture with an authentic sample).

Spectra 8. $^{31}P\{^1H\}$ NMR of (a) 5b with Extra dppm in Ethanol/Benzene and (b) 5b with added $CoBr_2.xH_2O$ in Ethanol/Benzene



Further addition, again under CO, of a similar amount of $NaBH_4$ leads to the reduction of both Co^I centers in **7** and the formation of the equilibrium

$$\mathbf{Co_2(CO)_4(\mu\text{-}dppm)_2\ (9)} \rightleftharpoons \mathbf{Co_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)_2\ (10)} \qquad \mathbf{[61]}$$

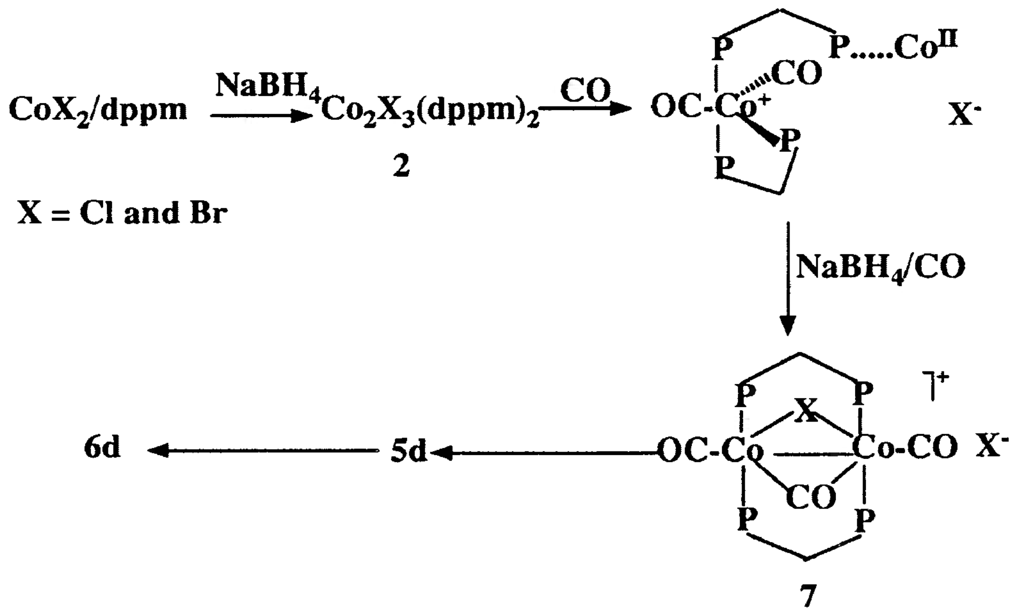
system as shown by the ^{31}P NMR spectrum and "spiking" with authentic[38] **9**. The conversion of **7** to **9** has been confirmed by the reaction of pure **7** with $NaBH_4$ (see Experimental Section). Exposure of this solution to an atmosphere of CO results in a disproportionation reaction and the formation of $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **6d**. It seems clear then that this is the principal route whereby **6d** is formed in the direct $Co^{II}/dppm/BH_4^-/CO$ reactions which have been reported elsewhere[37] and the sequence of events is summarized in **Scheme 19**.

When the molar ratio of $Co^{II}/NaBH_4$ in the above reaction is raised to 1 : 4, only free dppm (no Co-dppm complexes) can be detected by $^{31}P\{^1H\}$ NMR. This may be explained as mentioned in Section **I.2** of this Chapter.

4. Reactions of $[CoH(\eta^2\text{-dppm})_2X]X$ with CO or $CO/NaBH_4$

The discovery of vitamin B_{12}, which is regarded as a Co^{III} complex with an axially coordinated carbanion, stimulated interest in the study and preparation of Co^{III} compounds.[158] One of the interesting complexes obtained from the reactions of $Co^{II}/dppm/NaBH_4$ is the Co^{III} species $[CoH(\eta^2\text{-dppm})_2X]X$, **3**, and the further reactions of this compound with CO or $CO/NaBH_4$ are worth studying.

Scheme 19. Reaction Sequence of 2 with CO and CO/NaBH$_4$



A preliminary investigation by $^{31}P\{^1H\}$ NMR showed that no obvious reaction of [CoH(η^2-dppm)$_2$Br]Br, **3b**, in CH_2Cl_2 with CO takes place. However, compound **3b** suspended in ethanol/benzene can react further with NaBH$_4$ in the presence of CO to give a brown crystalline compound [Co$_2$(μ-Br)(μ-CO)(CO)$_2$(μ-dppm)$_2$]Br.4CH$_2$Cl$_2$, **7b**, (see Experimental Section). In the $^{31}P\{^1H\}$ NMR spectrum, **7b** shows a singlet due to the P atoms of bridging dppm at δ 52.2. The IR absorptions of **7b** occur at 1950(s), 1965(sh), 1910(s) and 1815(s) and indicate the presence of both terminal and bridging CO. The spectral properties of this compound **7b** are similar to those of the known compound [Co$_2$(μ-Cl)(μ-CO)(CO)$_2$(μ-dppm)$_2$]Cl, **7a.**[159]

The corresponding BPh_4 salt **7c** can be easily prepared from the metathetical reaction of **7b** with $NaBPh_4$. Complex **7c** shows identical spectral properties to **7a** and **7b**.

The following discussion may provide some clues to the possible mechanism for formation of the Co^{III} complexes, **3**. It is well known that Co^{I} complexes in less basic media can pick up a proton to form covalent hydrides[163] (Dfferent Co^{III} compounds have different requirements for its media. For example, the hydride $[CoH(CN)_5]^{3-}$ exists throughout the normal pH range and only gives up a proton to form $[Co(CN)_5]^{4-}$ in strongly alkaline solutions with a pK of about 18 -19, whereas the complex [Co(tspc)] is reversible protonated in aqueous solution.). The existence of the equilibrium

$$[Co^{I}]^{-} \quad + \quad H^{+} \quad \rightleftharpoons \quad Co\text{-}H \qquad [62]$$

has been demonstrated with several cobalt hydrides.[162] Since the further reactions of $[CoH(\eta^2\text{-dppm})_2X]X$, **3**, in ethanol with BH_4^-, which can act as strong base, lead to loss of proton in **3**, therefore, **3** are possibly derived from a Co^{I} intermediate, $[CoBr(\eta^2\text{-dppm})_2]$, followed by a proton abstraction from ethanol. This conclusion is consistent with observations recorded in references 18 and 19 which point out that the proton of **3** apparently comes from ethanol because **3** can be obtained very simply from the recrystallization of $Co_2X_3(dppm)_2$, **2**, in DMF in good yield when ethanol is allowed to diffuse into the solutions. The possibility that some of the ion $[Co(CO)(\eta^2\text{-dppm})_2]^+$ formed from Co^{II}/dppm/$NaBH_4$/CO reactions is derived from intermediates of the type outlined above therefore cannot be dismissed.

5. Conclusion

From the discussion outlined so far in this Section, it is clear that the Co-dppm-X complexes $CoX(\eta^1\text{-dppm})_3$, **1**, $Co_2X_3(dppm)_2$, **2**, and $[CoH(\eta^2\text{-dppm})_2X]X$, **3**, can be converted into Co-dppm-CO-X and Co-dppm-CO complexes in the presence of either CO only or with $CO/NaBH_4$, although some of these products have not yet been separated from the direct $Co^{II}/dppm/NaBH_4/CO$ reactions. Thus, most products obtained from the direct $Co^{II}/dppm/NaBH_4/CO$ reactions can also be obtained from the reactions of **1**, **2** or **3** with CO or $CO/NaBH_4$. It seems likely that compounds **1**, **2** and possibly **3** are precursors in these reactions and they can react further with CO to give the observed Co-dppm-CO-X and Co-dppm-CO complexes. This point is explored further in the next Section.

II. Mechanisms and Pathway of $Co^{II}/dppm/NaBH_4/CO$ Reactions

Section I of this chapter concentrated on the reactions of reduced Co/dppm species with CO. Several new Co-dppm-CO complexes were reported with full characterization and suggestions were made regarding possible routes whereby some of these products are formed in direct $Co^{II}/dppm/BH_4^-/CO$ reactions. These latter reactions are, however, extremely complex and this section explores such reactions in a much wider context.

As mentioned earlier, reactions of Co^{II} salts with $NaBH_4$ or $NaBH_3CN$ in the presence of dppm and CO have been shown to give several Co-CO-dppm complexes containing Co^{I}, Co^{0} and Co^{-1}. The nature of the major products is critically dependent upon the reaction conditions. Thus, if $NaBH_4$ is added to a Co^{II}/dppm/CO system in $EtOH/C_6H_6$ over 10-30 minutes, either or both of two solid products is initially obtained depending upon the conditions. These are the Co^{I}-Co^{-I} species $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **6d** and the binuclear complex $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**. The first of these, **6d**, can be converted (with loss of CO) into a mixture of **9** and $Co_2(\mu\text{-CO})_2(CO)_2(\mu\text{-dppm})_2$, **10**, by stirring a CH_2Cl_2/EtOH solution, a process similar to that recently observed[165] in a more general form in the synthesis of heterobimetallic-CO-dppm complexes. This mixture of isomers, can, in turn, be converted quantitatively into pure **10** by stirring a suspension of **9** in ethanol. This transformation can be reversed by crystallization of a solution of **10** in CH_2Cl_2 to give a mixture of **9** and **10** and the solution equilibrium **9** $\rightleftharpoons$ **10** has been studied in detail.[39] If reaction conditions are modified slightly, a fourth product, $Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm-BH}_2)$, **16** (which contains the first fully-characterized example of a $Co\text{-}BH_2$ bond), is formed[43] as a minor product together with **9** and **10**. If, however, the basic reaction is carried out with very rapid addition (ca. 1 min.) of $NaBH_4$ (but otherwise unmodified), the principal product is the diphenylphosphido-bridged system $Co_2(CO)_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})_2$.[60]

Clearly, although the above mentioned products are formed in one experimental step, several mechanistic steps must be involved. Furthermore, it is probable that those reactions leading to the formation of phosphido-bridged binuclear complexes follow a different mechanistic pathway from those leading to the other products. Thus, while the reduction of metal ions by $NaBH_4$ in the presence of CO has proved to be an extremely useful route to binuclear dppm-bridged carbonyl complexes, the mechanisms involved are poorly understood. The cobalt system, as outlined above, is particularly rich and complex and so an attempt has been made to determine the sequence of reactions which leads to each possible product.

1. Preliminary Studies

First of all, several simplified reactions were designed in order to better understand the $Co^{II}/NaBH_4$/dppm/CO reactions. These investigations were carried out by dividing the $Co^{II}/NaBH_4$/dppm/CO system into three simpler systems, **a)** $NaBH_4$/dppm with or without CO, **b)** $Co^{II}/NaBH_4$/CO, and **c)** Co^{II}/dppm/CO. All of these systems may provide some information which will hopefully lead us to understand better the mechanism of $Co^{II}/NaBH_4$/dppm/CO reactions.

a. Reaction of $NaBH_4$ and dppm

We know that if the basic reaction of $Co^{II}/NaBH_4$/dppm/CO is carried out with very rapid addition of $NaBH_4$, the principal product is the diphenylphosphido-bridged system $Co_2(CO)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-dppm})_2$.[60] The mechanistic pathway leading to the formation of the phosphido-bridged binuclear complexes is still not clear. Whether the dppm can be cleaved by $NaBH_4$ alone (unlikely) or whether the cleavage requires the coordination of dppm by Co with, perhaps, the presence of CO is not known. Furthermore, whether H_3B.dppm obtained frequently from $Co^{II}/NaBH_4$/dppm/CO reactions can be produced directly from the reaction of $NaBH_4$ with dppm should be studied as a possible intermediate for the formation of Co-BH_2-dppm complexes in these reactions.

In the simplest of these studies, a mixture of $NaBH_4$ and dppm in ethanol/benzene at room temperature or higher temperature (70°C) show no obvious reaction except for the formation of small amounts of dppm mono-oxide and dppm dioxide. Even in the presence of catalytic amounts of Co^{II}, the above reaction only shows small increases in the amounts of the two dppm oxides formed. This clearly indicates that the $NaBH_4$ cannot react with dppm alone and the cleavage of dppm must result from the interaction between Co^{II}-dppm and $NaBH_4$, perhaps in the presence of CO.

b. Reaction of $CoBr_2.4.7H_2O$ and $NaBH_4$

Since most products obtained from the $Co^{II}/NaBH_4$/dppm/CO reactions could be formed from direct reactions between $Co_2(CO)_8$ and dppm (more will be discussed later), it is of interest to know whether $Co_2(CO)_8$ or $[Co(CO)_4]^-$ (the anion of **6d**, mentioned earlier) could be produced in significant quantities under the mild conditions of the $Co^{II}/NaBH_4$/CO reactions. In this context, treatment of $CoBr_2.4.7H_2O$ with $NaBH_4$ in ethanol/benzene with CO passing gives a very finely divided black solid which precipitated out from solution immediately. The black solid is insoluble in all organic solvents and does not react further with dppm. It probably is a non-stoichiometric Co boride of the type formed in similar reactions in which CO is absent.[185] The black solid is formed even in the presence of dppm if the mole ratio of dppm to Co^{II} is less than 1 : 1. Formation of the black precipitate cannot be prevented even if the reaction is carried out at lower temperatures (-20°C), or if $NaBH_4$ is added very slowly, or even if $NaBH_3CN$ (a milder reducing agent) is added first, followed by $NaBH_4$, to the reaction solution. The IR spectra of the filtrates of these reaction solutions also indicate no trace of the existence of $Co_2(CO)_8$ or $[Co(CO)_4]^-$. This clearly indicates that Co^{II} can not be reduced by $NaBH_4$ directly under CO to produce $Co_2(CO)_8$ or $[Co(CO)_4]^-$ in the absence of dppm. The $[Co(CO)_4]^-$ component of compound **6d** therefore could come from the further reduction of **6a** or **6b** (or related species) and replacement of dppm with CO, and it should be borne in mind that the sequence outlined in **Scheme 19** (Section **I** of this chapter) is the most probable route of formation.

c. Reactions of Co^{II}/dppm and Co^{II}/dppm/CO

Co^{II} halide complexes with tertiary phosphines and diphosphines are well known.[166,167] Nevertheless, their solution behavior has not been extensively investigated.[168] A recent report[11] pointed out that reactions of $CoBr_2(PPh_3)_2$ at 25°C in benzene with $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 2 and 3), which have been followed spectrophotometrically and by conductivity measurements in CH_2Cl_2, include several steps. With dppm, a bridging mode of coordination on two metal atoms forms initially and this is followed by the formation of a chelating dppm ring without disruption of the bridged system as shown in **Scheme 1** (see Introduction).

It has been shown that $K_1 = (1.73 \pm 0.14) \times 10^9$ mol^{-2} L^2; $K_2 = (9.4 \pm 0.5) \times 10^{-2}$mol L^{-1} and $K_3 = (1.05 \pm 0.08) \times 10^{-2}$. Therefore the interaction between the Co^{II} species and dppm in the Co^{II}/dppm/NaBH$_4$/CO reactions should be very fast. Several pseudotetrahedral [CoX$_2$(η^2-dppm)] and [CoX(η^2-dppm)$_2$]X (X = Cl, Br, I and ClO$_4$) complexes have also been separated from the reactions of CoX$_2$ with dppm.[12] The further reduction of these Co^{II}-dppm complexes with NaBH$_4$ could therefore be based on species of the type shown in **Scheme 1**, [CoX(η^2-dppm)$_2$]X and [CoX$_2$(η^2-dppm)]. The easy formation of bridging and chelating Co^{II}-dppm species can account for the later and the quick formation of bridging or chelating Co-dppm-CO species such as Co$_2$(CO)$_4$(μ-dppm)$_2$, **9**, Co$_2$(μ-CO)$_2$(CO)$_2$(μ-dppm)$_2$, **10** and [Co(CO)(η^2-dppm)$_2$][Co(CO)$_4$], **6d**, under the usual conditions of the Co^{II}/dppm/BH$_4^-$/CO reactions.

It has been established for some time that Co^{II}-phosphine complexes can form unstable Co^{II}-phosphine-CO derivatives upon exposure to CO. The reactions of carbon monoxide with complexes of the type CoX$_2$(PR$_3$)$_2$ (PR$_3$ = tertiary phosphine, X = mononegative ion) under ambient conditions leads to the reversible formation of the five-coordinate adducts CoX$_2$(CO)(PR$_3$)$_2$. The stability of the adducts is strongly influenced by the nature of R and X.[154] The stability constants of the equilibria

$$\mathbf{CoX_2(PR_3)_2 \; + \; CO \; \rightleftharpoons \; CoX_2(CO)(PR_3)_2} \qquad \textbf{[63]}$$

have been measured for several complexes in C$_2$H$_4$Cl$_2$ at 25°C as shown in **Table 1**

(Abstracted from ref. 154)

Table 1.

Stability Constants (K, M^{-1}) at 25°C for the Equilibrium

$$Co(PR_3)_2X_2 \quad + \quad CO \rightleftharpoons Co(CO)(PR_3)_2X_2$$

X	$P(C_3H_7)_3$	$P(C_2H_5)_3$	$P(C_2H_5)_2Ph$	$P(C_2H_5)Ph_2$	PPh_3	$P(C_6H_{11})_3$
Cl	787±31	1232±63	203±5	6.8±0.2	b	b
Br	2371±117	2476±123	1020±41	103±2	2.9±1[c]	b
NCS	a	a	a	503±5	91±2	22±1

a: Not determined; b: Very small, not measurable; c: Estimated error

Generally, **Table 1** shows that the equilibrium lies very far to the left for bulkier, less basic phosphines such as PPh_3 (X = Cl). In the Co^{II}/dppm/$NaBH_4$/CO reactions, the exposure time of the Co^{II}/dppm ethanol/toluene solution to CO is so brief, and the dppm is sufficiently bulky, that the reduction of Co^{II}-dppm by $NaBH_4$ should occur before significant interaction of CO with the Co center takes place. Therefore, as briefly touched upon in Section I of this chapter, complexes **1**, **2** and **3** should be the first reduced products in the Co^{II}/dppm/$NaBH_4$/CO reactions.

2. Sequence of Products Obtained From Reactions of Co^{II}/dppm/$NaBH_4$/CO

As mentioned in the introduction to this section, a series of Co-dppm-CO products has been separated from Co^{II}/dppm/$NaBH_4$/CO reactions with the nature of the major product depending upon reaction conditions. In a further investigation carried out as part of the studies described herein, no new product was isolated from the reactions of $CoBr_2.4.7H_2O$ and $NaBH_4$ in the presence of dppm and CO even though factors such as temperature and reactant stoichiometries were varied considerably.

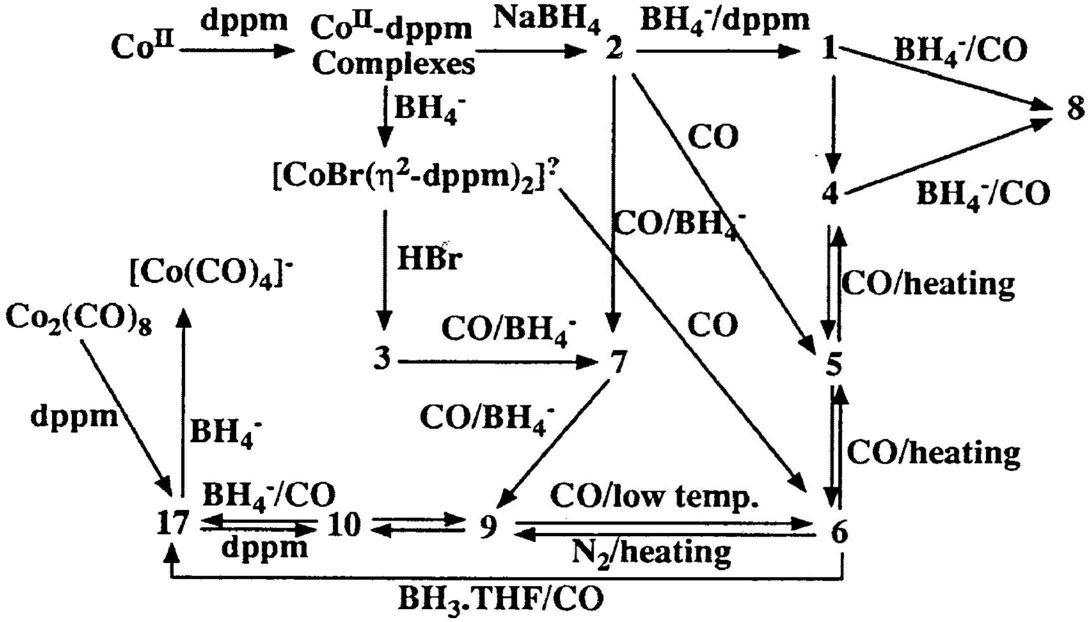
Thus, reaction of $CoBr_2.4.7H_2O$ with dppm and $NaBH_4$ in the ratio of 1 : 1 : 1 in the presence of CO gave $[Co(CO)(\eta^2\text{-dppm})_2]Br$, **6b**, as the major product as indicated by solution $^{31}P\{^1H\}$ NMR spectra. The product was separated and characterized as mentioned in section **I.1.c.** of this chapter. However, if the reaction of $CoBr_2.4.7H_2O$, dppm, $NaBH_4$ and CO is carried out in a ratio of Co^{II}/$NaBH_4$/dppm = 1 : 2 : 1, both the ion pair, $[Co(CO)(\eta^2\text{-dppm})_2]X$ (X = Br or $[Co(CO)_4]$), **6b** or **6d**, and the dimer, $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**, are major products as indicated by solution $^{31}P\{^1H\}$ NMR spectra and spiking with authentic **6d** and **9**.[5]

When the ratio of Co^{II}/$NaBH_4$ is increased to 1 : 4, all the peak intensities of the known products except $[Co_2(\mu\text{-CO})_2(CO)_4(\mu\text{-dppm})]$, **17**, in the $^{31}P\{^1H\}$ NMR spectrum decrease. When the Co^{II}/$NaBH_4$ ratio reaches 1 : 6, almost no peaks of Co-dppm-CO complexes can be detected by $^{31}P\{^1H\}$ NMR and the strongest signal is due to free dppm. As mentioned before(Section II.2 of this chapter), solution IR spectra show absorptions which could be due to $[Co(CO)_4]^-$ at 1890 and 2040cm^{-1}.

It is also worth mentioning that no anionic cobalt-dppm-CO complex, or $[Co(CO)_4]^-$ itself, could be precipitated from reactions of Co^{II}/$NaBH_4$/dppm/CO/Ph_4PBr in a variety of ratios and reaction conditions.

From the above discussion, it seems likely that Co^{II} reacts with dppm first to form bridging and chelating Co^{II}-dppm species. Then the Co^{II}-dppm complexes are reduced by BH_4^- to give complexes **1**, **2** and **3** via a [dppm-Co^{II}-H-BH_3] intermediate. The complexes **1**, **2** and **3** then react with CO or are reduced by $NaBH_4$ in the presence of CO to form a variety of Co-dppm-CO and Co-dppm-CO-X complexes. Finally, as the reaction proceeds further, all of these Co-dppm-CO complexes can be converted into $[Co(CO)_4]^-$ and free dppm. The complete process is summarized in **Scheme 20** and while some elements of **Scheme 20** may be somewhat speculative, the evidence suggests that, in broad outline, it is accurate.

Scheme 20. Possible Pathway of Reactions of Co^{II}/dppm/CO/NaBH$_4$



3. Equilibrium between the Dimers 9 and 10 and the Ion pair 6d

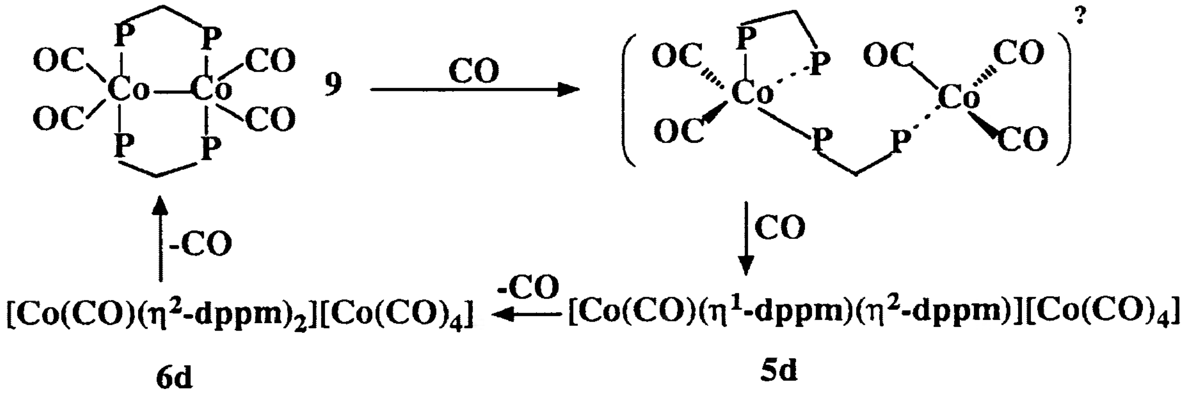
Normally, cationic-anionic complexes of the type $[Co(CO)_n(PR_3)_{5-n}][Co(CO)_4]$ (n = 1 - 4) are synthesized[25,169] from disproportionation reactions of phosphines or phosphites with $Co_2(CO)_8$ and the formation[38,39] of $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **6d**, in Co^{II}/dppm/BH_4^-/CO reactions might, at first sight (ignoring the evidence above), be assumed to fall into this category. Indeed, it has recently been shown[25] that $Co_2(CO)_8$ reacts with dppm rapidly (a few minutes) to give the salt $[Co(CO)_3(\eta^1\text{-dppm})][Co(CO)_4]$ and that this loses CO to give $Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-dppm})$, **17**. However, the evidence presented above and in the previous sections of this chapter shows that this is not the case and therefore the equilibrium **6d** $\rightleftharpoons$ **9** has been explored further.

Thus, it has already been found that benzene or CH_2Cl_2 solutions of the ion pair $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **6d**, can turn black slowly as the dimer $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**, is produced and there is an equilibrium between **9** and its isomer $Co_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})_2$, **10**, in solution.[39] In the work described herein, it has been found that **6d** can be easily converted into **9** by removing one CO with a N_2 stream in most solvents at room temperature.

It is interesting to note that the reverse reactions of benzene/ethanol solutions of the dimer **9** with CO to give the ion pairs **5d** (see **Scheme 21**), and **6d** (confirmed by spiking with authentic samples of **6d** and pure **5b**), are much slower than expected. The unexpected formation of **5d** gives us a clue regarding the sequence of steps in the conversion of **9** into **6d**. The probable steps are outlined in **Scheme 21**.

The conversion of **9** to a mixture of **5d** and **6d** can only be carried out in a protic

Scheme 21. Reactions of **9** with CO



solvent. In benzene or CH_2Cl_2 solution, no reaction between **9** and CO is observed. Therefore, **9** is stable in non-protic solvents whereas **5d** and **6d** are favoured in protic solvents.

Complex **9** appears to be a thermodynamically stable product whereas **6d** is a kinetically favoured product. Thus, the reaction of $Co^{II}/NaBH_4$ in a 1 : 2 ratio with dppm and CO at low temperature (-20°C), gives only the ion pair **6d**. If, however, the reaction is carried out at 0°C, peaks due to both the ion pair **6d** and the dimer **9** appear in the $^{31}P\{^1H\}$ NMR spectrum but the integral area of the dimer **9** is very small. If the reaction solution is allowed to reflux for 30 minutes under CO, the dimer **9** becomes the major product. When the ion pair **6d** is heated under reflux for a while (15 min.) in benzene in a CO atmosphere, it can be easily converted to the dimer **9**. Thus, at low temperatures, the equilibrium [64] seems to favor the ion pair **6d**, whereas higher temperatures favor formation of the dimer **9**.

$$[\mathbf{Co(CO)(\eta^2\text{-}dppm)_2][Co(CO)_4]} \rightleftharpoons \mathbf{Co_2(CO)_4(\mu\text{-}dppm)_2} \qquad [64]$$

4. Reactions of $Co_2(CO)_8$ and Dppm

Since it has already been briefly mentioned that cationic-anionic complexes related to **6d** are usually prepared by reactions of phosphines with $Co_2(CO)_8$, such reactions have been examined briefly as part of the study described in this chapter.

It has been demonstrated that the CO ligands of $Co_2(CO)_8$ can be replaced easily by phosphines.[171-173] Thus, $Co_2CO)_8$ reacts rapidly with dppm to give an unstable salt $[Co(CO)_3(\eta^1\text{-dppm})][Co(CO)_4]$ which converts quickly to corresponding neutral dimer $Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-dppm})$ in solution.[25] However, it is most unlikely that $Co_2(CO)_8$, which is normally formed from Co^{II} only under extremely forcing conditions,[170] could be formed in significant quantities under the mild conditions (room temperature, atmospheric pressure, short reaction times) of these Co^{II}/dppm/$NaBH_4$/CO reactions. Certainly, we have uncovered no evidence for the formation of $Co_2(CO)_8$ in our detailed studies[37,38,39,43,60] of this reaction system. Although a lot of work has been done on the reactions of $Co_2(CO)_8$ with dppm,[25] no Co-dppm-CO complexes similar to those obtained from the Co^{II}/dppm/BH_4^-/CO reactions have ever been obtained in previous work. It appeared at the time this work was started that there is no obvious connection between the two methods which give entirely different products. However, in a reexamination of the $Co_2(CO)_8$/dppm system it has been found that $Co_2(CO)_8$

reacts with dppm in benzene at -20°C to give an extremely unstable species, tentatively characterized as $[Co(CO)_3(\eta^1\text{-dppm})_2][Co(CO)_4]$, **18**, and $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})][Co(CO)_4]$, **5d**. Complex **18** cannot be separated from the solution because it converts to **5d** slowly in solution with time. Compound **18** has a similar $^{31}P\{^1H\}$ NMR spectrum (benzene solution) to that shown by the complex $CoBr(CO)_2(\eta^1\text{-dppm})_2$, **4b**, but has slightly different chemical shifts, [δ 57.41 (dd), -22.56 (dd)] and quite different coupling constants ($^2J_{PP} = 27.3$ and 74 Hz). Compound **18** provides important supporting evidence (in terms of the stability of the cation) for the existence of the intermediate $[Co(CO)_3(\eta^1\text{-dppm})_2]Br$ in the conversion of **5** to **4** under CO (see p.103).

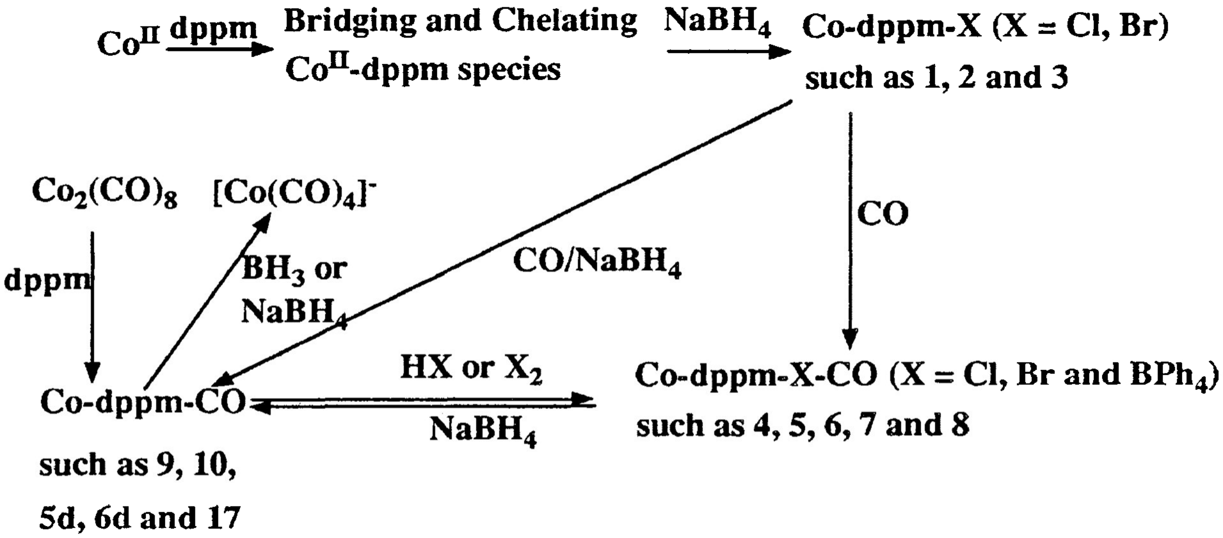
Complex **5d** is also unstable and converts first into **6d**, and then **9** in the recrystallization process. However, since the reactions of $Co_2(CO)_8$ with dppm are quite clear, only **18** and **5d** exist in the solution and the former will be converted to **5d** with time, pure **5d** can be obtained by simply removing most of the solvent with a N_2/CO stream followed by rapid addition of CO saturated Et_2O. The $^{31}P\{^1H\}$ NMR spectrum is identical to that of **5b**. Therefore, it is quite clear that in contrast to previous reports published in the literature[25,26], most products obtained from the Co^{II}/dppm/BH_4^-/CO system can also be obtained from the $Co_2(CO)_8$/dppm system.

Finally, it is necessary to mention again that a dppm ligand in $Co_2(CO)_4(\mu\text{-dppm})_2$, **9**, and $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, **6d**, can be removed by BH_3.THF to give $Co(\mu\text{-CO})_2(CO)_4(\mu\text{-dppm})$, **17**, which is the first product from the reaction of $Co_2(CO)_8$ with dppm.

In conclusion, the relationships between the Co^{II}/dppm/BH_4^- system, the

Co^{II}/dppm/BH_4^-/CO system and the $Co_2(CO)_8$/dppm system are quite clear and are summarized in **Scheme 22.**

Scheme 22. Relationship Between The Reaction Systems, Co^{II}/dppm, Co-dppm-X, Co-dppm-CO-X, Co-dppm-CO and $Co_2(CO)_8$/dppm



III. Synthesis of Heterobimetallic Complexes

Heterobimetallic complexes are particularly interesting for their potential to exhibit different reactivities at the two different metal sites and unusual chemical and physical properties arising from the presence of different metals. Having two different metal atoms in the same molecule can result in a different electron population on the two metal atoms. This is particularly important in the context of catalytic systems.[3,4,35,36]

Shaw and his co-workers have been particularly active in preparing homo- and hetero-bimetallic compounds bridged by dppm using a strategy based on metallation[174-176] and transmetallation[177-179] of binuclear frameworks. Similarly, Kubiak's group[82,83,84] has used the cradle nickel complex, $Ni_2(\mu\text{-CNMe})(CNMe)_2(\mu\text{-dppm})_2$, for which the structure is similar to that of $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$, as a starting material in such studies and several heterometallic complexes such as $\{[Ni_2(\mu\text{-CNMe})(CNMe)_4(\mu\text{-dppm})\}_2Hg][NiCl_4]$,[82] $[Ni_2Pd(CNMe)_6(\mu\text{-dppm})_2]^{2+}$,[83] $[NiPt(\mu\text{-CNMe})(CNMe)(\mu\text{-dppm})_2Cl][Cl]$,[84] and $[NiAu(CNMe)_2(\mu\text{-dppm})_2]Cl$,[85] have been synthesized and characterized.

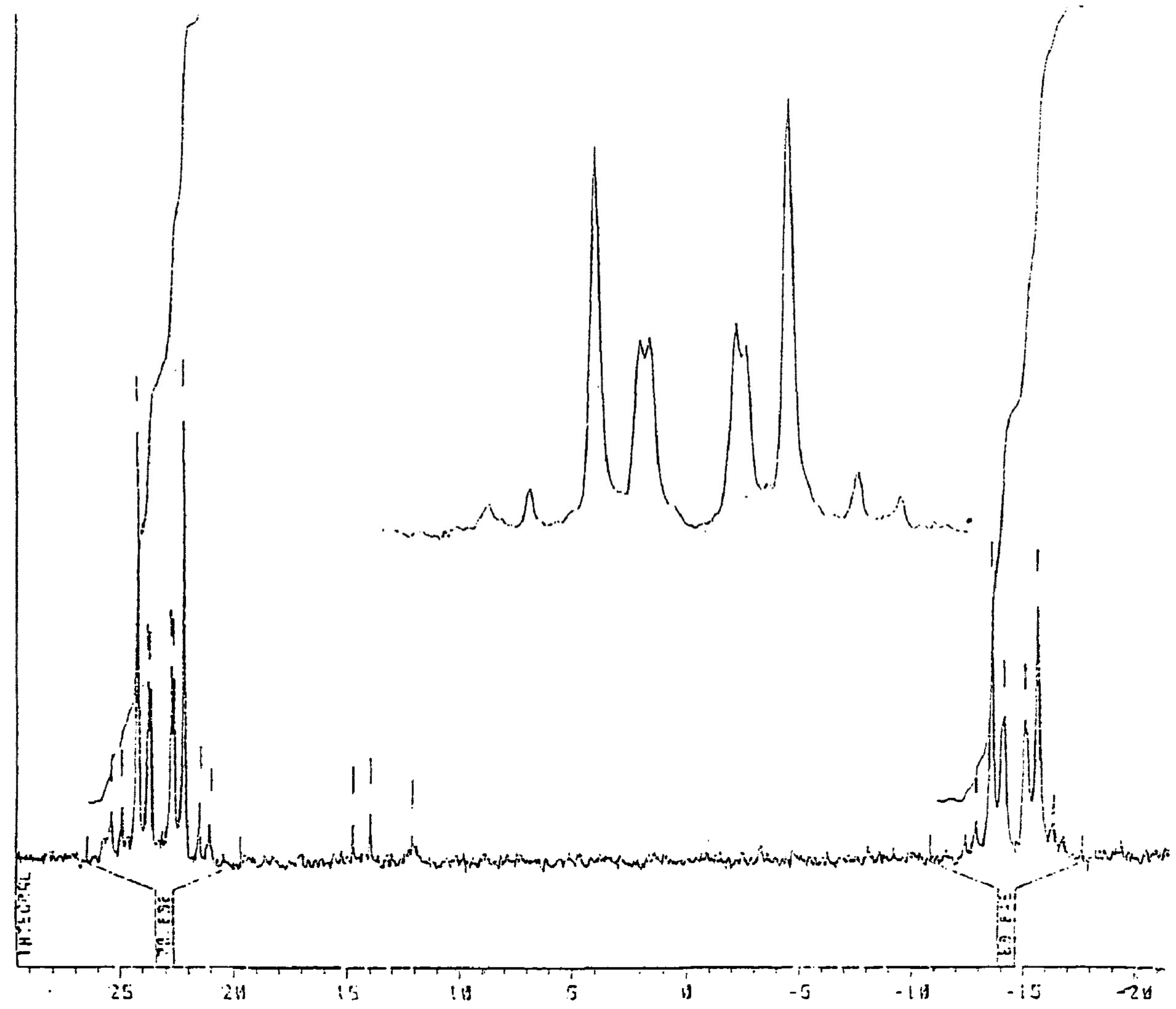
Several Co-CO-dppm complexes containing monocoordinated dppm have been reported earlier in this chapter and these are obvious starting points for bimetallic syntheses. Such studies have been carried out but greater success has been achieved with related Ni-CO-dppm complexes and these reactions will therefore be discussed first. Thus, as noted earlier (see Introduction), $Ni(CO)_2(\eta^1\text{-dppm})_2$, **11**, and $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ have been prepared from Ni^{II}/dppm/BH_4^- or BH_3CN^-/CO reactions.[53] There is considerable interest[176,180] at present in using complexes containing monodentate (or bridging) dppm as precursors to prepare bimetallic systems and there is obvious potential for the use of $Ni(CO)_2(\eta^1\text{-dppm})_2$. Indeed, this compound reacts very rapidly with $PtCl_2(COD)$, $NiCl_2.6H_2O$, $Rh_2Cl_2(CO)_4$, and $Mo(CO)_5(THF)$ in CH_2Cl_2 and a variety of bimetallic complexes have been isolated.[10] For example, $[PtNiCl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ has been obtained and its crystal structure shows that both the Ni and Pt atoms are each bonded to a terminal chlorine atom although the overall electronic structure appears to be that of a Ni^0-Pt^{II} system.[81] Complex **11** is worth further study in terms of its synthetic potential for heterobimetallic syntheses and further study of the reactions of **11** with other metals, especially with other d^{10} metal salts, has been undertaken.

1. Reaction of $Ni(CO)_2(\eta^1\text{-dppm})_2$ with $Cu(MeCN)_4ClO_4$

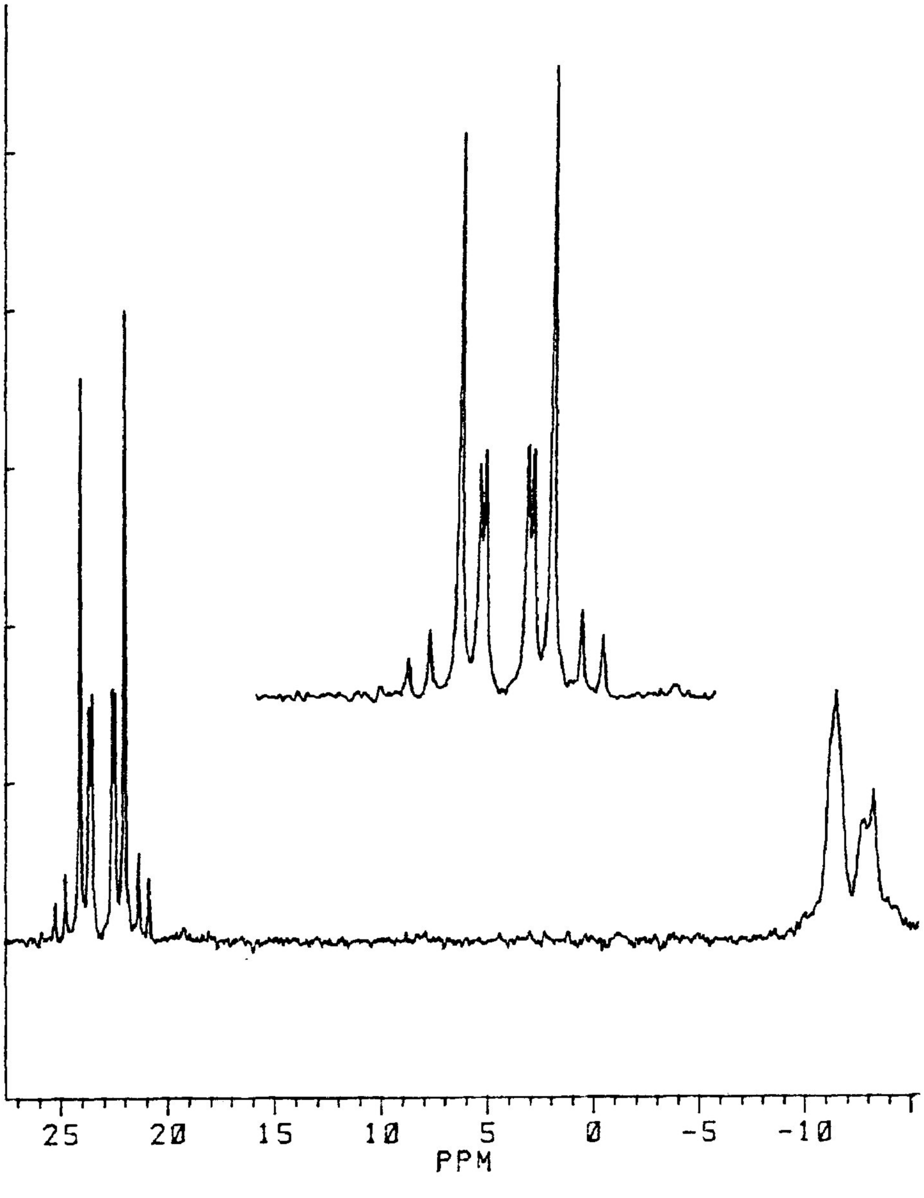
Treatment of $Ni(CO)_2(\eta^1\text{-dppm})_2$, **11**, in benzene with $Cu(MeCN)_4ClO_4$ in MeCN afforded **12** (see **Figure 14**) as a yellow-green precipitate. A yellow-green crystalline solvate **12a** can be obtained from recrystallization in CH_2Cl_2 and the non-solvated material **12b** can also be obtained from the direct crystallization of the filtrate of the reaction solution upon addition of hexane. The products **12a** and **12b** have been characterized by microanalysis and by IR, ^1H and ^{31}P NMR spectroscopy. The IR spectra (ν_{CO} 2000 (s), 1918 (s) cm^{-1}) of **12a** and **12b** is similar to that of the starting material **11**, and therefore the enviroment about Ni is probably similar in the two complexes **11** and **12**.

The value of ν_{ClO_4}, 1088 (s, br) cm^{-1} in the IR spectra of **12a** and **12b** indicates that the ClO_4 group is not coordinated.[182] Both IR (**12a**, ν_{CN} 2275, 2318 cm^{-1}; $Cu(MeCN)_4ClO_4$, ν_{CN} 2272, 2335 cm^{-1}; Free MeCN, ν_{CN} 2251, 2293 cm^{-1}) and ^1H NMR (δ 1.94) spectra indicate clearly that MeCN is still contained in the products **12a** and **12b**. The $^{31}P\{^1H\}$ NMR spectra of **12a** and **12b** show a complex AA'XX' spin system at low temperature (202K) (see **Spectrum 9**), although at room temperature the $^{31}P\{^1H\}$ NMR spectra of **12a** and **12b** (see **Spectrum 10**) show broadening at the

Spectrum 9. $^{31}P\{^1H\}$ NMR of 12a at 202K in CD_2Cl_2



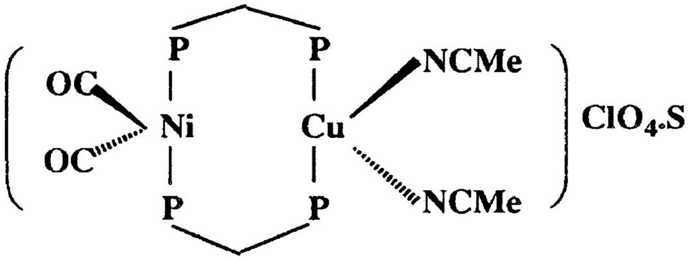
Spectrum 10. $^{31}P\{^1H\}$ NMR of 12a at 298K in CD_2Cl_2



peaks corresponding to Cu-P-CH_2-P because of the influence of the quadrupolar effect of ^{63}Cu.

The spectroscopic and analytical data suggest the formation of $[NiCu(CO)_2(\mu\text{-dppm})_2(MeCN)_2]ClO_4$ which is related to the known[85] d^{10} - d^{10} system, $[NiAu(CNMe)_2(\mu\text{-dppm})_2]Cl$. A possible structure for the complex is shown in **Figure 13.**

Figure 13. Structure of 12



S = 0.4CH_2Cl_2, 12a; no S 12b.

It has not yet been possible to grow crystals of **12** which are suitable for X-ray analysis.

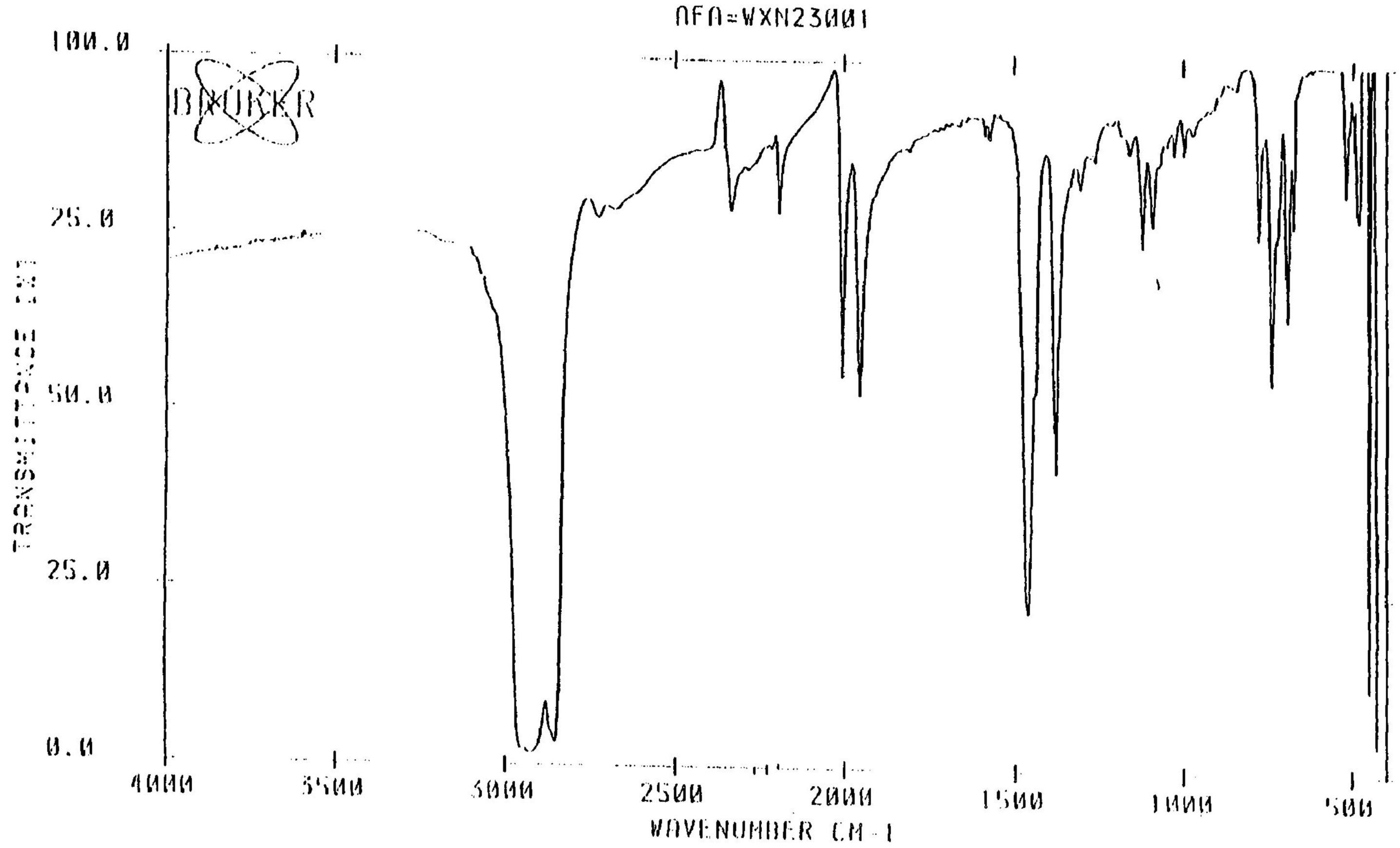
The corresponding BPh_4^- or PF_6^-salts, $[NiCu(CO)_2(\mu\text{-dppm})_2(MeCN)_2]X.CH_2Cl_2$ (X = BPh_4, **12c**; X = PF_6, **12d**) can be prepared by metathetical reactions of compound **12a** with an excess of either $NaBPh_4$ or $NaPF_6$ in MeCN. The spectroscopic properties of **12c** and **12d** are identical to those of **12a**. The results provide further evidence for an ionic formulation of the complexes **12**.

The compounds **12a** and **12b** do not react further with PPh_3 in CH_2Cl_2 under a CO atmosphere as indicated by the $^{31}P\{^1H\}$ NMR spectra of the solutions. If dppm is added to a solution of **12a**, this complex decomposes into the Ni complexes **11** and $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$ and the Cu complex, $[Cu_2(\mu\text{-dppm})_2][ClO_4]_2$, as also indicated by a $^{31}P\{^1H\}$ NMR spectrum of the solution.

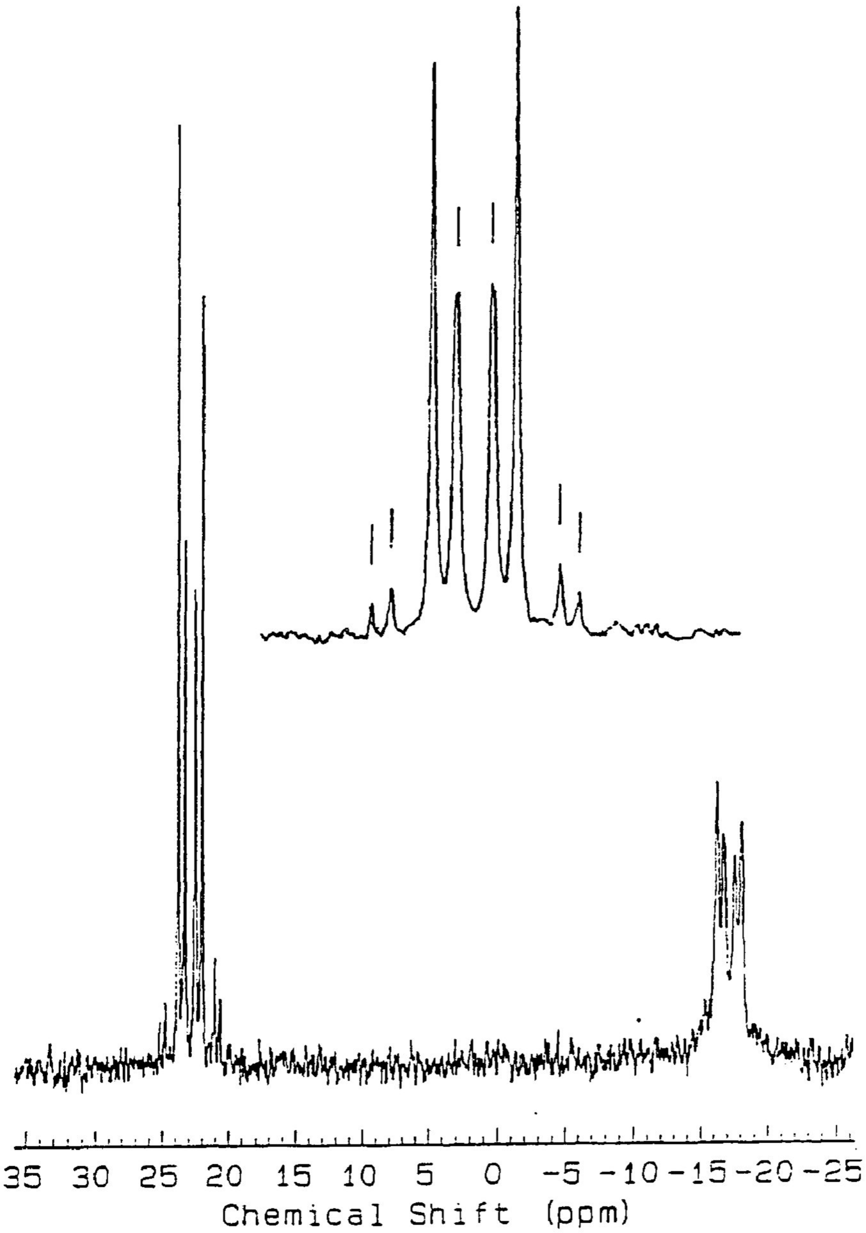
2. The $NiCl_2$/dppm/$NaBH_3CN$/$CuCl_2$ Reaction System

It is interesting to note that a similar compound, $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].S$, **13** ($S = CH_2Cl_2$), is isolated in up to 66.2% yield in a single experimental step by addition of $CuCl_2.2H_2O$ to a benzene/ethanol solution containing $Ni(CO)_2(\eta^1\text{-dppm})_2$, $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$, free dppm and $NaBH_3CN$ obtained from the reaction of the system $NiCl_2.6H_2O$/dppm/$NaBH_3CN$/CO (ratio of Ni^{II} : dppm : $BH_3CN^- = 1 : 3.5 : 5)^{53}$ with an excess of CO. Yellow-green crystalline **13** can be obtained as a CH_2Cl_2 solvate (presence of the CH_2Cl_2 is confirmed by MS and ^1H NMR spectra) from recrystallization in CH_2Cl_2. The IR spectrum of **13** (ν_{CO} 2000 (s); 1958 (s) cm^{-1}) is similar to those of **12** except for the BH_3CN group absorptions at ν_{BH} 2320(s)cm^{-1} and ν_{CN} 2280 (sh), 2190 (s) cm^{-1} (see **Spectrum 11**). The $^{31}P\{^1H\}$ NMR spectrum of **13** is also a complex AA'XX' spin system (see **Spectrum 12**). The spectroscopic and analytical data suggest the possible structure of **13** should be similar to that of **12a**.

Spectrum 11 IR of 13



Spectrum 12 $^{31}P\{^{1}H\}$ NMR of 13 in CD_2Cl_2 at Room Temperature



This has been confirmed recently by an X-ray study[193] for which an ORTEP structure is shown in **Figure 14** which shows the Ni atom to be four-coordinate in a tetrahedral geometry while the Cu atom is three-coordinate and trigonal with the Ni-Cu-phosphine framework in a cradle type of arrangement. A skeletal view of the molecule is presented in **Figure 15**, and shows more clearly that one of the CO ligands attached to Ni is tilted towards Cu, although the distance of Cu-C_1 (2.704Å) is too great for this CO to be regarded as a bridging ligand. Also, the metal centers are too far apart (Ni-Cu = 3.167Å) for any metal-metal interaction. Crystallographic data are given in **Tables 2**, **3** and **4**.

Complex **13** crystallizes in the triclinic space group P-1 with unit cell dimentions of a 11.411(7) Å, b 14.937(6) Å, c 17.045(6) Å, α 79.66(3)°, β 76.34(5)°, γ 71.27(4)°, Volume 2656.4(22)$Å^3$ (Estimated standard deviations in the least significant digits are given in parentheses). The crystal size (mm) was 0.10 × 0.20 × 0.60. Unit cell dimensions were obtained from 25 reflections with 2θ angle in the range of 40.00° - 50.00°. The intensity data were collected on an Enraf-Nonius CAD 4 diffractometer, using the $\theta/2\theta$ scan mode. Bond lengths, bond angles and atomic positional parameters for the coordination sphere of $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$, **13**, are shown in **Tables 2**, **3** and **4** repectively.

Table 2. Bond Lengths(Å) in the Coordination Sphere of $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$, 13

Cu - Ni	3.167	P(2) - C(1C)	1.854

Figure 15 ORTEP drawing of [NiCu(CO)$_2$(μ-dppm)$_2$(BH$_3$CN)].CH$_2$Cl$_2$, 13

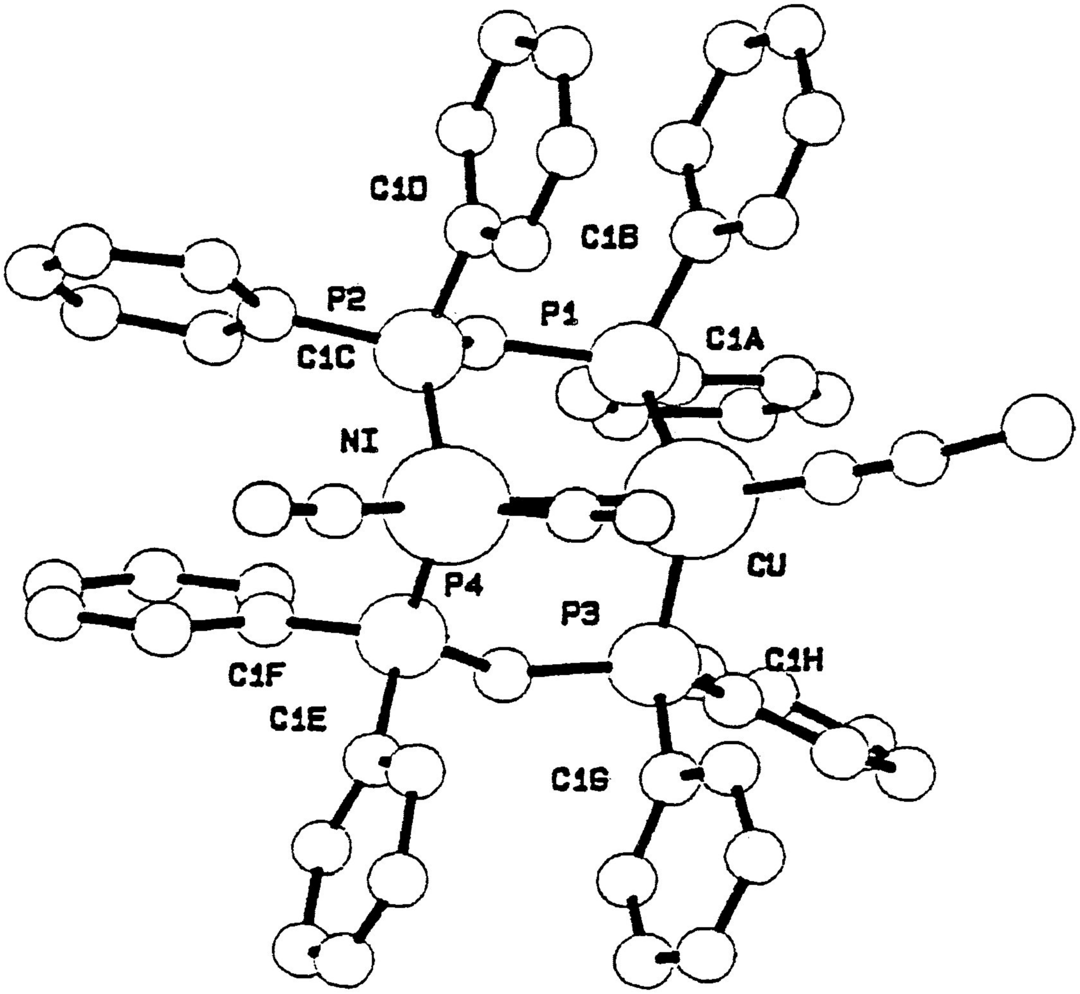
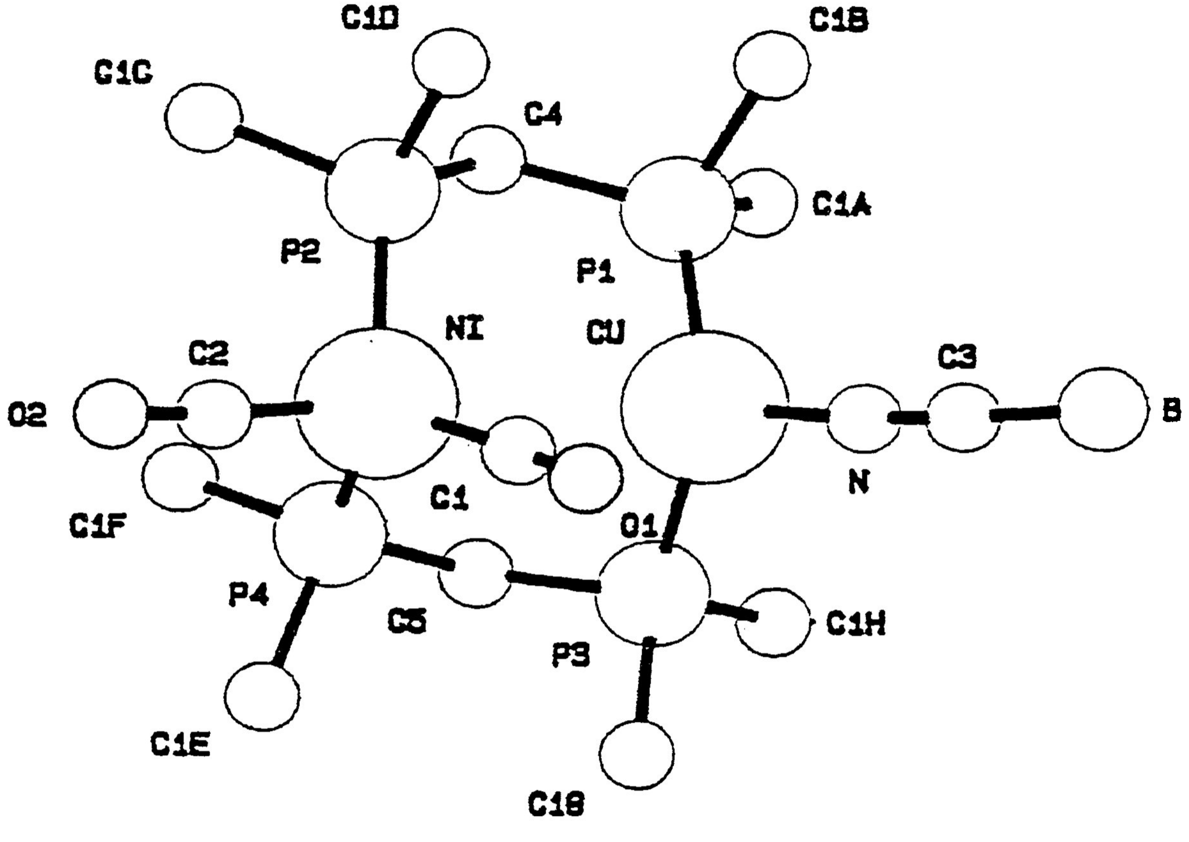


Figure 16 Skeletal view of [NiCu(CO)$_2$(μ-dppm)$_2$(BH$_3$CN)].CH$_2$Cl$_2$, 13. Phenyl rings have been omitted for clarity.



Cu - P(1)	2.243	P(2) - C(1D)	1.820
Cu - P(3)	2.242	P(3) - P(4)	3.060
Cu - C(1)	2.704	P(3) - C(5)	1.845
Cu - N	1.909	P(3) - C(1G)	1.792
Ni - P(2)	2.213	P(3) - C(1H)	1.827
Ni - P(4)	2.216	P(4) - C(5)	1.844
Ni - C(1)	1.762	P(4) - C(1E)	1.801
Ni - C(2)	1.755	P(4) - C(1F)	1.849
P(1) - P(2)	3.035	C(1) - O(1)	1.144
P(1) - C(4)	1.844	C(2) - O(2)	1.104
P(1) - C(1A)	1.859	N - C(3)	1.200
P(1) - C(1B)	1.804	C(3) - B	1.583
P(2) - C(4)	1.841		

Table 3. Bond Angles (deg) in the Coordination Sphere of the $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$, 13

Ni - Cu - P(1)	90.9	P(1) - P(2) - C(4)	34.6
Ni - Cu - P(3)	88.7	P(1) - P(2) - C(1C)	134.7
Ni - Cu - C(1)	33.8	P(1) - P(2) - C(1D)	91.3
Ni - Cu - N	121.3	C(4) - P(2) - C(1C)	100.2
P(1) - Cu - P(3)	117.5	C(4) - P(2) - C(1D)	104.0

P(1) - Cu - C(1)	114.3	C(1C) - P(2) - C(1D)	101.3
P(1) - Cu - N	116.4	Cu - P(3) - P(4)	88.3
P(3) - Cu - C(1)	98.1	Cu - P(3) - C(5)	108.9
P(3) - Cu - N	116.5	Cu - P(3) - C(1G)	121.8
C(1) - Cu - N	88.3	Cu - P(3) - C(1H)	115.1
Cu - Ni - P(2)	84.7	P(4) - P(3) - C(5)	33.9
Cu - Ni - P(4)	86.0	P(4) - P(3) - C(1G)	92.7
Cu - Ni - C(1)	58.5	P(4) - P(3) - C(1H)	135.7
Cu - Ni - C(2)	164.8	C(5) - P(3) - C(1G)	103.1
P(2) - Ni - P(4)	109.5	C(5) - P(3) - C(1H)	101.8
P(2) - Ni - C(1)	115.1	C(1G) - P(3) - C(1H)	101.8
P(2) - Ni - C(2)	103.7	Ni - P(4) - P(3)	92.0
P(4) - Ni - C(1)	117.8	Ni - P(4) - C(5)	120.5
P(4) - Ni - C(2)	102.7	Ni - P(4) - C(1E)	113.0
C(1) - Ni - C(2)	106.2	Ni - P(4) - C(1F)	115.5
Cu - P(1) - P(2)	87.5	P(3) - P(4) - C(5)	34.0
Cu - P(1) - C(4)	113.6	P(3) - P(4) - C(1E)	100.9
Cu - P(1) - C(1A)	113.7	P(3) - P(4) - C(1F)	134.9
Cu - P(1) - C(1B)	116.7	C(5) - P(4) - C(1E)	103.0
P(2) - P(1) - C(4)	34.5	C(5) - P(4) - C(1F)	102.2
P(2) - P(1) - C(1A)	139.0	C(1E) - P(4) - C(1F)	100.0
P(2) - P(1) - C(1B)	100.5	P(1) - C(4) - P(2)	110.9
C(4) - P(1) - C(1A)	105.3	P(3) - C(5) - P(4)	112.1

C(4) - P(1) - C(1B)	105.9	Cu - C(1) - Ni	87.7
C(1A) - P(1) - C(1B)	100.1	Cu - C(1) - O(1)	107.2
Ni - P(2) - P(1)	95.0	Ni - C(1) - O(1)	164.8
Ni - P(2) - C(4)	114.7	Ni - C(2) - O(2)	176.1
Ni - P(2) - C(1C)	115.4	Cu - N - C(3)	176.1
Ni - P(2) - C(1D)	118.7	N - C(3) - B	174.8

Table 4. Positional Parameters for $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)].CH_2Cl_2$, 13

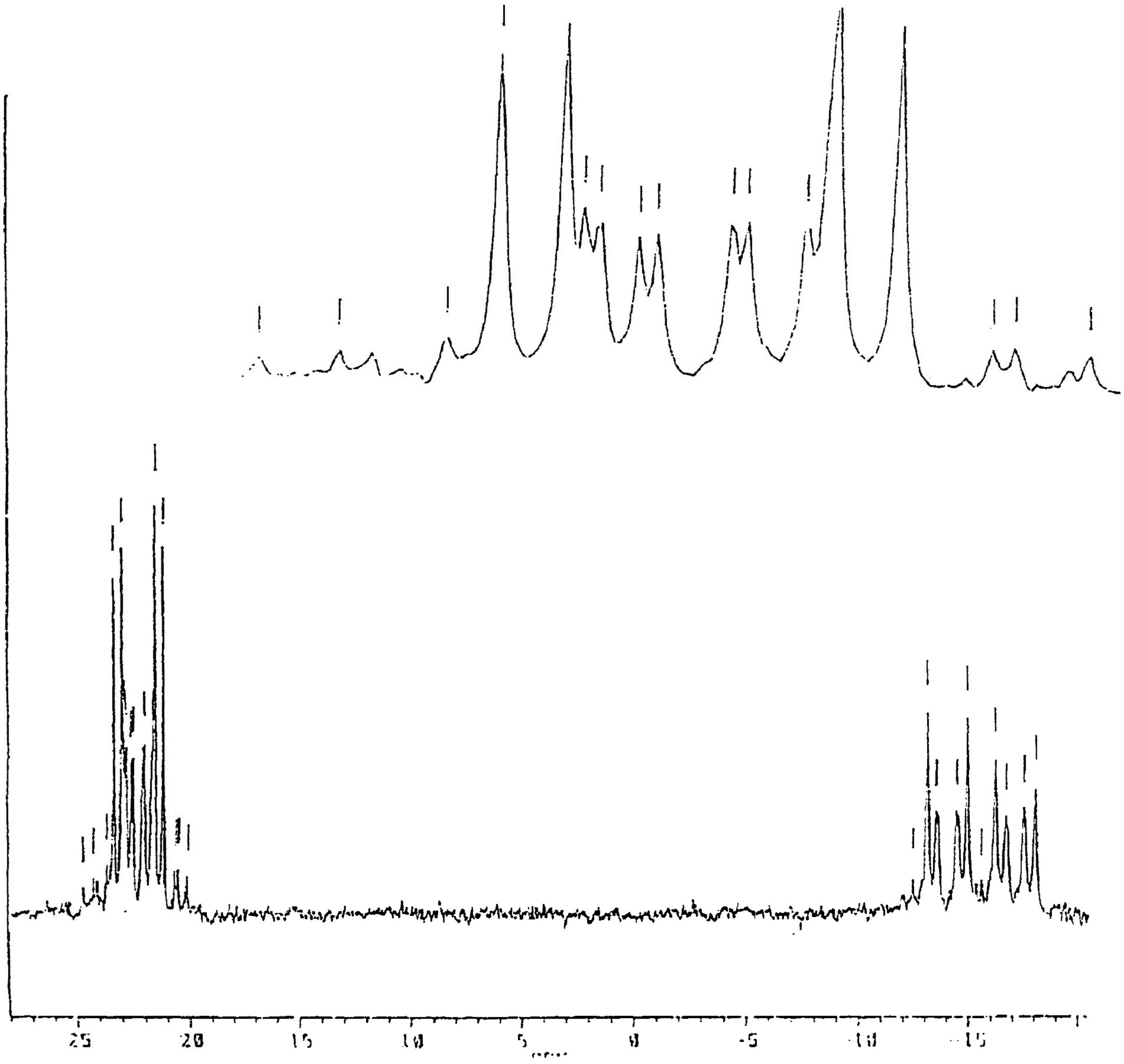
Atom	**x**	**y**	**z**
Cu	0.51167	0.26618	0.21112
Ni	0.63429	0.10869	0.34321
P(1)	0.69131	0.22770	0.11939
P(2)	0.78659	0.05816	0.23954
P(3)	0.48914	0.37696	0.29098
P(4)	0.66882	0.22604	0.38885
C(4)	0.82832	0.15325	0.16406
C(5)	0.63258	0.34700	0.33420
C(1)	0.48052	0.12394	0.32936
O(1)	0.38406	0.11500	0.33109
C(2)	0.66342	0.01534	0.42154
O(2)	0.68611	-0.04646	0.46762

N	0.36258	0.26506	0.17938
C(3)	0.27335	0.26105	0.15597
B	0.16060	0.26005	0.11735
C(1A)	0.73907	0.33233	0.06136
C(1B)	0.68998	0.16793	0.03673
C(1C)	0.94286	-0.00740	0.26584
C(1D)	0.76774	-0.02304	0.17881
C(1E)	0.58557	0.24525	0.49110
C(1F)	0.83214	0.20541	0.40181
C(1G)	0.36478	0.39853	0.37820
C(1H)	0.48271	0.49569	0.23811

Metathetical reactions of the above compound **13** with an excess of either $NaBPh_4$ or $NaPF_6$ in MeCN produce mixtures of unreacted **13** and $[NiCu(CO)_2(\mu\text{-dppm})_2(MeCN)_2]X$ (X = BPh_4, PF_6; **12b, 12c**). The complexes **12b** and **12c** display quite different chemical shifts in the Cu-P region (-13.9 ppm for **12b**) compared with -17 ppm for **13** in the $^{31}P\{^1H\}$ NMR spectrum (see **Spectrum 13**).

However, the conversion of **12a** to **13** is a fairly clean reaction. Thus, treatment of a toluene/acetonitrile solution of **12a** with an excess of $NaBH_3CN$ (1 : 2.5 ratio) with CO passing gives **13** in high yield (70%). This may imply that the geometry of the Ni-Cu dimer is more suitable with three-coordinated Cu in **13** than with

Spectrum 13 $^{31}P\{^1H\}$ NMR of a Mixture of 13 and 12b in MeCN at Room Temperature



four-coordinated Cu in **12a**. This also can account for the fact that compound **13** is more air-stable than **12** (compound **13** can be exposed to air for one week with only ~50% decomposition, whereas **12b** decomposes in one day). Furthermore, a $^{31}P\{^1H\}$ NMR spectrum of compound **13** in CH_2Cl_2 shows that no further reactions occur when PPh_3 is added under CO atmosphere.

3. Reactions of Either $Ni(CO)_2(\eta^1\text{-dppm})_2$, 11, or $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ with Ag^I salts

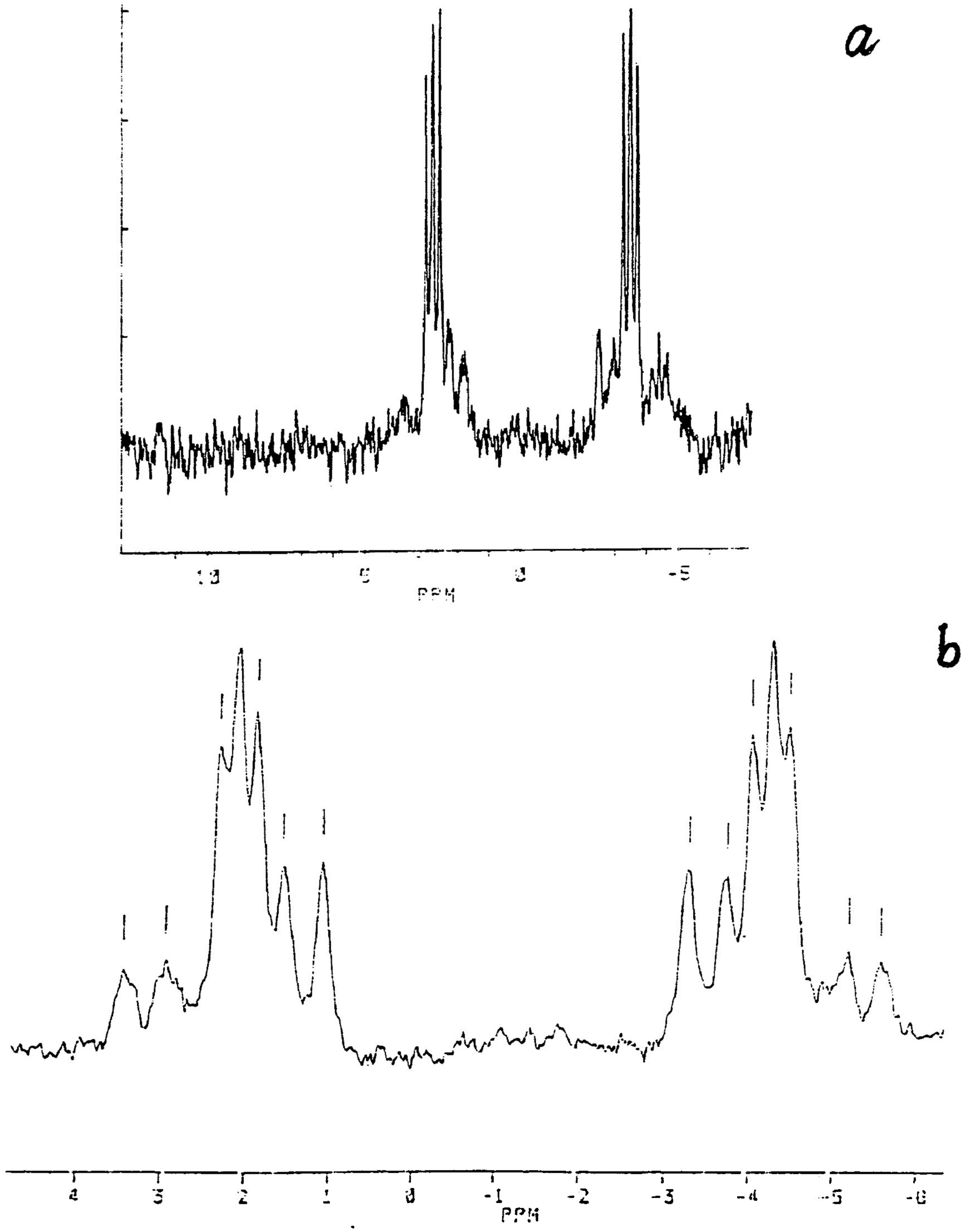
The successful synthesis of the bimetallic compounds **12** and **13** suggested the extension of this method to other d^{10} metal salts. However the reactions between **11** and Ag^I, Au^I, Hg^{II} or Zn^{II} give quite different results from those of obtained with Cu^I salts. For example, reactions between equivalent amounts of $Ni(CO)_2(\eta^1\text{-dppm})_2$, **11**, in benzene and $AgNO_3$, $Ag(PPh_3)_2NO_3$ or $Ag(diphos)NO_3$ in MeCN, were studied both at ambient and lower temperatures (-10°C). Only $[Ag_2(\mu\text{-dppm})_3]X_2.CH_2Cl_2$ ($X = NO_3$, **14a**) could be obtained from the reactions. The $^{31}P\{^1H\}$ NMR spectrum of **14a** in CD_2Cl_2 at ambient temperature shows three doublets centered at δ 7.65 ppm. Some complexes of apparently similar structure such as $[Ag_2(\mu\text{-dppm})_3]X_2$ ($X = O_3SCF_3$, **14b**; AsF_6, **14c**)[145,146] are known. However, the $^{31}P\{^1H\}$ NMR spectrum of **14b** at ambient temperature shows only a broad peak at δ 2.7 ppm[145] while that of **14c** shows a doublet centered at δ 5.9 ppm[146]. It is evident that there is the onset of an exchange process in complexes **14b** and **14c** when the probe is at ambient temperature. The exchange rates decrease with decreasing temperature[145] and are influenced by the properties of X. From X = O_3SCF_3, **14b**, X = AsF_6, **14c** to X = NO_3, **14a**, the exchange rates decrease. The spectra (see **Spectrum 14**) of type **14** complexes at low temperatures arise from the superposition of three different spin systems: $([A]_3X)_2$, $([A]_3Y)_2$ and $[A]_3[A^*]_3XY$, attributable to the isotopomers $[^{107}Ag_2(\mu\text{-dppm})_3]^{2+}$ (abundance 26.9%), $[^{109}Ag_2(\mu\text{-dppm})_3]^{2+}$ (23%) and $[^{107}Ag^{109}Ag(\mu\text{-dppm})_3]^{2+}$ (49.9%).[145]

Similar reactions of $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ with $AgNO_3$ give virtually identical results to those obtained from the reactions of **11** with $AgNO_3$. However, treatment of $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ with an equivalent amount of $[Ag_2(\mu\text{-dppm})_2][NO_3]_2$ leads to an orange solution and the $^{31}P\{^1H\}$ NMR spectrum of which shows an AA'XX' pattern consistent with the formation of an Ni-Ag bimetallic system. Unfortunately, separation of this complex has not yet been achieved and further careful work is still in process.

4. Reactions of $CoX(\eta^1\text{-dppm})_3$, 1, $CoX(CO)_2(\eta^1\text{-dppm})_2$, 4, $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]X$, 5, or $[Co(CO)(\mu\text{-dppm})_2]X$, 6, with metal salts

There is obvious potential for the preparation of bimetallic compounds from

Spectrum 14 $^{31}P\{^{1}H\}$ NMR of 14a at 298K (a) and 202k (b) in CD_2Cl_2



$CoX(\eta^1\text{-dppm})_3$, **1**,[18] and $CoX(CO)_2(\eta^1\text{-dppm})_2$, **4**. Since the complexes $[Co(CO)_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]X$, **5b**, (X = Br) and $[Co(CO)(\eta^2\text{-dppm})_2]X$, **6b**, (X = Br), **6c**, ($X = BPh_4$) can be converted into complex **4** by passage of CO and heating as was discussed earlier, it may also be possible to use them to synthesize novel bimetallic complexes.

a. Reactions of $CoBr(\eta^1\text{-dppm})_3$, 1b, with $RhCl_3.3H_2O$

Treatment of a benzene solution of **1b** with ethanolic $RhCl_3.3H_2O$ produced a greenish crystalline compound. The product is difficult to dissolve in most organic solvents except DMSO. Since the compound is a paramagnetic species, no $^{31}P\{^1H\}$ NMR signal was observed. However, while both scanning electron energy dispersive X-ray microanalysis spectra and X-ray fluorescence spectroscopy of this compound indicate that there are Co, Rh, Br, Cl, and P present in the compound, the formulation is still not clear and further studies are in progress.

Other efforts to produce bimetallic complexes using **1b** also have been made. However, no bimetallic complex has yet been separated, or characterized by spectroscopic methods from, for example reactions of **1b** in benzene with metal salts, such as $Pt(COD)Cl_2$ in CH_2Cl_2, $NiCl_2.6H_2O$ in ethanol and $Cu(MeCN)_4ClO_4$ in MeCN, in 1 : 1 ratio at 0°C. Because of the problem of NMR studies on paramagnetic species, attention was therefore turned to reactions which could yield diamagnetic Co-M systems.

b. Reactions of $CoX(CO)_2(\eta^1\text{-dppm})_2$, 4, and $[Co(CO)(\eta^2\text{-dppm})_2]X$, 6, with $Rh_2(CO)_4Cl_2$

Treatment of $CoCl(CO)_2(\eta^1\text{-dppm})_2$, **4a** in benzene with $Rh_2(CO)_4Cl_2$ in dichloromethane produced the known[79] compound $[CoRh(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]Cl$, **15a**, which was found to be identical in all respects(IR, ^{31}P NMR and Elemental Analysis) with an authentic sample prepared[79] by treatment of $CoRh(CO)_3(\mu\text{-dppm})_2$ with $HgCl_2$.

The same product was also obtained from reactions of **6a** with $Rh_2(CO)_4Cl_2$ under CO and it is interesting to note also that even $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$, **6c**, which is fairly difficult to convert into **4** in the pure state can also react with $Rh_2(CO)_4Cl_2$ at room temperature to give $[CoRh(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]BPh_4$, **15b**, in an identical procedure. Therefore the presence of metal ions which can readily coordinate with phosphorus atoms will assist the ring-opening of complexes of type **6**.

c. Reactions of 4, 5 and 6 with $Cu(MeCN)_4ClO_4$

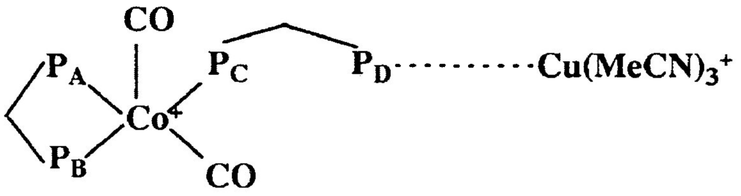
Efforts to prepare Co^I-Cu^I bimetallic complexes have also been made by reacting $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$, **6c**, with $Cu(MeCN)_4ClO_4$. The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution at room temperatures shows signals at δ 50.1 (t), J = 25.8Hz, -2.3 (br), -18.24 (br) (see **Spectrum 15**), but at -85°C the spectrum becomes similar to that of **5b** with δ P_A at 12.3(dd), δ P_B at -12.8(dd), δ P_C at 47.8(dt) and δ P_D at δ -20.4(m) (J_{AB} = 113.0Hz, J_{AC} = 109.0Hz, J_{BC} = 55.2 Hz, J_{CD} = 51.9 Hz) (see

Spectrum 16). Therefore, the formation of Co-Cu complexes under these conditions apparently does not occur.

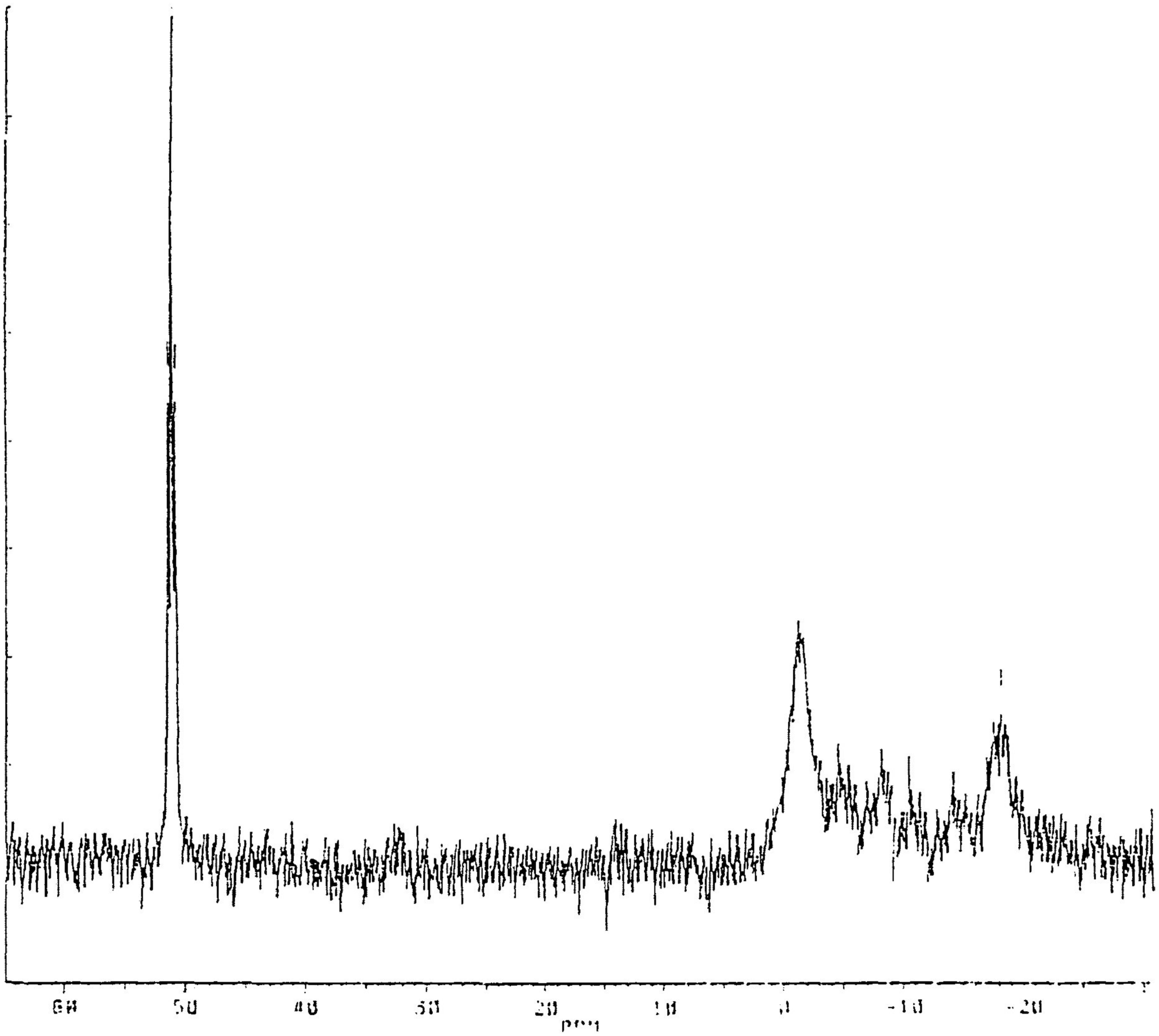
Indeed, all of these attempts to isolate heterobimetallic complexes failed. Instead, work up of the solutions resulted in the isolation of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4](ClO_4)_2$ or recovery of the starting material **6c**. Reactions of **4** or **5** with $Cu(MeCN)_4ClO_4$ gave similar results.

Since these $^{31}P\{^1H\}$ NMR spectra at room and low temperatures are similar to those of the **2a/CO** system, the most reasonable Co-Cu species which might form in solution is probably that shown in **Figure 16**.

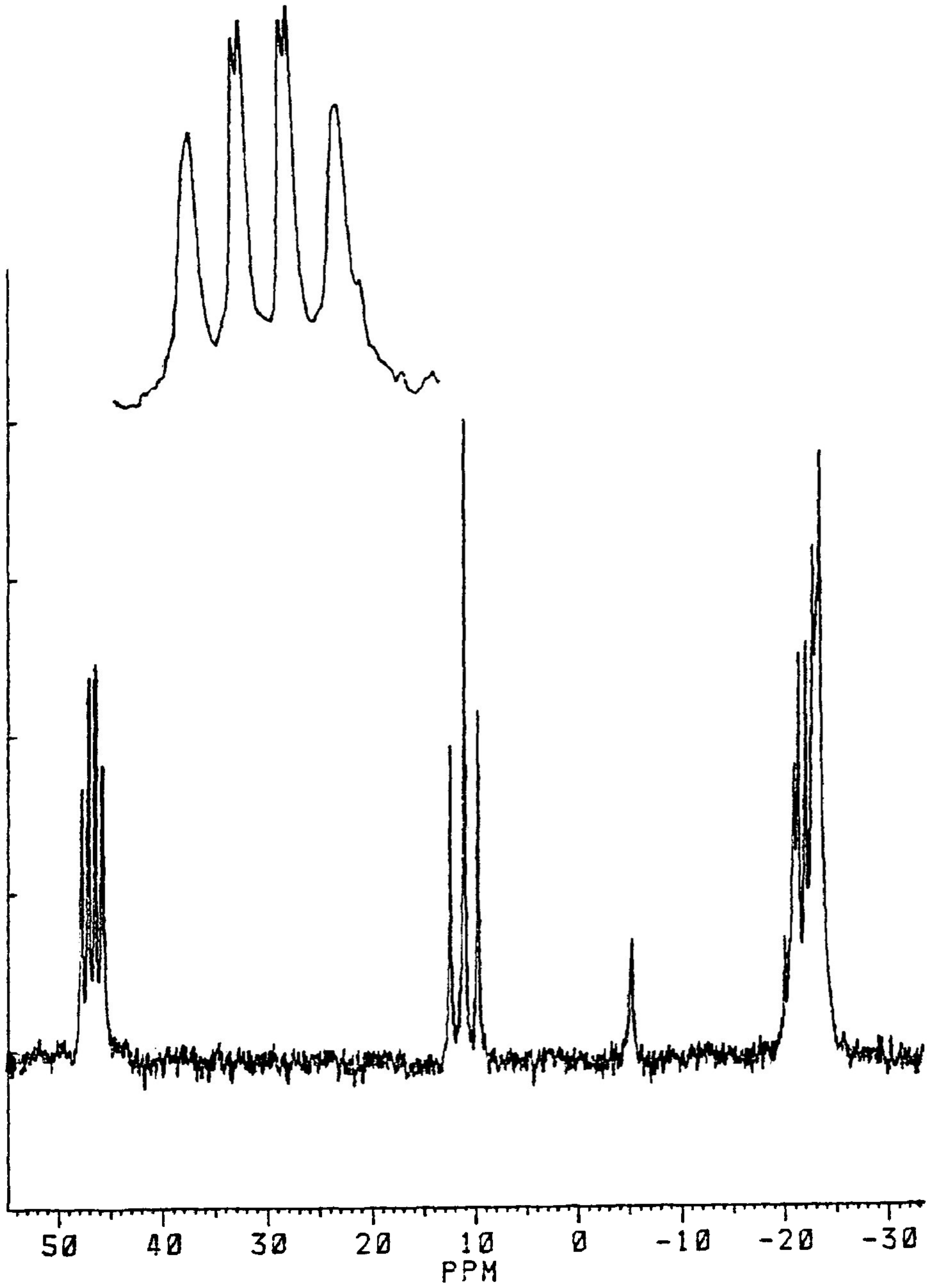
Figure 16. Possible Structure of Co-Cu Species In THF/MeCN Solution



Spectrum 15 **Reaction Solution $^{31}P\{^1H\}$ NMR of 6c with $Cu(MeCN)_4ClO_4$ at 298K in THF/MeCN**



Spectrum 16 Reaction Solution $^{31}P\{^1H\}$ NMR of 6c with $Cu(MeCN)_4ClO_4$ at 202K in THF/MeCN



However, no further direct evidence for such a structure has been obtained.

d. Other Attempts to Prepare Bimetallic Compounds

Several other efforts have been made to prepare bimetallic complexes. These were unsuccessful but the attempts are briefly listed below.

i. No evidence for Co-Pt complexes was obtained from reactions of **4a**, **6a** or **6c** with $Pt(COD)Cl_2$ in methylene chloride under CO or N_2.

ii. No bimetallic complex was observed in the reaction of $[CoH(\eta^2\text{-dppm})_2X]X$ with $Mo(CO)_6$ in a 1 :1 ratio in MeCN.

iii. The formation of a bimetallic complex was not observed from the reactions of **4**, **5** or **6** with metal compounds, such as $Mo(MeCN)_3(CO)_3$, $NiCl_2.6H_2O$, VCl_3, $CoCl_2.6H_2O$, $ZnCl_2$ and $CdCl_2$ in 1 : 1 ratios in CH_2Cl_2 and EtOH.

iv. Some reactions of mixed metal salts and $NaBH_4$ in the presence of dppm have been studied. No bimetallic complex was observed in the reactions of $CoBr_2.4.7H_2O$ and compounds, such as $Mo(CO)_6$, $NiCl_2.6H_2O$, K_2PdCl_6, $CuCl_2.2H_2O$, with $NaBH_4$ in EtOH (added slowly) in the presence of dppm and CO (ratio of Co^{II}/metal salts/$NaBH_4$/dppm = 1 : 1 : n : 2, (n = 1 - 4) in ethanol/benzene).

v. Some reactions between compounds, such as such as $Cu(MeCN)_4ClO_4$ in acetonitrile, $NiCl_2.6H_2O$, $Ni(CO)_4$, $PdCl_2$, $Cr(NO_3)_3.9H_2O$, VCl_3 or K_2PdCl_6-$NaBH_4$ (1 : 2), and the reaction solution of $CoBr_2.4.7H_2O$/dppm/$NaBH_4$/CO also have been studied in 1 : 1 mole ratio of Co : M (M = Ni, Pd, Cr, V and Pd) under a CO atmosphere. No bimetallic complex has been separated or observed spectroscopically.

vi. Some efforts to prepare trimetallic clusters also have been made by using **7b.** No such trimetallic complex could be separated, or observed by spectroscopic methods, from reactions of **7b** and metal salts, such as $Cu(MeCN)_4ClO_4$, $Ni(PPh_3)_2Br_2$, $Ni(CO)_4$ in a 1 : 1 ratio in CH_2Cl_2.

IV. Studies Regarding to the Formation of $[Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm-}BH_2)]$, 16

Transition metal complexes containing M-BH_2 units are rare in the literature despite intensive research in transition metal-borane chemistry.[41] However, the first stable metallaborane complex has been prepared in very low yield from Co^{II}/dppm/BH_4^-/CO reactions as mentioned in section **II** of this chapter and in the Introduction chapter.[43] Since M-BH_2 complexes have great potential in a variety of catalytic reactions,[41] high yield synthetic routes to such systems are desirable and the mechanism of formation of **16** in the reactions noted above needs to be established. Several attempts to establish the mechanism of formation of **16** and to design new routes to this complex were therefore made. These are summarized below.

1. Variation of the Reaction Conditions of the Co^{II}/dppm/$NaBH_4$/CO System

A reinvestigation of this reaction, which is known to give the borane complex **16,** was carried out by varying the reaction conditions such as time, temperature, molar ratios of reactants, rate of BH_4^- addition, etc. However, changing the time of the reaction from 0.5 h to 24 h, the reaction temperature from -20°C to refluxing in toluene/ethanol, and the $Co^{II}/NaBH_4$ ratio from 1 : 1 to 1 : 6, in a series of reactions gave no detectable amounts of compound **16.** It seems unlikely that **16** is formed following the normal reduction route. Some unusual intermediate could exist in the reaction system in small quantities and studies involving possible intermediates were carried out. These are recorded below.

2. Reactions of Co-dppm-CO complexes with BH_3.THF

Since the reducing agent $NaBH_4$ can release BH_3 and H^- when it reacts with metal ions, BH_3 is a very possible species to react with Co-CO-dppm complexes. Since numerous Co^0 and Co^I complexes may be present in solutions resulting from Co^{II}/dppm/BH_4^-/CO reactions, it seemed reasonable to study reactions between Co-dppm-CO compounds and both BH_3 and BH_4^- as possible new high-yield routes to **16.**

a. Reactions of $Co_2(CO)_4(\mu\text{-dppm})_2$, 9, and

$[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$, 6d, with BH_3.THF

Complex **9** in benzene and **6d** in THF react rapidly and very cleanly with BH_3.THF to give the red crystalline compound $Co_2(\mu\text{-CO})_2(CO)_4(\mu\text{-dppm})$, **17**, for which the structure has been established.[26] In addition, dppm.BH_3 and H_3B.dppm.BH_3 (characterized from the ^{31}P NMR spectra) are formed, but no trace of **16** was observed.

b. Reactions of $CoBr(CO)_2(\eta^1\text{-dppm})_2$ and Other Complexes with BH_3.THF

Treatment of a benzene solution of either $CoBr(CO)_2(\eta^1\text{-dppm})_2$, **4a**, or $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$, **6c**, with BH_3.THF in a 1 : 2 ratio under a CO atmosphere leads quickly to the formation of a white precipitate and a green solution. The white solid was identified as a mixture of H_3B.dppm.BH_3 and dppm.BH_3 from a ^{31}P NMR spectrum spiked with authentic samples.[161]

It seems that in these reactions BH_3 is simply abstracting dppm from the Co-CO-dppm complexes to form the air-stable dppm-BH_3 adducts as mentioned in Section I of this chapter. In these reactions again no trace of compound **16** was observed and it is not yet clear what happened to the Co^I species.

3. Reactions of $Co(CO)_4BH_2$.THF and dppm

The reaction

$$Co_2(CO)_8 \quad + \quad 2BH_3.THF \quad \longrightarrow \quad 2\,Co(CO)_4BH_2.THF \quad + \quad H_2 \qquad [65]$$

has been demonstrated by spectroscopic and chemical means to occur cleanly at -15°C in THF.[42] Since both BH_3 and $Co_2(CO)_8$ could exist in the Co^{II}/dppm/$NaBH_4$/CO reaction system, $Co(CO)_4BH_2$ is another possible intermediate in the formation of complex **16**. This possibility was investigated as follows.

The reaction of $Co(CO)_4BH_2.THF$ with dppm in THF appears to be very complex but still no sign of compound **16** was observed. Though most products from the reaction are known and can be identified by spiking with authentic samples, several products are still uncharacterized and appear in ^{31}P NMR spectra as δ 53 (s), 44.8 (d) J = 96.6, -25 (m) and 6.7 (br). The products which have been identified by authentic sample spiking techniques include the ion pair **6d** (^{31}P NMR, δ -5.5 (s)), the Co-Co dimer **9** (δ 36.1 (s)), **17,** (δ 60.1 (s)), $[Co(CO)(\eta^1\text{-dppm})(\eta^2\text{-dppm})][Co(CO)_4]$, **5d,** (δ 51.7 (dt) J = 24.4 and J = 56.9 Hz, -2.3 (br, s), -27 (d)) (see Experimental), BH_3.dppm (δ 15.1 (br), -27 (d) J = Hz), BH_3.dppm.BH_3 (δ 15.2 (br)) and free dppm (δ -22 (s)). Among these, **5d** is the major product.

Although no products containing BH_2^- were observed, more careful studies are still in progress because several factors will affect the formation of the $Co(CO)_4BH_2.THF$[42].

4. Reactions of $[H_2B(\eta^2\text{-dppm})]I$ with $Co_2(CO)_4(\mu\text{-dppm})_2$ or $Co_2(CO)_8$

The reaction of monoiodoborane with dppm produces what is probably a boronium iodide salt, $[H_2B(\eta^2\text{-dppm})]I$[162] which is a possible intermediate in the formation of complex **16**. However, $^{31}P\{^1H\}$ NMR spectra showed that there is no reaction between $[H_2B(\eta^2\text{-dppm})]I$ and $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$.

Similarly, $Co_2(CO)_8$ in benzene does not react with $[H_2B(\eta^2\text{-dppm})]I$ in THF in a 1 : 4 ratio or with BH_3.dppm/H_3B.dppm.BH_3 in THF also in a 1 : 4 ratio. These reactions rule out the possibility of this route to form compound **16**.

5. Reactions of dppm.BH_3 and H_3B.dppm.BH_3 with $Co^{II}/NaBH_4/CO$

Since H_3B.dppm.BH_3 and dppm.BH_3 are observed in $Co^{II}/NaBH_4$/dppm/CO reactions, it is possible that they are intermediates in the formation of **16**. In a final series of experiments, the same reaction conditions were used to synthesize compound **16** except that dppm.BH_3 was present instead of dppm, but again, no sign of the presence of compound **16** was observed. Instead, **6d**, **7b**, **9** and **17** were obtained and pure complex **7b** was separated in 16% yield.

From these experiments, no clearly defined route to the formation of compound **16** has been found although further study of the possibility that $Co(CO)_4BH_2$ is an intermediate is worth while. Other possibilities to be explored include the reaction of BH_2I with **5d** or **6d**, and the reaction of BH_2I with Co^{II} followed by treatment with dppm in the presence of $NaBH_4$ and CO.

Suggestions for Further Work

Although the main pathway of Co^{II}/dppm/$NaBH_4$/CO reactions has been established in these studies, there are some points which are still not clear and, therefore, some more careful work is needed to resolve the following points.

1. When excess amounts of $NaBH_4$ (Co^{II} : $NaBH_4$ ratios is 1 : 4 or up) is used in the Co^{II}/dppm/$NaBH_4$/CO reactions, the peaks which show in the $^{31}P\{^1H\}$ NMR spectrum of the reactions at the ratio Co^{II} : $NaBH_4$ of 1 : 2 disappear. Whether the final reduced product that Co-dppm-CO compounds convert into is $[Co(CO)_4]^-$ is still not clear.
2. Does electron transfer from the reducing agent $NaBH_4$ to Co^{II} occur via a Co-H-BH_3 intermediate ? If so, can it be isolated ?
3. Although the reactions of $Co_2(CO)_8$ with dppm first give $[Co(CO)(\eta^1\text{-dppm})(\eta^2\text{-dppm})][Co(CO)_4]$, **5d**, an unidentified brown compound occurs during the recrystalization process. Its $^{31}P\{^1H\}$ NMR spectrum shows a singet at δ 44.2 ppm and its IR spectrum shows that only terminal CO is present with absorptions at 1874 (s), 1895 (s), 1910 (s), 1930 (s), 1956 (s), 1990 (s), 2006 (s) cm^{-1}. Since the singlet at δ 44.2 ppm was also observed in the $^{31}P\{^1H\}$ NMR spectrum of the Co^{II}/dppm/$NaBH_4$/CO reactions, identification of this compound will provide some additional information on both the mechanism of the Co^{II}/dppm/$NaBH_4$/CO reactions and on the further reactions of **5d**.
4. In the reactions of $CoBr(CO)_2(\eta^1\text{-dppm})_2$, **4a**, or $[Co(CO)(\eta^2\text{-dppm})_2]BPh_4$, **6c**, with BH_3.THF in a 1 : 2 ratio, BH_3 is simply abstracting dppm from the **4a** or **6c** to

form the dppm-BH_3 adducts. It is not clear what happened to the remaining Co^I species.

5. In this study, no clue was discovered for elucidating the mechanism of the reactions which produce the phosphido-complexes, $Co_2(\mu\text{-}H)(CO)_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2$, $Co_2(\mu\text{-}H)(CO)_4(\mu\text{-}PPh_2)(\mu\text{-dppm})$ and $[Ni_2(CO)_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2]^+$. The GC-MS technique may provide a powerful tool for us to understand the mechanism of these reactions by monitoring the gases released and identifying any small organic compounds which are produced. The TLC and liquid column chromatography may also be used to find out what kinds of organic compounds or even complexes also exist in these reactions.

6. While extensive work has been done on reactions of $Ni(CO)_2(\eta^1\text{-dppm})_2$, **11**, with $Cu(MeCN)_4ClO_4$ and $CuCl_2.2H_2O$, there is still great potential for the use of **11** to synthesize new heterobimetallic compounds, particularly with different d^{10} metals such as Ag^I, Au^I and Hg^{II}. The nature of the starting metal salts will be important to obtain stable heterobimetallic complexes and therefore they should be chosen carefully.

7. Finally, $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$, which is similar to Kubiak's compounds, $Ni_2(\mu\text{-}CNMe)(CNMe)_2(\mu\text{-dppm})_2$, may also be used as a starting material to prepare heterobimetallic complexes with transition metal salts

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