A Simple Route to New

Palladium-Carbonyl-Bis(diphenylphosphino)methane Complexes.

by

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submitted to

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ABSTRACT

The method of synthesizing metal-carbonyl-dppm complexes [dppm = bis(diphenylphosphino)methane] devised by Holah and Hughes has been extended to include palladium. Specifically, reductions of palladium salts by $NaBH_4$ in the presence of dppm and CO lead to any one or more of five different palladium-dppm complexes. Two of these complexes, $\mathbf{Pd_2(\mu\text{-}dppm)_2(\mu\text{-}CO)Cl_2}$, **1**, and $\mathbf{Pd_2(\mu\text{-}dppm)_3}$, **2**, were identified spectroscopically and have been previously prepared by other less convenient routes.

Three new palladium complexes are also reported. The hexameric $\mathbf{Pd_6(\mu\text{-}dppm)_3(\mu\text{-}CO)_6}$, **3**, has been identified spectroscopically and crystallographically. The X-ray crystal structure of **3** shows that crystals of this complex lie in the space group $Pna2_1$ and are orthorhombic with unit cell dimensions of a, 39.836(13) Å; b, 15.587(4) Å; c, 12.1654 Å. The other two unidentified complexes **4a** and **5a** were only partially characterized spectroscopically. Two possible structures, $\mathbf{[Pd_3(\mu\text{-}dppm)_3(\mu_3\text{-}CO)Cl_3]Cl}$ and $\mathbf{Pd_3(\mu\text{-}dppm)_3(\mu_3\text{-}CO)(\mu_3\text{-}Cl)Cl_3}$, are proposed for **4a** and these proposals are based largely on spectroscopic and

analytical evidence. An X-ray quality crystal of **4a** has been obtained very recently. It has been found to diffract satisfactorily and data are currently being collected as of this report. The unidentified complex **5a** was characterized only partially. Complex **5a** is a fluxional molecule at room temperature and is thought to contain at least 3 Pd trimeric units. The inter-relationships between **3**, **4a** and **5a** are discussed.

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ABBREVIATIONS

Bu	butyl
COD	1,5-cyclooctadiene
dba	dibenzylidene acetone
dmf	N,N-dimethylformamide
dmpm	bis(dimethylphosphino)methane
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	bis(diphenylphosphino)propane
Et	ethyl
Me	methyl
OAc	acetate
PBu_3	tributylphosphine
PCy_3	tricyclohexylphosphine
Ph	phenyl
PPh_3	triphenylphosphine
THF	tetrahydrofuran
THT	tetrahydrothiophene

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INTRODUCTION

Monodentate and polydentate tertiary phosphine ligands play a very important role in coordination chemistry.[1] They strongly bind to transition metal complexes in various, (especially low) oxidation states[2], thus stabilizing them. The reactivity of these phosphines may be altered by varying the substituents on the phosphorus.[3] In the case of bidentate phosphines of the type $Ph_2P(CH_2)_nPPh_2$ the backbone length may be varied[2] (n = 1 to 6).

These ligands can either act as monocoordinate ligands, leaving one phosphorus free, or dicoordinate ligands forming chelate or bridging complexes.[2] In forming chelate complexes the optimum ring size is five; therefore, dppe (n = 2) is the best chelating ligand.

The chelate properties of the phosphines decrease as the length of the backbone increases. This can be easily visualized in the example of $[RhCl(CO)\{Ph_2P(CH_2)_nPPh_2\}]$ complexes, which are dimers, when n = 1, 3 and 4, but it is a chelate monomer when n = 2.[4]

Particular attention has been paid to bis(diphenylphosphino)methane (dppm), where n = 1,

because of its usefulness in homogeneous and heterogeneous catalysis.[3] Dppm can act as a bridging ligand locking two metals together in close proximity and thereby promoting organometallic reactions which involve two metal centers. The role of the ligand then is to prevent dimer dissociation thereby promoting binuclear reactions. The bridging mode of coordination of dppm also allows for the formation of metal-metal[5,6] bonds and the insertion of small molecules between two metal centers.[7,8]

As mentioned before, dppm can also act as a monodentate ligand leaving one phosphorus free, which is an active site for further reactions.

This thesis is concerned with the preparation and structure elucidation of palladium compounds with dppm and CO as ligands. The following discussion provides information about the general synthetic procedure used and also about palladium chemistry, upon which the research, described in the Results and Discussion section, was based.

I. Recent Approaches to Dppm and Dppm-CO Complexes of Nickel and Cobalt.

It is well known that dppm can stabilize metal

carbonyl complexes in various oxidation states.[2,9] For instance, dppm has been found to stabilize a variety of mononuclear and dinuclear cobalt complexes in various oxidation states.[10]

Generally metal-carbonyl-phosphines are synthesized via two separate routes, specifically reacting metal carbonyls with phosphines or reacting low oxidation state metal-phosphine complexes with CO. However, both of these methods have disadvantages. For example metal carbonyls are generally very toxic, they usually are in a form that makes them difficult to work with, they are expensive, and in some cases not readily available (for example palladium carbonyls are unknown). The alternative route requires the synthesis of low oxidation state metal-phosphine complexes which can be very tedious.

It is partially for these reasons that Holah and Hughes have developed a one step synthesis for preparing low oxidation state metal-carbonyl-phosphines.[10] Basically, the method involves the reduction of metal salts in the presence of a phosphine and CO, using a suitable reducing agent, usually $NaBH_4$ or $NaBH_3CN$. They have found that the products formed depend crucially on the reaction conditions such as: reaction times, stoichiometric ratios and the rate of addition of reducing agent.

The following discussion is a survey of the work that has been done using this one step synthesis. The method has been applied extensively to Co and Ni salts and the work has been extended to other metal salts such as Rh, Pd, Ag, Cu and Mn salts. It has recently been established in this work that similar $Fe/NaBH_4$ reactions do not lead to reduction. However, reductions of Fe salts in the presence of dppm and CO using $LiAlH_4$ gave a variety of carbonyl and hydrido iron(II) chelate dppm complexes.[11]

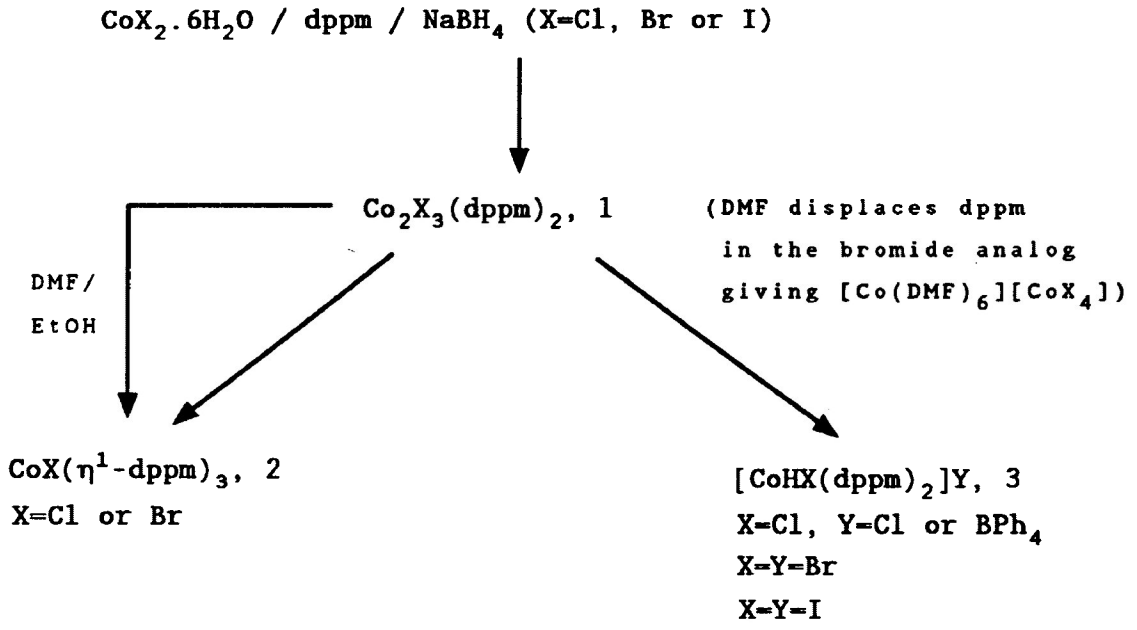
1. Dppm Complexes of Cobalt.

It was found[12,13,14,15] that reductions of Co(II) with $NaBH_4$ in the presence of bulky phosphines such as PPh_3, PCy_3, etc., or bidentate phosphines of the type $Ph_2P(CH_2)_nPPh_2$ ($n \geq 2$) lead to a variety of reduced Co-phosphine complexes. However, when similar reactions were carried out using bidentate phosphines with n = 1 (dppm), the situation becomes more complicated and a variety of Co-dppm complexes may be formed in oxidation states ranging from (III) to (0).[12,22]

The outcome of these reactions depends on the reaction conditions such as stoichiometric ratios of the reagents, the rate of addition of a reducing agent

($NaBH_4$ or $NaBH_3CN$), and the reaction time. The reactions involving $NaBH_4$ are very complex and difficult to control. However, when $NaBH_3CN$ is used, the reactions are generally slower and easier to handle.

Reductions of Co(II) ions by $NaBH_4$ or $NaBH_3CN$ in the presence of dppm leads to the formation of various cobalt complexes which are presented in Schemes 1, 2 and 3.[16]



Scheme 1.

Synthesis of Co-dppm complexes using $NaBH_4$.

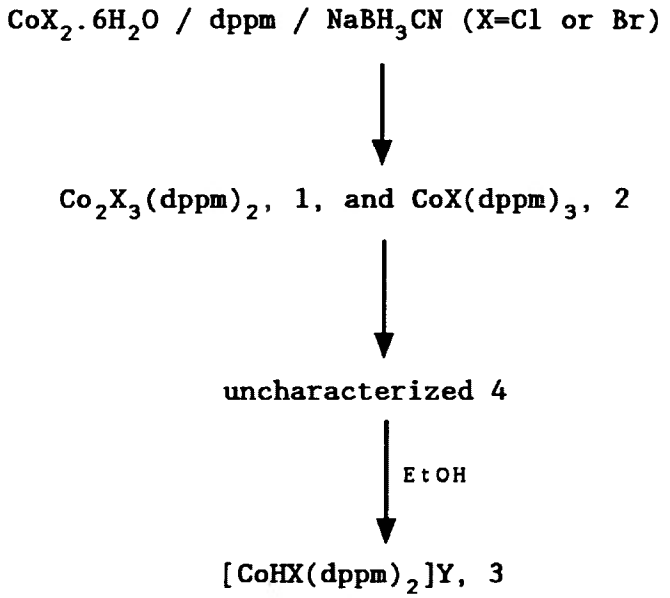
As can be seen in Scheme 1, reductions of Co(II) chloride, bromide or iodide in the presence of dppm leads to the formation of the mixed oxidation state 1 of unknown structure. The chloride version of this

compound produces dark green crystals that are twinned. It was thought that this complex would possess an A-frame type structure. However, magnetic moment measurements revealed that **1** has five unpaired electrons which would make such a structure implausible. If **1** is dissolved in DMF, dppm ligands are slowly displaced producing a species containing coordinated DMF. Compound **2**, containing high spin, tetrahedrally coordinated Co(I) can be obtained by two separate routes. For example, if one attempts to recrystallize **1** from DMF/EtOH, **2** is produced in high yields. The second method involves **1** as an intermediate to **2** when Co(II) salts are reduced by $NaBH_4$ in the presence of dppm. A second product, compound **3**, is also produced in this reaction.

Another route leading to the synthesis of **3** is presented in Scheme 2. If the milder reducing agent $NaBH_3CN$ is used to reduce cobalt(II) salts in the presence of dppm, **3** may be produced. However, the reaction proceeds through different intermediates. En route to the formation of **3**, **1** and **2** appear as intermediates, along with an uncharacterized compound **4**. If **4** is dissolved in ethanol, **3** is formed.

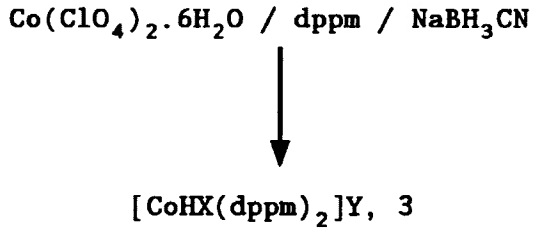
The final route (see Scheme 3) to the formation of **3** involves reductions of cobalt perchlorate salts in the presence of dppm by $NaBH_3CN$. Its interesting to note

that 3, which contains a Co(III) centre, is being produced from Co(II) in a strongly reducing environment.



Scheme 2.

Synthesis of Co-dppm complexes using $NaBH_3CN$.



Scheme 3.

Synthesis of $[CoHX(dppm)_2]Y$ from cobalt perchlorate.

2. Co-Dppm-CO Complexes.

It is known that cobalt-carbonyl substituted monotertiary phosphine complexes may be prepared simply by reacting $Co_2(CO)_8$ with the phosphine. Brown et al.[17] found that when they reacted, for example, L=PBu_3 or PPh_3 with **$Co_2(CO)_8$**, **5**, the product obtained was **$Co_2(CO)_7L$**, **6**. As well, complex **5** may be reacted with ditertiary phosphines,[17] L-L, such as dppm or dmpm, to yield **[Co(L-L)(CO)$_3$][Co(CO)$_4$]** which slowly loses CO and converts to a neutral dimer, **Co_2(L-L)(CO)$_6$** (see equation 1). Complex **6** will disproportionate to yield an ionic compound **[Co(PBu_3)$_2$(CO)$_3$][Co(CO)$_4$]**, **7**. Upon heating,[18] **7** may be transformed into **[LCo(CO)$_3$]$_2$**.

$$[Co(L\text{-}L)(CO)_3][Co(CO)_4] \xrightarrow{-CO} Co_2(L\text{-}L)(CO)_6$$

Equation 1.

Much of the interest in preparing Co-ditertiary phosphine-CO complexes lies in their use as catalysts.[19]

Meanwhile, Holah and Hughes have been interested in synthesizing Co-dppm-CO complexes via reductions of Co(II) salts by $NaBH_4$ or $NaBH_3CN$ in the presence of dppm and CO.

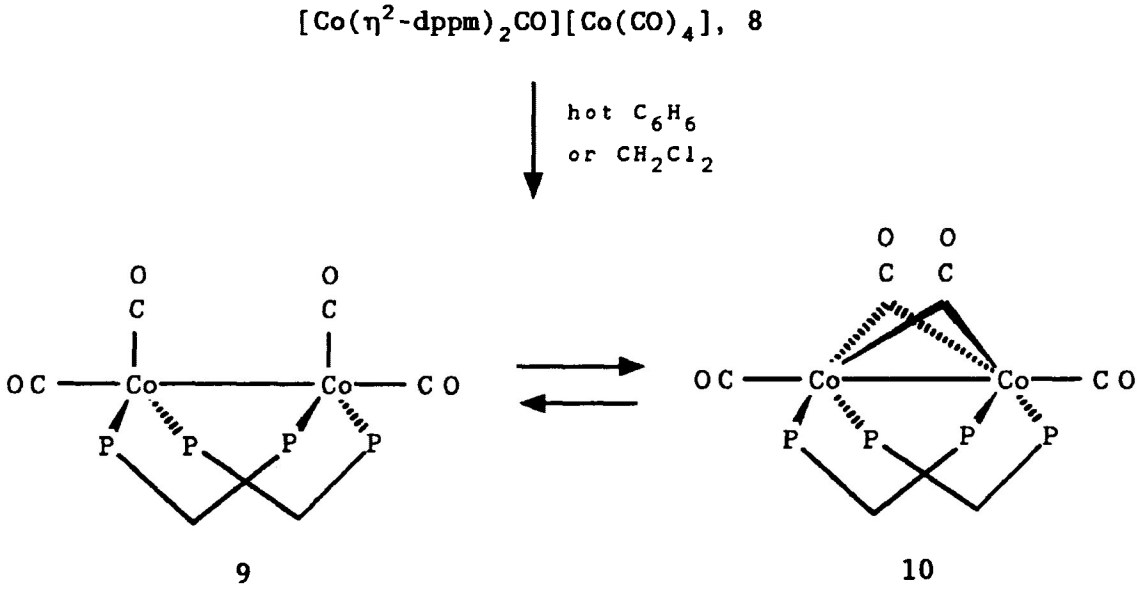
For example, by varying the reaction conditions

slightly, they have obtained and fully characterized at least six different monomeric and dimeric cobalt complexes.[10] The following discussion will focus on five of these compounds, while the sixth will be discussed in a later section.

The formation of three of these complexes largely depends on the rate of addition of $NaBH_4$. One such compound, **$[Co(\eta^2\text{-dppm})_2CO][Co(CO)_4]$**, **8**, may be obtained when a solution of Co(II) and dppm saturated with CO is treated with $NaBH_4$ over 30 minutes. X-ray crystallography has shown that the cation of **8** is a distorted trigonal bipyramid.[20] (It should be noted that this cation may be prepared by other less direct routes).[20,21] If the time of addition of $NaBH_4$ is decreased to 10 minutes, a dimeric Co(0) species **$Co_2(\mu\text{-dppm})_2(CO)_4$**, **9**, containing dppm in a cradle-like arrangement, may be formed. As well, complex **9** may be converted[22,23,24] to an isomer, complex **10**, **$Co_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(CO)_2$**, upon stirring a suspension of **9** in ethanol. Compound **10** also contains the dppm ligands in a cradle-like arrangement and it can be converted back to **9** by simply dissolving it in CH_2Cl_2 or C_6H_6. Both complexes are in rapid equilibrium with one another at room temperature in solution. It was observed[23] that at lower temperatures, **10** is favoured; this is evident from the ^{13}C NMR of both **9** and **10**. The

^{13}C NMR of **9** shows only a singlet corresponding to terminal CO, while at lower temperatures, the ^{13}C NMR of **10** shows both terminal and bridging CO. The structures of both complexes were confirmed by X-ray crystallography.[22]

Compound **9** may be prepared by a less direct route which involves the heating of **8** in benzene or dichloromethane (see Scheme 4). Again, complex **10** is in rapid equilibrium with complex **9** upon its formation.



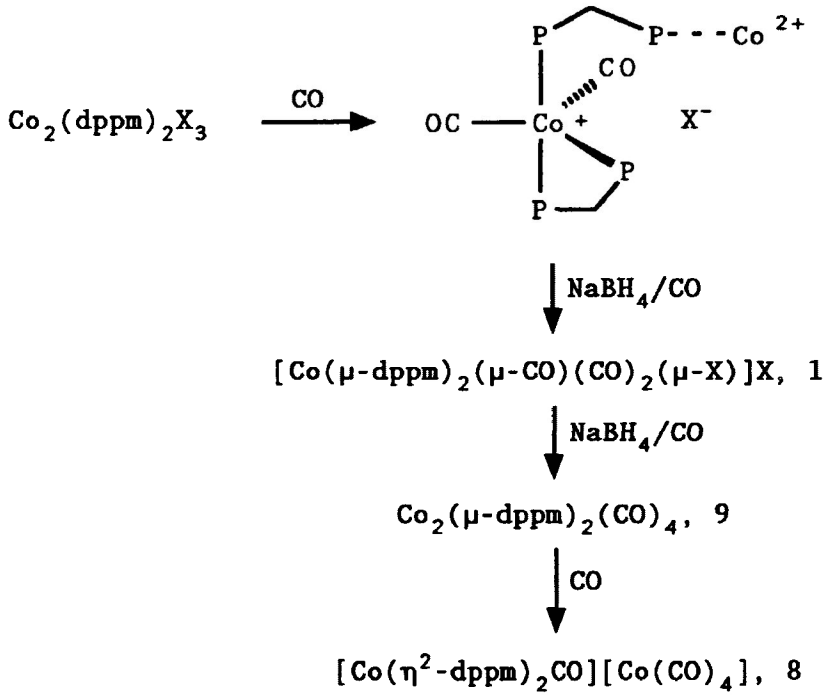
Scheme 4.

A less direct route to the synthesis of 9 and 10.

When the addition time of $NaBH_4$ is decreased to 5 minutes and the amount of dppm and $NaBH_4$ are slightly increased, a fourth product, specifically **[Co(η²-dppm)(η¹-dppm)(CO)₂]X** (X=Br or BPh_4), **11**, may be

isolated. The ^{31}P NMR of this complex shows it to be fluxional.[20]

An alternative route[20] to synthesizing **11** (see Scheme 5) involves treatment of the previously discussed $Co_2(dppm)_2X_3$ (X=Cl or Br) with CO. It is formed here with an equimolar amount of Co(II) and shows[20] unusual ^{31}P NMR properties under these conditions.



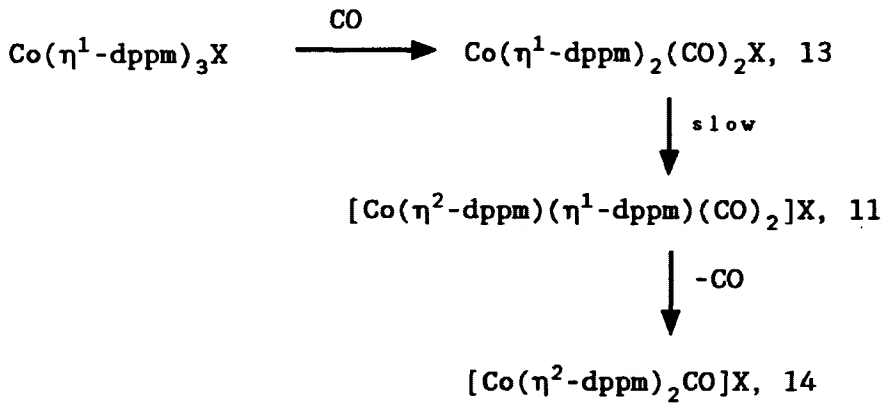
Scheme 5.

Reductions of $Co_2(dppm)_2X_3$ in the presence of CO and $NaBH_4$ leading to a variety of products.

If **11** is further treated with CO and $NaBH_4$, the cobalt complex, **$[Co_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2(\mu\text{-X})]X$**, complex **12**, is ultimately produced which, as well, may be further reduced by $NaBH_4$ and CO to give **9**. Compound **8** is

formed when **9** undergoes disproportionation in the presence of CO.[10]

Yet another route[20] to producing **11** (see Scheme 6) involves treatment of **Co(η^1-dppm)$_3$X** (previously discussed) with CO. It has been found that the reaction proceeds through an intermediate complex, specifically **Co(η^1-dppm)$_2$(CO)$_2$X** (X=Cl or Br), **13**. In solution, the coordinated halide is displaced by one of the free phosphorus atoms of one of the monocoordinated dppm ligands. If **11** is left to stand, it undergoes a loss of CO to yield **14**, **[Co(η^2-dppm)$_2$CO]X** (X=Cl, Br or BPh_4).



Scheme 6.

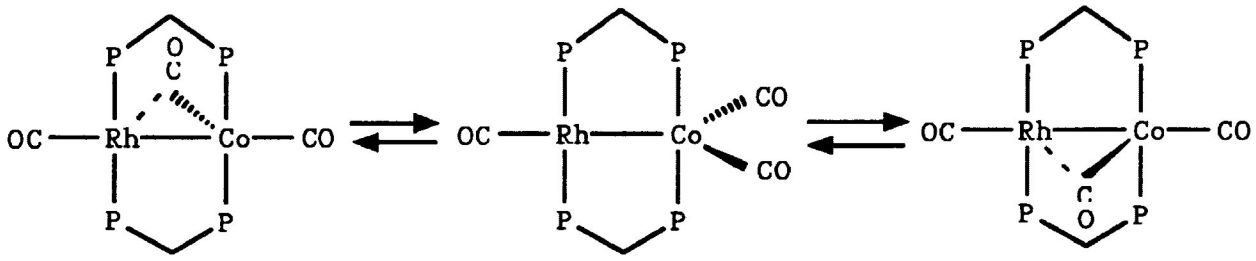
Synthesis of complex 11 from Co(η^1-dppm)$_2$(CO)$_2$X.

3. Co-M-Dppm-CO Complexes

Two methods explored in preparing heterobimetallic

compounds containing cobalt involve (1) a direct reduction of mixtures of transition metal salts in the presence of dppm and CO, and (2) reactions of monomeric Co-dppm-CO complexes with other metal complexes.[10,25]

For example, if a mixture of Co(II) and Rh(III) salts is rapidly reduced in the presence of dppm and CO, the complex **$CoRh(\mu\text{-}dppm)_2(CO)_3$, 15,** is formed.[26] The X-ray crystal structure of **15** shows that one of the CO ligands on the cobalt atom is semi-bridged to the rhodium atom. At room temperature, **15** is fluxional (see Scheme 7); however, at lower temperatures (ca. 228 K) the fluxionality may be "frozen out".

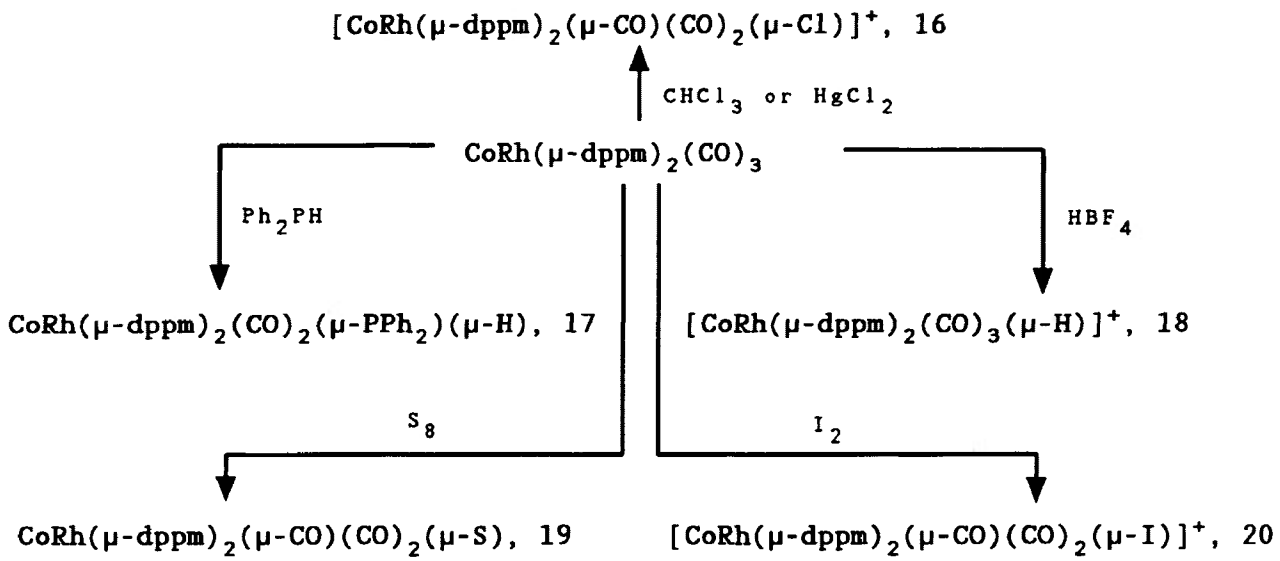


Scheme 7.

Fluxionality of $CoRh(\mu\text{-}dppm)_2(CO)_3$.

It should be noted that **15** is also produced when **$[Rh(\eta^2\text{-}dppm)_2(CO)][Co(CO)_4]$** undergoes loss of CO.[25]

The chemistry of **15** has been found to be quite rich[26] (see Scheme 8). Complex **15** reacts with a variety of compounds to produce several different Rh-Co species.



Scheme 8.

Reactions of complex 15 with various compounds.

An alternative method of synthesizing heterobimetallic compounds (specifically those containing cobalt) is to use Co(0) or Co(I) complexes containing CO and monocoordinated dppm.[10]

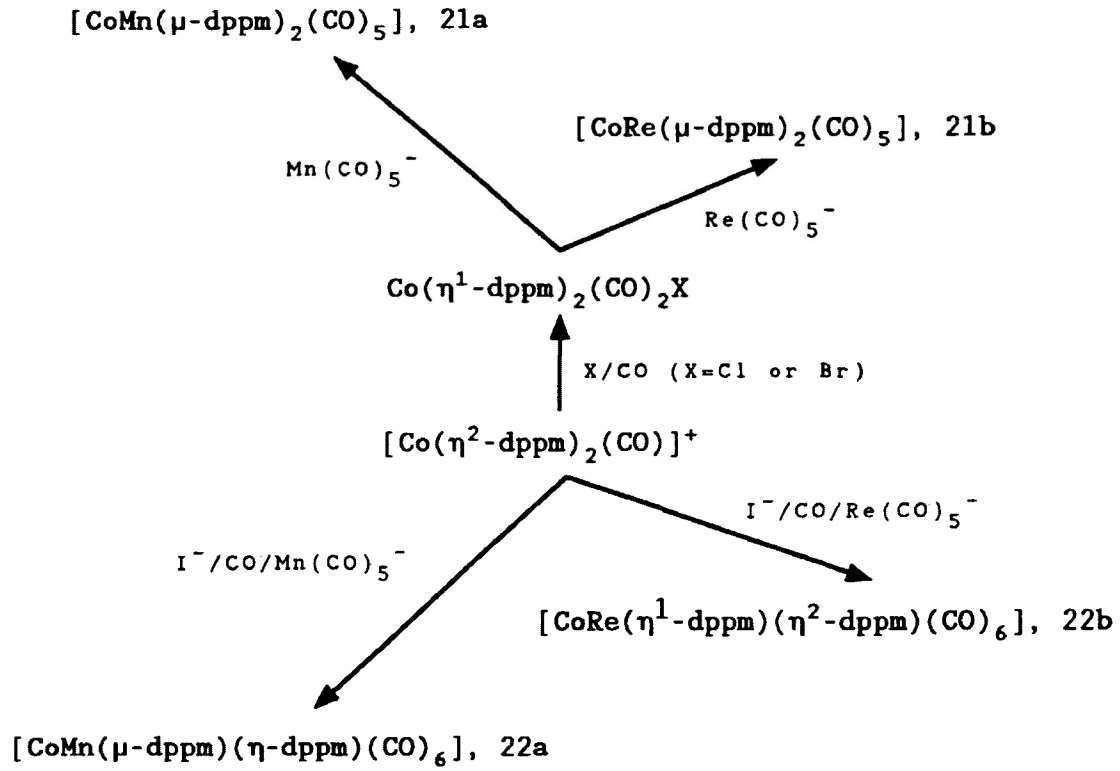
For instance, the previously discussed complex **$Co(\eta^1\text{-dppm})_2(CO)_2X$** (X=Cl) has been found to be quite useful in preparing heterobimetallic compounds. When this Co(I) species is reacted with $Rh_2(CO)_4Cl_2$, the Co-Rh complex **$[CoRh(\mu\text{-dppm})_2)(\mu\text{-CO})(CO)_2(\mu\text{-Cl})]X$** (X=Cl), **16**, is formed,[20] and this may also be prepared via a different route (refer to Scheme 8).

Other complexes prepared[25] from reactions between **$Co(\eta^1\text{-dppm})_2(CO)_2X$** (X=Cl) and $Na[M(CO)_5]$ (M=Mn or Re)

include **[CoMn(μ-dppm)$_2$(CO)$_5$]**, **21a**, and **[CoRe(μ-dppm)(CO)$_5$]**, **21b** (see Scheme 9).

Compound **21a** has been characterized crystallographically and it was found that the Mn atom adopts a distorted octahedral geometry whereas the Co atom adopts a trigonal bipyramidal arrangement. The ^{13}C NMR of **21a** shows that this compound contains fluxional CO ligands.[25] As well, the fluxionality of the dppm ligands of **21a** is evident from the ^{1}H NMR since a broad resonance assigned to the methylene protons of dppm appears, as opposed to two peaks corresponding to two non-equivalent protons. When **21a** is reacted with $CHCl_3$, CCl_4 or I_2, the Co-Mn complexes **[CoMn(μ-dppm)$_2$(μ-CO)(CO)$_3$(μ-X)]X** (X=Cl or I) may be formed. The analogous compound **21b** was synthesized in the same manner and was characterized spectroscopically. It, too, is thought to be a fluxional species since the resonance due to the methylene protons of dppm becomes broader as the temperature is dropped.[25]

If **[Co(η^2-dppm)$_2$CO]$^+$** is used[25] in the reactions with $[M(CO)_5]^-$ (M=Mn or Re) instead of **Co(η^1-dppm)$_2$(CO)$_2$X**, two other products may be obtained, the Co-Mn complex **[CoMn(η^1-dppm)(μ-dppm)$_2$(CO)$_5$]**, **22a**, and the Co-Re complex **[CoRe(η^1-dppm)(η^2-dppm)(CO)$_6$]**, **22b**[25] (see Scheme 9).



Scheme 9.

Reactions of $Co(\eta^1\text{-dppm})_2(CO)_2X$ and $[Co(\eta^2\text{-dppm})_2CO]^+$ with $M(CO)_5^-$ (M=Mn or Re).

It is thought that **22a** is a precursor to **21a**, since in solution, **22a** readily converts to **21a**. The ^{31}P and ^1H NMR of **22b** closely resemble the ^{31}P and ^1H NMR of **21b**.[25]

While transition metal complexes containing BH_2 units as ligands are quite rare, heterobimetallic cobaltaborane complexes are even more rare.[27] In fact, only two cobaltaborane complexes have been reported.[27,28] The first isolated cobaltaborane complex, **$[CoBH_2(THF)(CO)_4]$**, was characterized

spectroscopically at low temperatures. However, at room temperature, this complex decomposes quite rapidly.[28] The second cobaltaborane complex, specifically **[Co(μ-dppm)(η^1-dppm)(CO)$_2$BH$_2$]**, **23**, may be obtained as a minor product from reductions of Co(II) salts by $NaBH_4$ in the presence of dppm and CO.[27] (see Figure 1).

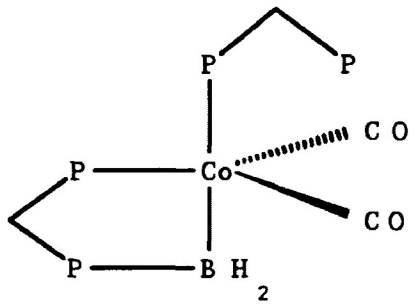


Figure 1. Cobaltaborane complex, 23.

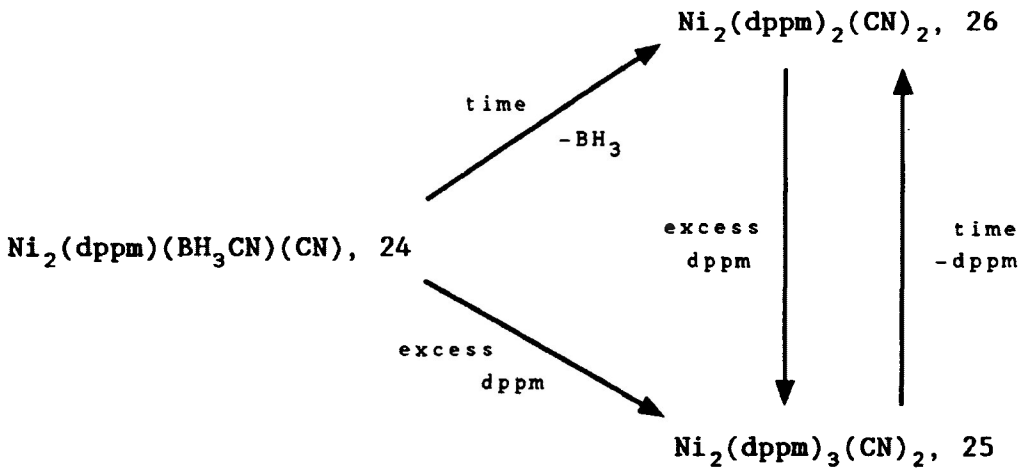
Complex **23** has been identified crystallographically and the Co centre has been found to adopt a distorted trigonal bipyramidal arrangement.[27] The stability of **23** is thought to be attributed to the bridging dppm.

4. Dppm Complexes of Nickel.

As mentioned in preceding sections, reactions involving Co(II) salts, dppm and $NaBH_4$ or $NaBH_3CN$ lead to the formation of a variety of products. Similar reactions between Ni(II) salts and $NaBH_3CN$ in the

presence of dppm leads to the formation of several different Ni(I) complexes.[29] These reactions generally are accompanied by cleavage of the C-B bond in $NaBH_3CN$ to produce Ni-CN complexes.

From these reactions, three Ni(I)-dppm complexes have been isolated. These are **$Ni_2(dppm)_2(CN)(BH_3CN)$, 24**, **$Ni_2(dppm)_3(CN)_2$, 25**, and **$Ni_2(dppm)_2(CN)_2$, 26**. The complex obtained from these reactions (either **24**, **25** or **26**) largely depends on the reaction times.[29] As well, complexes **25** and **26** are interconvertible depending on the reaction conditions (see Scheme 10). When Ni(II) salts are reduced in the presence of dppm by $NaBH_3CN$, compound **24** may be formed. However, if **24** is left in solution for a long period of time, it undergoes B-C bond cleavage, thus losing BH_3 and producing **25**. When



Scheme 10.

Interconversions between compounds 24, 25 and 26.

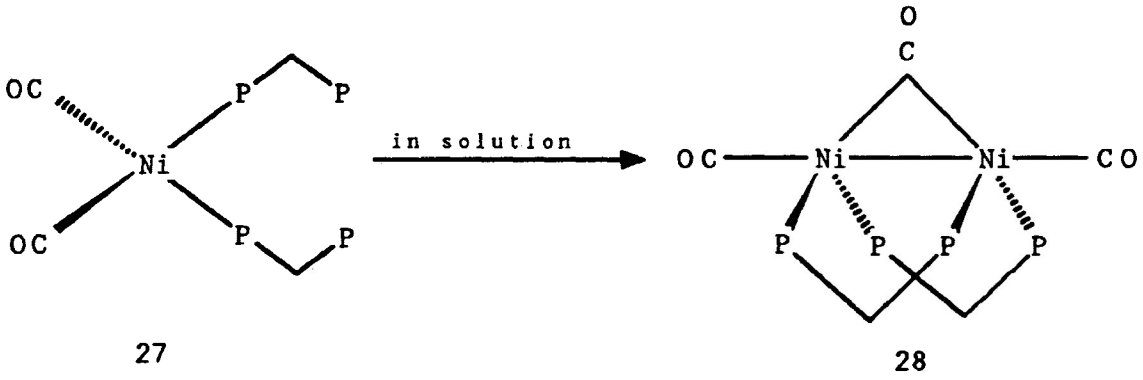
an excess of dppm is added to a solution containing **24**, compound **25** is slowly formed with the loss of BH_3. Compound **25** also decomposes over time with a loss of dppm to produce compound **26**. Complex **26** is also formed from Ni(II) reductions by $NaBH_3CN$ in the presence of dppm. This four-coordinate complex may be converted to complex **25** simply by reacting it with an excess of dppm.

5. Ni-Dppm-CO Complexes.

If the reactions involving Ni(II) reductions in the presence of dppm are extended to include carbon monoxide, various monomeric and dimeric Ni(0) species may be obtained. Generally, the reactions involve $NaBH_4$ or $NaBH_3CN$ as the reducing agent and depending on which one is used, different products may be obtained.[30]

For example, if Ni(II) is reduced by $NaBH_3CN$ in the presence of dppm and CO, a monomeric Ni(0) species **$Ni(\eta^1$-dppm$)_2(CO)_2$**, **27**, containing monocoordinated dppm, is formed. The complex is only stable at low temperatures or in the presence of an excess of dppm.[31] Complex **27** possesses also an un-coordinated phosphorus atom which makes it a very reactive species, specifically in the synthesis of heterobimetallic complexes (which will be discussed later).

In the case where Ni(II) is reduced by the more active reducing agent, $NaBH_4$, the complex **$Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2$**, **28**, having a cradle type geometry, is formed. Even though other routes[32,33,34] have been developed for the synthesis of **28**, this method appears to be the simplest. Complex **28** can be formed in solution from the decomposition of **27**, according to Equation 2. Complex **28** has been found to be a very reactive species.[30] It reacts with HCl and I_2 and is very reactive towards O_2 producing the monoxide of dppm.



27 28

Equation 2.

6. Ni-M-Dppm-CO Complexes.

The two methods previously discussed in synthesizing heterobimetallic systems containing cobalt may also be applied to nickel systems as well. For example, if in the reaction involving the reduction of Ni(II) (in the presence of dppm and CO) by $NaBH_3CN$, one

molar equivalent of $CuCl_2$ is added, the complex **$NiCu(\mu\text{-dppm})_2(CO)_2(NCBH_3)$, 29**, may be formed (see Figure 2). The X-ray structure reveals that the dppm ligands in **29** adopt a cradle-like geometry.[10] This complex is not very interesting from a catalytic point of view since it lacks a metal-metal bond, which is generally essential in reactions catalyzed by binuclear and metal cluster catalysts.

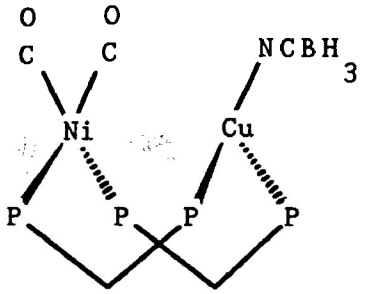


Figure 2. $NiCu(\mu\text{-dppm})_2(CO)_2(NCBH_3)$, 29.

As mentioned before, complex **27** has been found to be quite useful in heterobimetallic syntheses due to the free, uncoordinated, phosphorus atoms of the monocoordinated dppm ligands.[31] Compound **27** has been found to react with various transition metal complexes such as $Rh_2Cl_2(CO)_4$, $Mo(CO)_5(THF)$, $NiCl_2.6H_2O$, $Cu(NCMe)_4ClO_4$ and $PtCl_2(COD)$.

For example, in the reaction between **27** and $PtCl_2(COD)$, the heterobinuclear complex **$NiPt(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$, 30**, may be formed quite easily

(see Figure 3). The X-ray structure of **30** indicates the presence of a Pt-Ni bond. This would appear to imply that complex **30** contains Ni(0) and Pt(II).

In reactions of **27** with various d^{10} complexes such as $[Cu(NCMe)]ClO_4$, the ionic complex **$[NiCu(\mu\text{-dppm})_2(CO)_2(NCMe)_2]ClO_4$, 31,** can be formed[10] (see Figure 4).

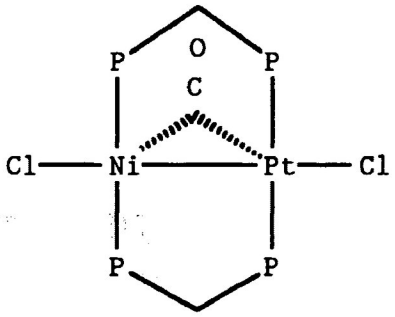


Figure 3. $NiPt(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$, 30.

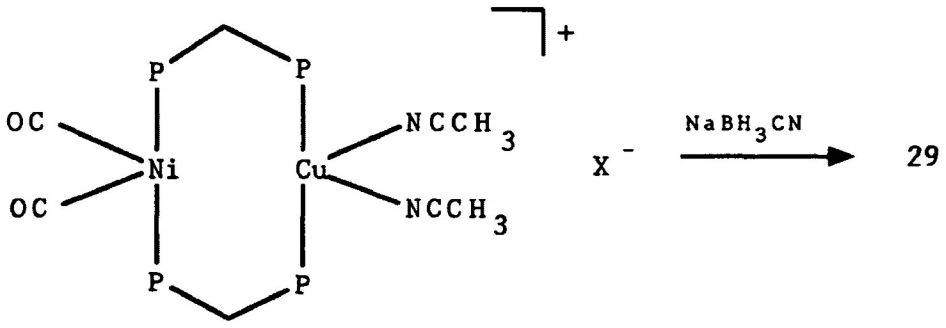


Figure 4. Conversion of complex 31 to complex 29.

An X-ray structure of **31** has not yet been

determined but it is thought that it resembles the structure of **29**. As well, while the copper in **29** is three coordinate, it is four coordinate in **31**. Complex **31** may be converted to complex **29** simply by treating it with $NaBH_3CN$. Finally, as with **29**, complex **31** is not very interesting in terms of catalysis, again due to the absence of a metal-metal bond.

Attempts at synthesizing other heterobimetallic complexes using d^{10} systems have so far not been very successful. For example, reactions involving **27** and Ag(I) appear to yield a Ni(0)-Ag(I) complex that is stable only at low temperatures.[10] However, if **28** is reacted with Au(I), specifically, $ClAu(Me)_2S$, **[NiAu(μ-dppm)$_2$(CO)$_2$]Cl** is thought to be produced. This complex has been identified spectroscopically and is thought to be analogous to $[NiAu(\mu\text{-dppm})_2(CNMe)_2]Cl$,[35] which is formed when $Ni_2(\mu\text{-dppm})_2(\mu\text{-CNMe})(CNMe)_2$ is reacted with $(PPh_3)AuCl$.

II. Cobalt and Nickel Mediated P-C Bond Cleavage in Dppm.

It is well known that certain transition metal complexes have the ability to catalyze the scission of the P-C bond in various tertiary phosphines.[36] As

well, it has been established[36] that the ease of P-C cleavage follows the order $P\text{-}C_{sp} > P\text{-}C_{sp^2} > P\text{-}C_{sp^3}$. Generally, the conditions under which P-C scission occurs are extremely forced. For example, P-C bond cleavage in dppm has been reported usually to occur in strongly alkaline solutions,[37] or at high temperatures.[38] However, Hughes and Holah have developed a one-step synthesis to producing phosphido-bridged complexes under comparatively mild conditions.

As previously discussed, reductions of Co(II) and Ni(II) salts in the presence of dppm and CO produce a wide variety of monomeric and dimeric complexes. The outcome of these reactions largely depends on three basic factors; specifically, the reaction conditions, the reactant ratios and finally, the rate of addition of the reducing agent. In the case of the last point, rapid addition of $NaBH_4$ results in the formation of phosphido-bridged complexes.[10,39]

For example, when $NaBH_4$ is rapidly added (about 1 minute) to a CO saturated solution of Co(II) and dppm, the complex $\mathbf{Co_2(\mu\text{-}dppm)(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}H)}$,[39] **32**, is formed (see Figure 5), which has been identified spectroscopically. If the procedure is modified somewhat[39] and the reducing agent is added over a longer period of time (about 10 minutes), two products may be

obtained; specifically **32** and the known[40] $Co_2(\mu\text{-dppm})(CO)_4(\mu\text{-}PPh_2)(\mu\text{-H})$. Another route leading to the formation of **32** involves refluxing the complex $Co_2(\mu\text{-dppm})_2(CO)_4$ under dihydrogen.[39] It appears, then, that such procedures provide short, convenient routes to metal-mediated P-C bond cleavage.

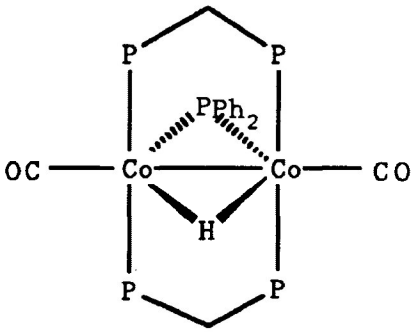


Figure 5. $Co_2(\mu\text{-dppm})(CO)_2(\mu\text{-}PPh_2)(\mu\text{-H})$, 32.

The complex **$[Ni_2(\mu\text{-dppm})_2(CO)_2(\mu\text{-}PPh_2)]X$** (X=Cl or BPh_4), **33** (see Figure 6), was also prepared in a

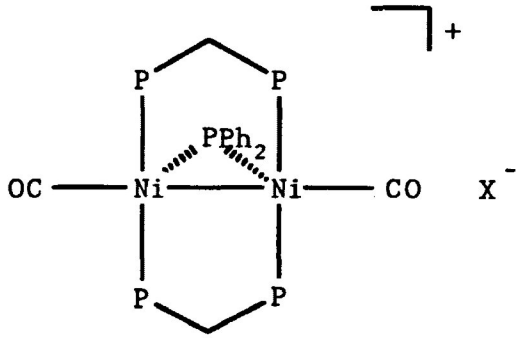


Figure 6. $[Ni_2(\mu\text{-dppm})_2(CO)_2(\mu\text{-}PPh_2)]X$, 33, (X = Cl, BPh_4).

somewhat similar manner as the phosphido-bridged cobalt complexes.[10,39] However, this complex may also be formed (inadvertently) in an attempt to synthesize heterobimetallic systems containing cobalt and nickel.[10,39] Although the product of this synthesis is unexpected, it is a convenient route to producing **33** in good yields. Such a complex is a rare example of a cationic species containing a phosphido-bridge.

The mechanism of the formation of these complexes containing a phosphido-bridge has been under extensive investigation.[41] While the literature cites several examples[37,38,42] of P-C bond cleavage in dppm, generally only one bond is cleaved and both fragments are incorporated into the final product. However, in one case[43] involving a dimeric iron carbonyl species bridged by the $-CHCO_2Et$ unit, both of the P-C bonds in dppm undergo scission leading to the formation of ethyl acrylate.

An important observation in the reactions involving the synthesis of the phosphido-bridged cobalt and nickel compounds is that a Ph_2PCH_2- fragment has never been isolated or observed.[10] This would seem to indirectly imply that both P-C bonds in dppm undergo cleavage in these reactions.[41] Furthermore, it is thought that if a double cleavage does, in fact, occur, the methylene

species produced probably reacts with CO in the reaction medium producing ketene. Since the reactions are generally carried out in solvent systems containing ethanol, it is quite probable that the ketene reacts with ethanol producing ethyl acetate, which has now been observed.[41]

III. Palladium-Dppm, Palladium-Dppm-CO and Palladium-M-Dppm/CO Complexes

1. Pd-Dppm Monomeric Complexes.

The general interest behind the preparation of palladium complexes lies in their ability to act as catalysts.[44,45,46] Thus, a wide variety of mononuclear, dinuclear and polynuclear palladium complexes has been synthesized using many different ligands.

Since the work reviewed in the Results and Discussion section largely deals with palladium-dppm-CO binuclear and cluster complexes, the following discussion will emphasize previous work that has been done in the field of palladium binuclear and cluster chemistry. Only a brief discussion will be given on mononuclear palladium complexes.

As previously mentioned, palladium can exist in

various oxidation states; specifically 0, I, II and IV. One monomeric complex that includes Pd in a +2 oxidation state is **$PdCl_2(\eta^2$-dppm)**, **34**, which was first synthesized by Steffen and Palenik.[47,48] This complex has been identified by X-ray structure analysis and the Pd was found to be in a square planar environment.

Denise and Sneeden[46] found that if **34** is treated with $NaBH_4$ in the presence of dppm, the Pd(0) complex, **$Pd(\eta^2$-dppm)$_2$**, **35**, may be formed. Alternatively, **35** may also be formed when **34** and **$PdCl_2(PhCN)_2$** is heated with $NaBH_4$ in the presence of dppm. The same group also found that the halide coordinated to **34** may easily be displaced. For example, when **34** is treated with $AgBF_4$ and dppm in the appropriate solvent, halide coordinated to **34** may be displaced by dppm in solution producing **$[Pd(\eta^2$-dppm)$_2](BF_4)_2$** (see Equation 3).

$$PdCl_2(\eta^2\text{-dppm}) \xrightarrow[\text{acetone or methanol}]{AgBF_4/\text{dppm}} [Pd(\eta^2\text{-dppm})_2](BF_4)_2$$

Equation 3.

Similarly, Balch *et al.*[49] found that the halide ligands in **34** may also be exchanged or displaced by other halide ions from another Pd(II)-dppm-halide complex (see Equation 4). As well, the triborane ligand ($B_3H_8^-$) has been found to easily displace halide

in **34**.[50] For example, when **34** is reacted with $[Me_4N][B_3H_8]$, both chloride ions may be displaced producing **Pd(η^2-dppm)B_3H_7**.

$$Pd(\eta^2\text{-dppm})X_2 + Pd(\eta^2\text{-dppm})Y_2 \rightleftharpoons 2\ Pd(\eta^2\text{-dppm})XY$$

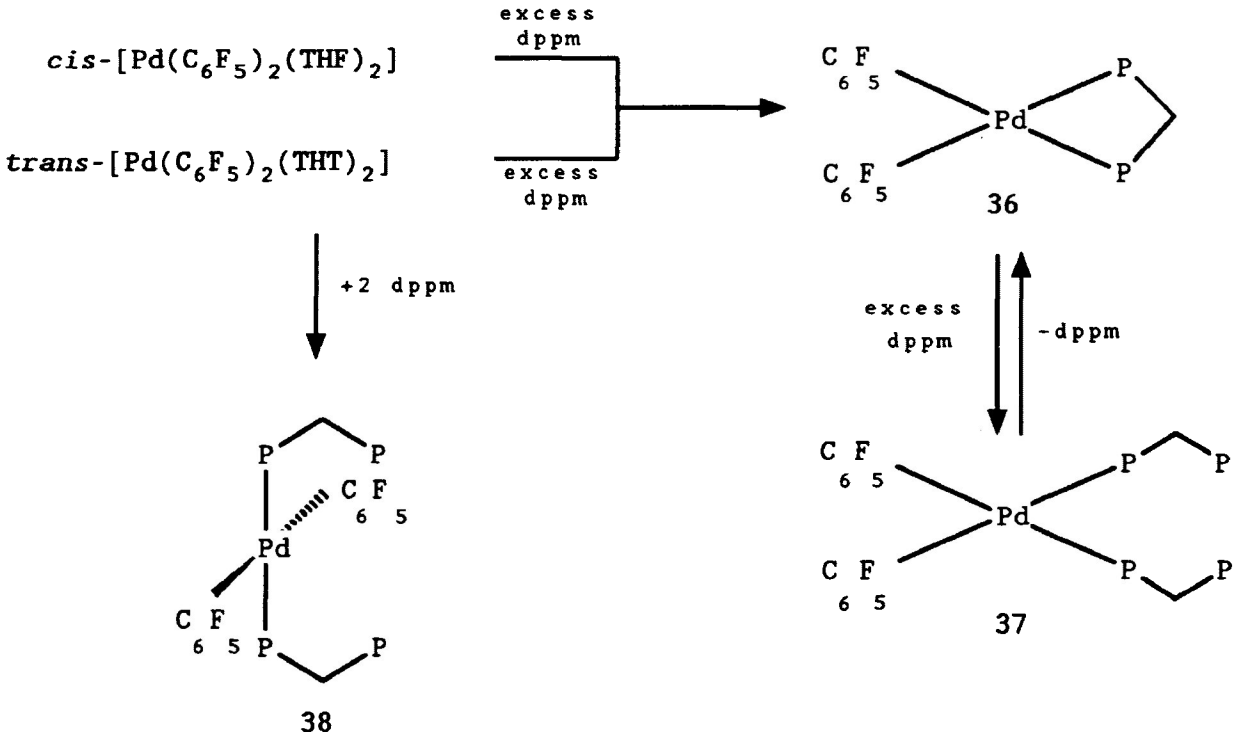
(X=Y=Cl, Br or I)

Equation 4.

Palenik *et al.*[48] found that in a series of mononuclear Pd(II)-phosphine-thiocyanate complexes, the mode of coordination of the thiocyanate ligands appears to be sterically directed and is not a function of electronic effects. Phosphines of the general type $Ph_2P(CH_2)_nPPh_2$ were used and they found that if the backbone was increased (from n=1,2 then 3) the mode of coordination of SCN^- changed from S,S for n=1 in **Pd(η^2-dppm)(SCN)$_2$**, to S,N for n=2 in the complex **Pd(η^2-dppe)(SCN)(NCS)**, to finally N,N for n=3 in the complex **Pd(η^2-dppp)(NCS)$_2$**. Each complex was identified by X-ray analysis.

In their investigations of the coordinating ability of dppm, Usón *et al.*[51] have prepared numerous monomeric complexes that were characterized by IR and ^{31}P spectroscopy. They have found that the mode of coordination of dppm (chelate, monodentate or bridging)

depends on the molar ratio between Pd and dppm (see Schemes 11 and 12). Thus, if one reacts the complex *cis*-$[Pd(C_6F_5)_2THF)_2]$ with dppm in a 1:1 molar ratio, the complex **Pd(η^2-dppm)(C_6F_5)$_2$, 36,** may be formed. If complex **36** is further treated with an excess



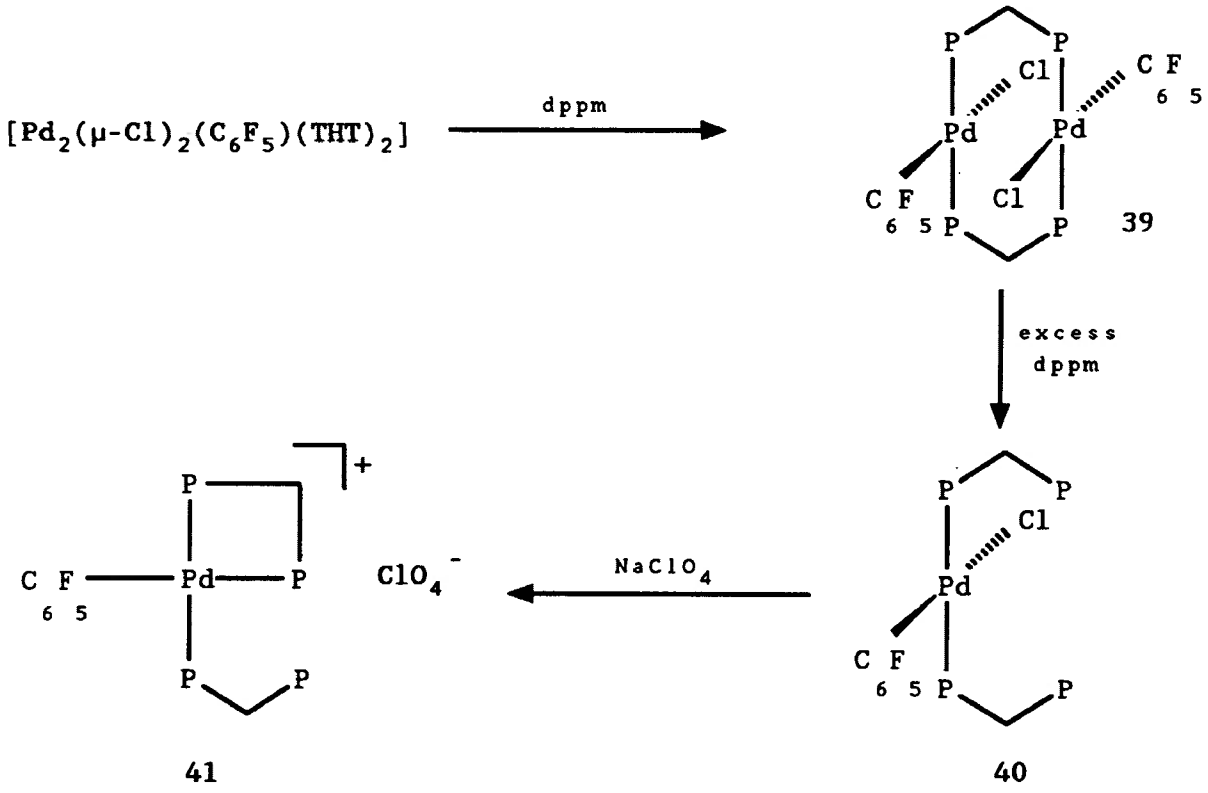
Scheme 11.

Modes of coordination of dppm in various Pd complexes.

of dppm, the monocoordinated *cis*-**Pd(η^1-dppm)$_2$(C_6F_5)$_2$, 37,** may be formed. Complex **36** can also be produced if the complex *trans*-$[Pd(C_6H_5)_2(THT)_2]$ is treated with an excess of dppm. From the reaction between *trans*-$[Pd(C_6F_5)_2(THT)_2]$ and dppm in a 1:2 molar ratio, the compound *trans*-**Pd(η^1-dppm)$_2$(C_6F_5)$_2$, 38,** is obtained.

It can be seen that in complex **36**, the C_6F_5 ligands are in a *cis* position whereas in complex **38** they adopt a *trans* configuration.

The same research group (see Scheme 12) also reacted the complex $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(THT)_2]$ with dppm in a 1:1 molar ratio and the complex ***trans,trans*-[Pd$_2$(μ-dppm)$_2$Cl$_2$(C$_6$F$_5$)$_2$]**, **39**, was formed. If **39** is further treated with excess dppm,



Scheme 12.

Modes of coordination of dppm in different monomeric and dimeric Pd complexes.

the mononuclear complex *trans*-**Pd(η^1-dppm)$_2$Cl(C_6F_5)**, **40**, may be formed. On treatment of **40** with $NaClO_4$, the cationic complex **[Pd(η^2-dppm)(η^1-dppm)(C_6F_5)]ClO_4**, **41**, (see Scheme 12) is formed. Finally, it is worth noting that complexes **38** and **40** possess uncoordinated phosphorus atoms, which have been shown to have a high reactivity towards other electrophilic centres.

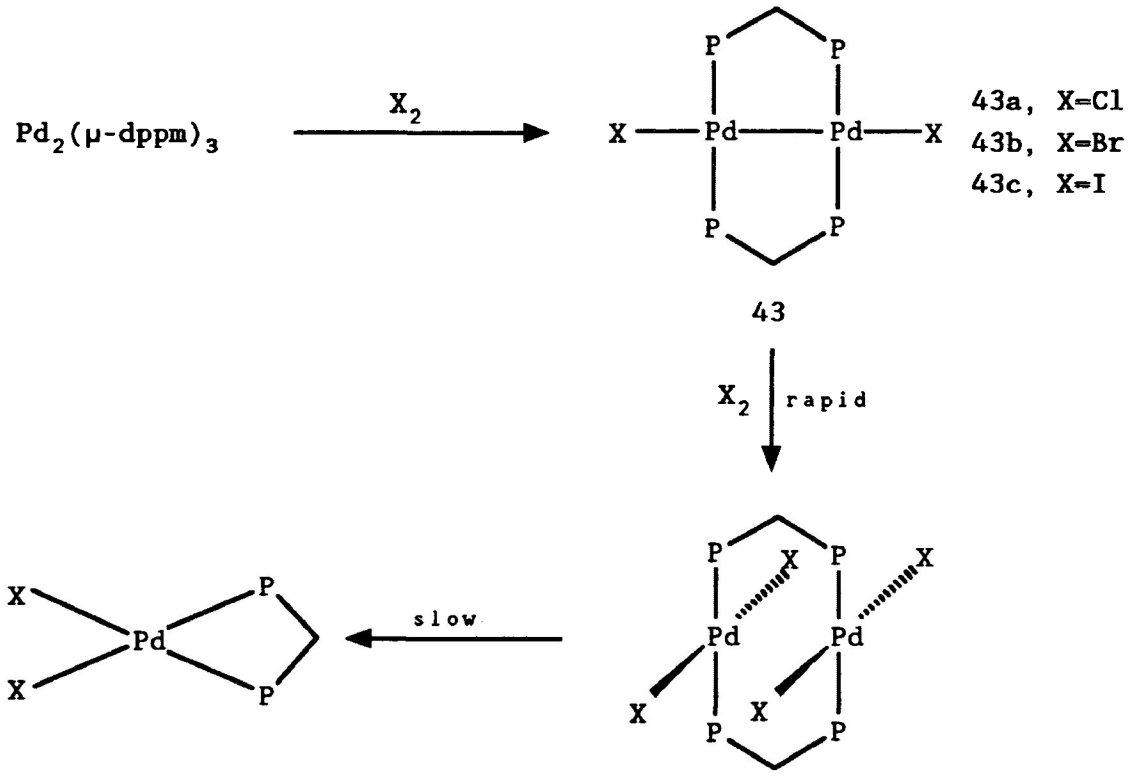
2. Pd-Dppm-CO Dimeric Complexes.

Although there is a variety of monomeric Pd complexes known containing dppm as a chelate or monocoordinated ligand, generally, dppm has a greater tendency to act as a bridging ligand. Thus, there are a great many more dimeric palladium compounds cited in the literature that contain dppm as a bridging ligand. Many of these dinuclear compounds are important from a catalytic point of view since they mimic those reactions which may occur on metal (palladium) surfaces (even more so with polynuclear complexes).

One Pd complex in which dppm acts as a bridging ligand is the complex **Pd_2(μ-dppm)$_3$**, **42**, originally synthesized by Stern and Maples.[44] In the synthesis of **42**, $PdCl_2(\eta^1\text{-dppm})_2$ was reacted with dppm and hydrazine. Another synthesis leading to the formation of **42** was the reaction between the uncharacterized $Pd_2H_x(dppm)_2$ and

dppm.[45] Compound **42** was fully characterized by X-ray diffraction and it was found that each of the Pd(0) atoms is trigonally coordinated by dppm. This thesis also reports a very rapid one-step synthesis leading to the formation of complex **42** (see Experimental Section).

Compound **42** can undergo oxidative addition reactions[52] in which Pd(I) and Pd(II) complexes are formed. Thus, if halogen X_2 (X=Cl, Br or I) is reacted with **42** under stoichiometric control, $\mathbf{Pd_2(\mu\text{-}dppm)_2X_2}$, **43**, is formed (see Scheme 13). The structure of



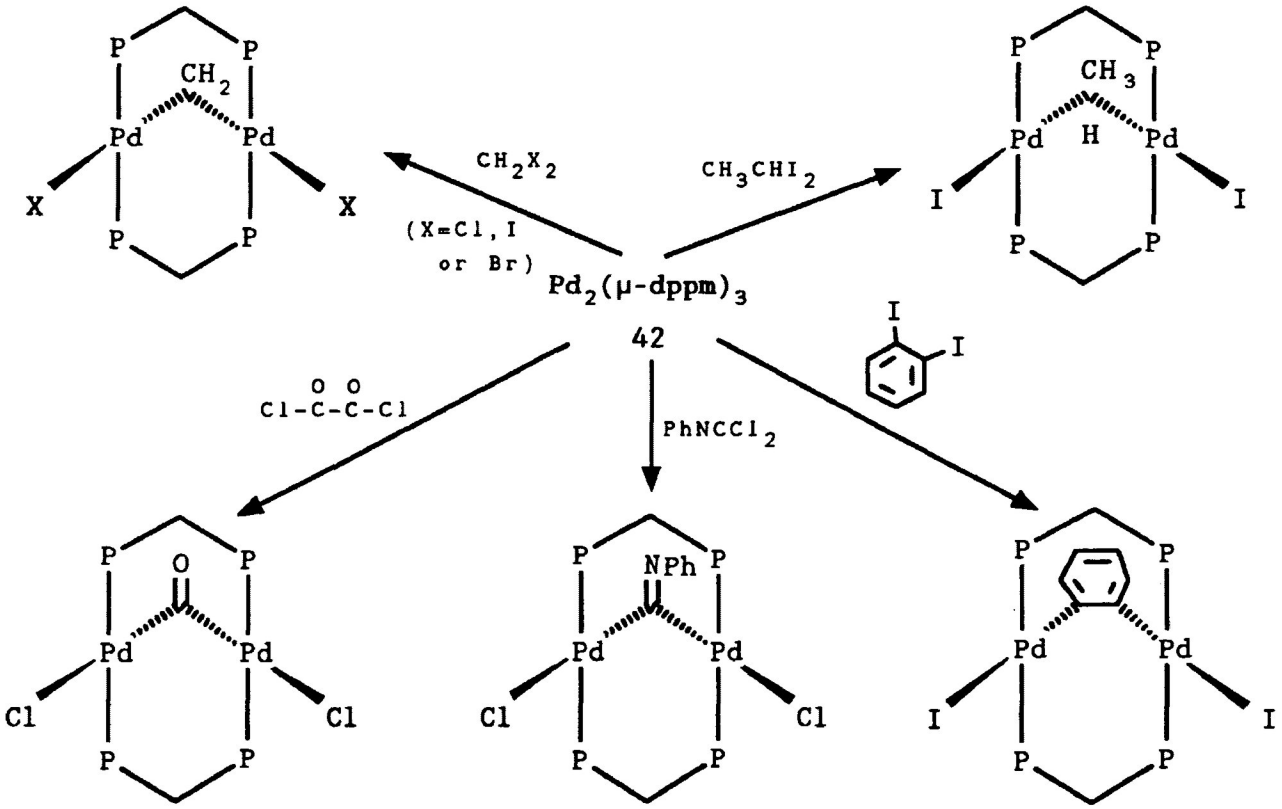
Scheme 13.

Oxidation of $Pd_2(\mu\text{-}dppm)_3$ by halogen molecules.

complex **43** was determined crystallographically and it

consists of two Pd(I) atoms directly bonded together; as well, each of the palladium atoms adopts square planar geometry. Complex **43** can be further oxidized to yield $PdX_2(\eta^2\text{-dppm})$, which proceeds through an intermediate $Pd_2(\mu\text{-dppm})_2X_4$ (also see Scheme 13) which was identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

In the case where halogen is substituted for



Scheme 14.

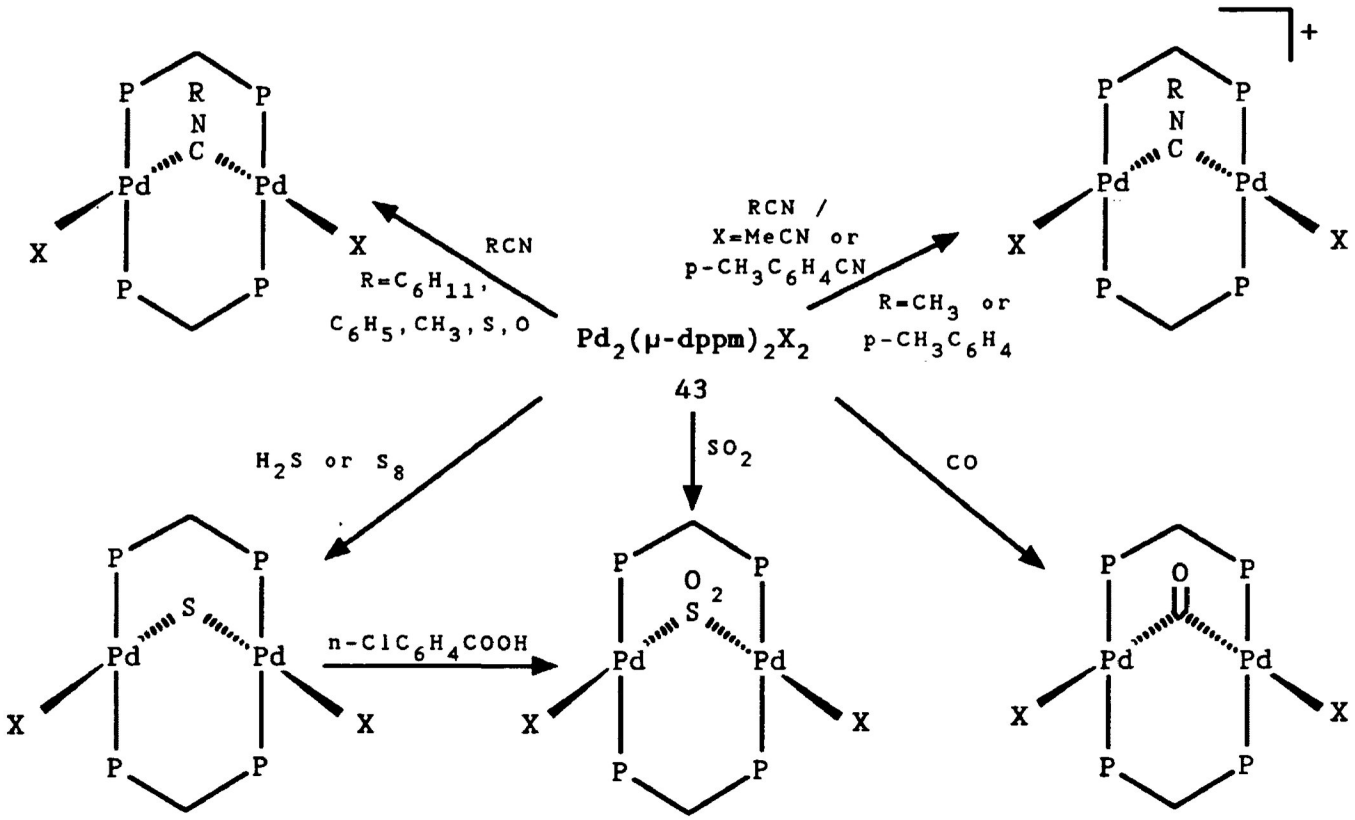
Oxidative addition to complex 42 by various organic dihalide compounds.

organic dihalide molecules,[53] **42** undergoes two-centre, three fragment oxidative addition producing A-frame type

complexes with a loss of dppm (see Scheme 14).

Finally, complex **42** will also catalyze hydrogenation reactions of unsaturated molecules[44] such as, for example ethylene, propylene, butadiene and acetylenes, just to name a few.

The previously mentioned compound **43** possesses a Pd-Pd single bond with each palladium atom having sixteen electrons. Therefore, the insertion of small



Scheme 15.

Insertion of S, SO_2, H_2S, RCN and CO into the metal-metal bond of $Pd_2(\mu\text{-dppm})_2X_2$.

molecules such as sulfur, sulfur dioxide,[54,55] hydrogen

sulfide,[56] isocyanides,[57,58] and carbon monoxide[57,59] (see Scheme 15) into metal-metal bonds results in the formation of A-frame type complexes. Generally, many[55] of the compounds were characterized by IR, NMR (^1H) and electron spectroscopy while several were identified by X-ray analysis. (The complex $Pd_2(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$ in Scheme 15 may also be produced via a simple one-step route which will be discussed in the Results and Discussion section of this thesis).

Complex **43** is also useful in certain catalytic reactions[46] depending on the solvent. Thus, **43** catalyzes, for example, the synthesis of diethyl formamide when the reaction is performed in diethylamine/benzene and under CO_2 and H_2.

Furthermore, dinuclear palladium complexes have also been found to undergo reductive elimination reactions.[60,61] For example, in the complex $[Pd_2(\mu\text{-dppm})(\mu\text{-Cl})H(CH_3)]^+$, **44**, it is thought that chloride and hydride undergo rapid exchange with one another. If **44** is heated, methane is reductively eliminated giving **43**; if **44** is reacted with CO at low temperatures, acetaldehyde is eliminated.[61]

3. Pd-M-Dppm and/or CO Complexes.

While much work has been done investigating

palladium homobinuclear compounds containing dppm and other stabilizing ligands, there is an increasing interest in investigating the synthesis and properties of heterobimetallic palladium complexes bridged by dppm. By having different metals in the same complex, the reactivity of the molecule is made variable due to different electron densities on the metal atoms involved.[62] It is for this reason that heterobinuclear complexes are thought to be useful in catalysis and, thus, have generated much interest lately.[63]

It has only been recently that mixed binuclear compounds containing palladium have been prepared and studied.[64] One such compound, prepared by Pringle and Shaw,[64] is a binuclear complex containing palladium and platinum, bridged by dppm (see Figure 7).

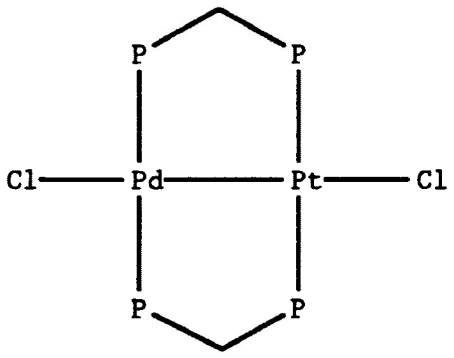
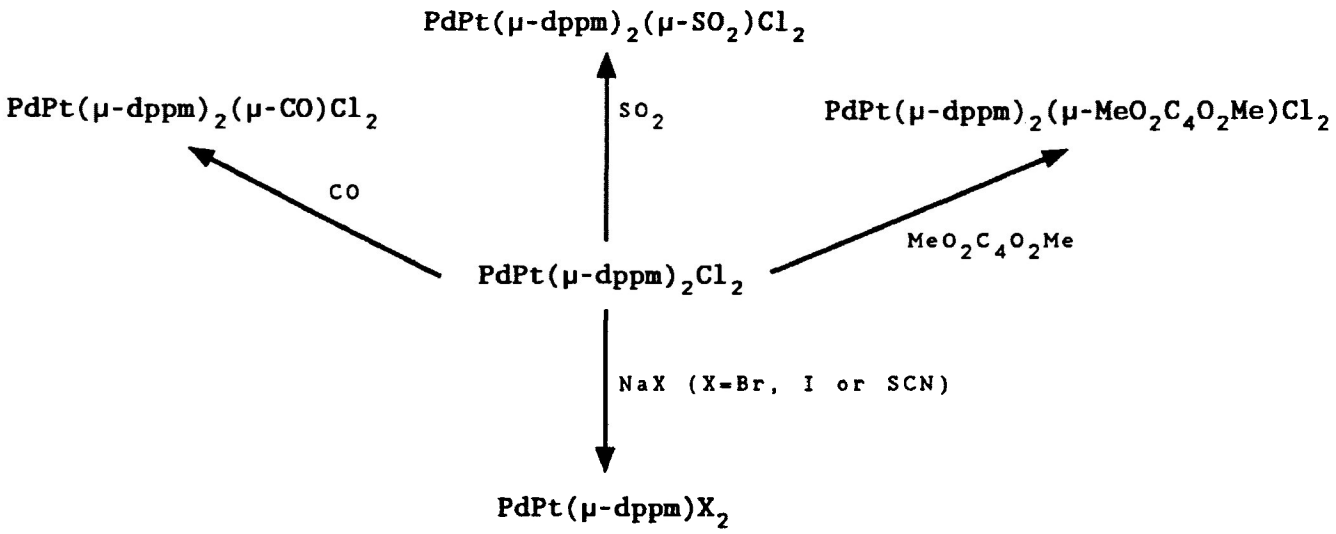


Figure 7. $PdPt(\mu\text{-}dppm)_2Cl_2$.

The complex $PdPt(\mu\text{-}dppm)_2X_2$ (X=Cl), **45**, was found to be quite stable against disproportionation, which is

attributed to the strong dppm bridge.[64] Complex **45** was also found to undergo a variety of ligand exchange reactions with various alkali metal salts, again, without undergoing disproportionation[65] (see Scheme 16). When CO or SO_2 is bubbled through solutions of **45**, or if a solution of **45** is treated with $MeO_2C_4O_2Me$, insertion into the Pd-Pt bond was found to occur[65] producing various A-frame species, again, without undergoing disproportionation (see Scheme 16).



Scheme 16.

Reactions of $PdPt(\mu\text{-dppm})_2X_2$ with alkali metal salts and other molecules.

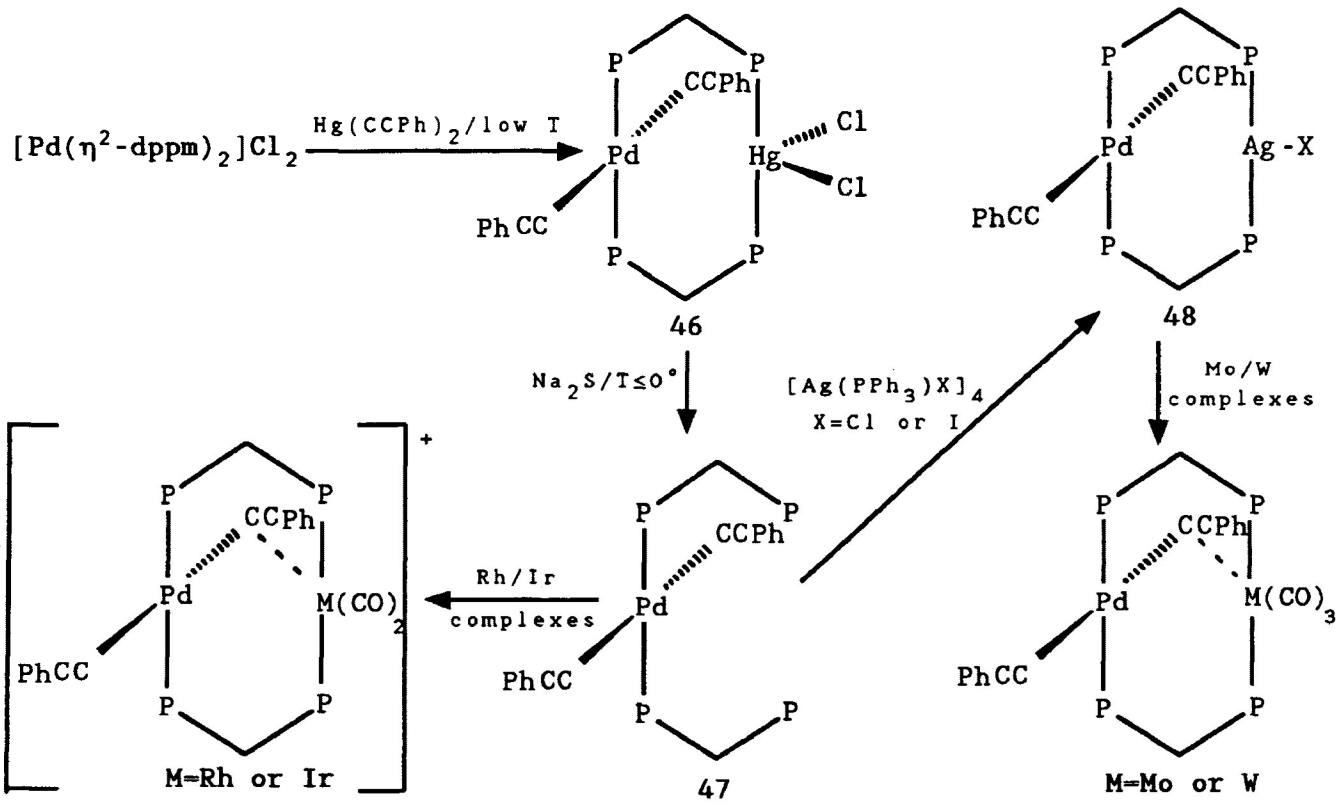
Shaw et al. have also produced a variety of other heterobinuclear compounds containing palladium,[66] which they have characterized spectroscopically. For example

when $[Pd(\eta^2\text{-dppm})_2]Cl_2$ (generated *in situ*) is treated with $Hg(CCPh)_2$ at low temperatures, the binuclear complex **$PdHg(\mu\text{-dppm})_2(CCPh)_2Cl_2$, 46**, may be formed. If **46** is reacted with Na_2S, ***trans*-$[Pd(\eta^1\text{-dppm})_2(CCPh)_2]$**, **47**, is formed in high yields (see Scheme 17).

Complex **47** was found to be quite useful in synthesizing heterobimetallic compound due to the *trans* arrangement and the uncoordinated phosphorus atoms of the dppm ligands. For example, treatment of **47** with $[Ag(PPh_3)X]_4$ (X = Cl, I) produces the heterobimetallic complex **$PdAg(\mu\text{-dppm})_2(CCPh)_2X$ (X=Cl or I), 48.** If **47** is reacted with $Rh_2Cl_2(CO)_4$, the ionic **$[PdRh(\mu\text{-dppm})_2(CO)(CCPh)_2]X$ (X=Cl)** is formed. Similarly, treatment of **47** with Ir_2Cl_2(cyclo-octene) and CO also produces the ionic complex **$[PdIr(\mu\text{-dppm})_2(CCPh)_2(CO)]X$ (X=Cl).** It is thought that one of the acetylide ligands on the Pd bridges both metals in the Pd-Rh and Pd-Ir complexes since this ligand was found to interact with both metals in similar Pt-Ir complexes[67] (see Scheme 17).

Finally, if the mixed Pd-Ag complex **48** (X=Cl)is reacted with $Mo(CO)_3(C_7H_8)$ or *fac*-$[W(CO)_3(NCMe)_3]$,[66] the mixed metal complexes **$PdM(\mu\text{-dppm})_2(CO)_3(CCPh)_2$ (M=Mo or W)** may be formed. Again, it is thought that one of the acetylide ligands on the palladium interacts with the other metal (Mo or W) in these binuclear complexes (see

Scheme 17).



Scheme 17.

Synthesis of heterobinuclear complexes containing palladium.

Shaw et al. have also synthesized a mixed Pd-Fe binuclear complex using an Fe(II) precursor containing a monocoordinated dppm ligand.[68] Specifically, when the complex $FeI_2(CO)(\eta^2\text{-dppm})(\eta^1\text{-dppm})$ is reacted with $Pd(dba)_2$ under CO, the complex **$PdFe(\mu\text{-dppm})_2(CO)_2I_2$, 49,** is formed; it may also be formed by reacting $Fe(CO)_4(\eta^1\text{-dppm})$ with the complex $Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2$.

If **49** is protonated by HBF_4, the ionic species **[PdFe(μ-dppm)$_2$(CO)$_2$I$_2$(μ-H)]BF$_4$** is formed; when methyl isocyanide is added to a solution containing **49**, the CO ligands on the iron are displaced, giving the ionic species **[PdFe(μ-dppm)$_2$I(MeNC)$_3$]I**; finally, when t-butyl isocyanide is reacted with **49**, the iodide ligand on the iron centre is displaced, producing **[PdFe(μ-dppm)$_2$(CO)$_2$I(Bu^{t}NC)]I**. All complexes were characterized by elemental and spectroscopic analysis.

Mixed-metal binuclear palladium complexes containing manganese[69] and nickel[63] have also been synthesized. For example, when **43** is reacted with $Mn(CO)_4^-$ at low temperatures, the complex **PdMn(μ-dppm)$_2$(CO)$_3$** is formed along with a mixed metal cluster containing palladium and manganese. Similarly, if $PdCl_2(PhCN)_2$ is treated with $Ni(CO)_2(\eta^1\text{-dppm})_2$, the complex **PdNi(μ-dppm)$_2$(μ-CO)Cl$_2$** is formed.

IV. Palladium Clusters containing Dppm.

Generally, palladium has the ability to form coordinatively unsaturated cluster complexes; hence, it is interesting from a catalytic point of view. Palladium has a tendency to form metal-metal bonds in cluster complexes and, thus, provides stability in such

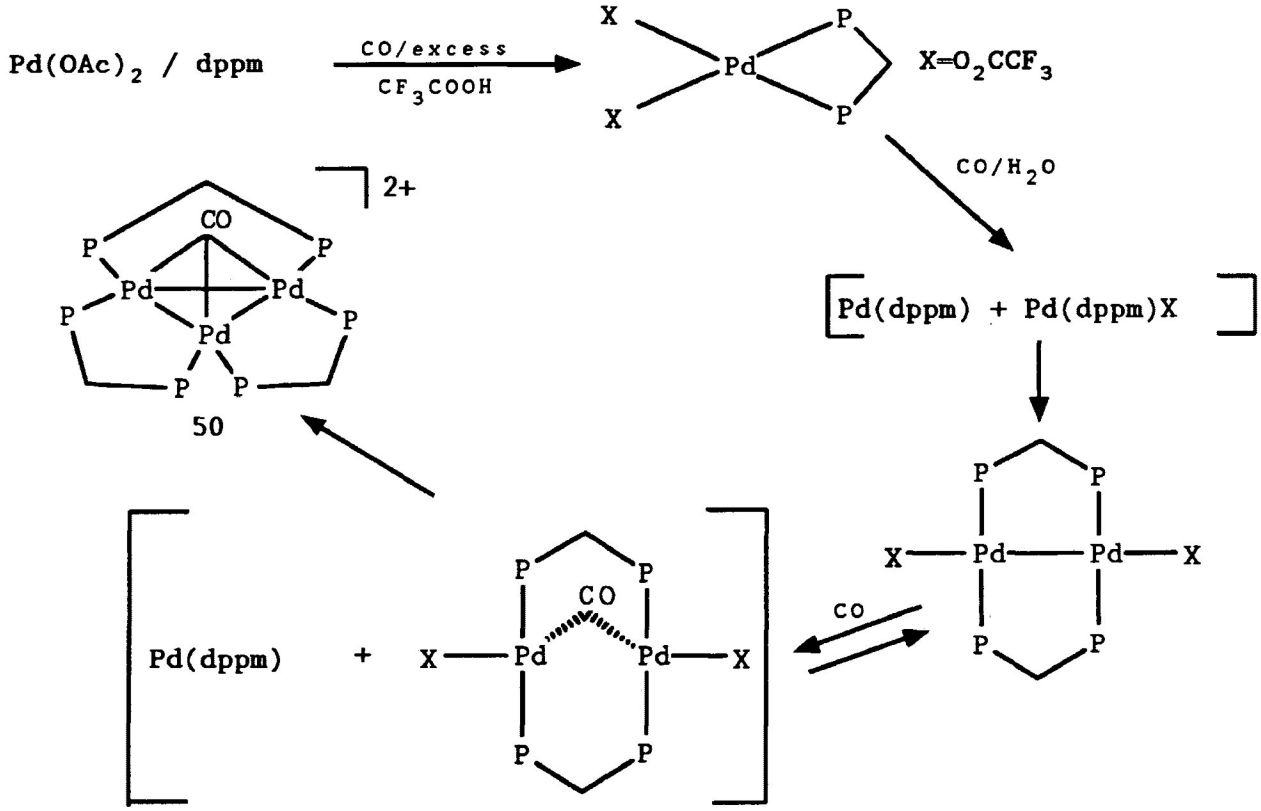
compounds. However, the use of bridging ligands such as CO, SO_2 and bridging phosphines (specifically, dppm) are quite useful in that they provide further stability against fragmentation.[70]

While a variety of palladium cluster complexes containing various phosphines and CO are known,[71] very few palladium clusters stabilized by dppm have been reported.

One example[72] of a palladium-CO-dppm cluster is the trimeric $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$, **50**. The X-ray structure of **50** shows the Pd_3P_6 moiety to be essentially planar, with dppm bridging each side of the basic Pd_3 unit. As well, X-ray analysis shows the CO ligand capping the Pd_3 unit and the stretching frequency of this triply bridging CO was reported[72] to be around 1820 cm^{-1}.

The mechanism of the formation of **50** has been studied extensively by Puddephatt et al.[73] Generally, complex **50** is synthesized from $Pd(OAc)_2$, dppm and CO with an excess of CF_3COOH. The mechanism (see Scheme 18), which was monitored by NMR, involves several intermediates, some of which have been isolated and fully characterized.[73] The intermediate species, Pd(dppm), is thought to exist in solution, but is too short lived to be observed or isolated; as well, it is possible that this complex may also contain coordinated

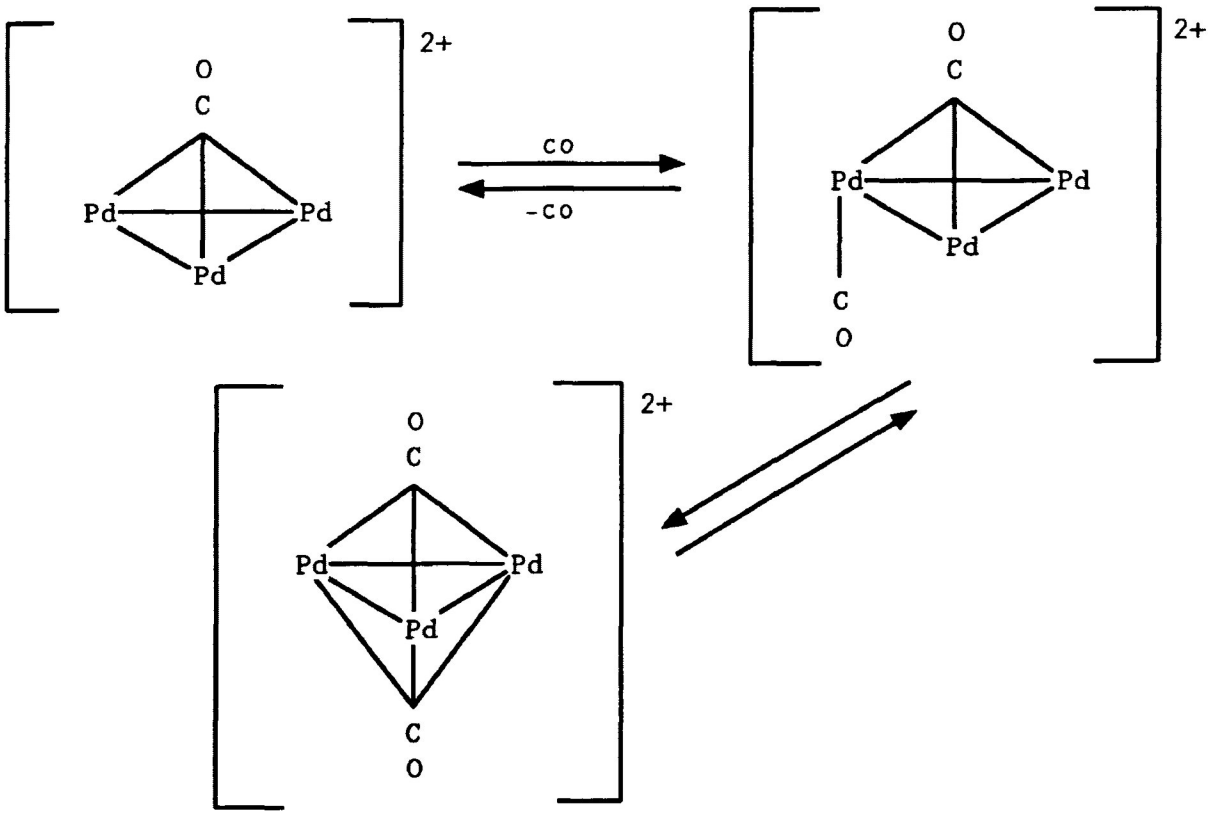
CO, which would provide additional stabilization.[73]



Scheme 18.

Mechanism of the formation of $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$, complex 50.

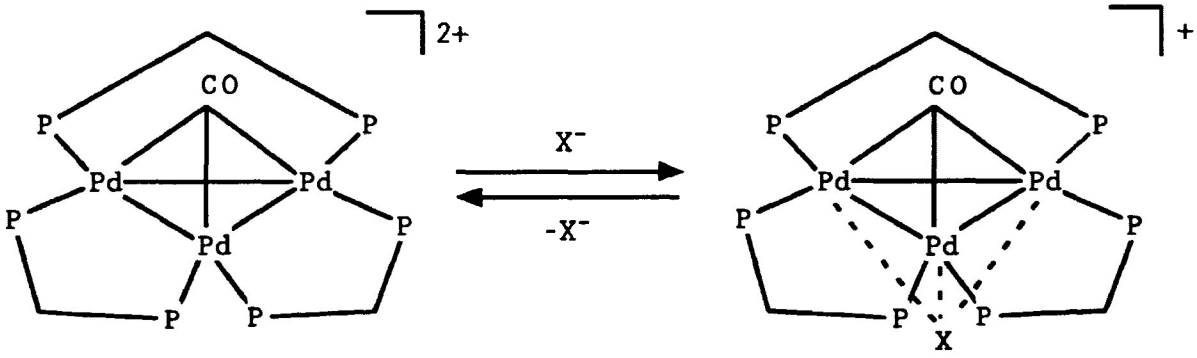
Reactions of **50** with CO[70] were monitored at low temperatures (see Scheme 19) by NMR and IR spectroscopy. It was found that CO reversibly adds to **50** to produce a $Pd_3(\mu_3\text{-CO})_2$ moiety which was evident from NMR studies. However, it is apparent that the $Pd_3(\mu_3\text{-CO})_2$ unit is in equilibrium with a separate $Pd_3(\mu_3\text{-CO})CO$ moiety, which was observed in the low temperature IR spectrum.



Scheme 19.

Reactions of 50 with CO.

Puddephatt et al.[74] also investigated (Scheme 20)



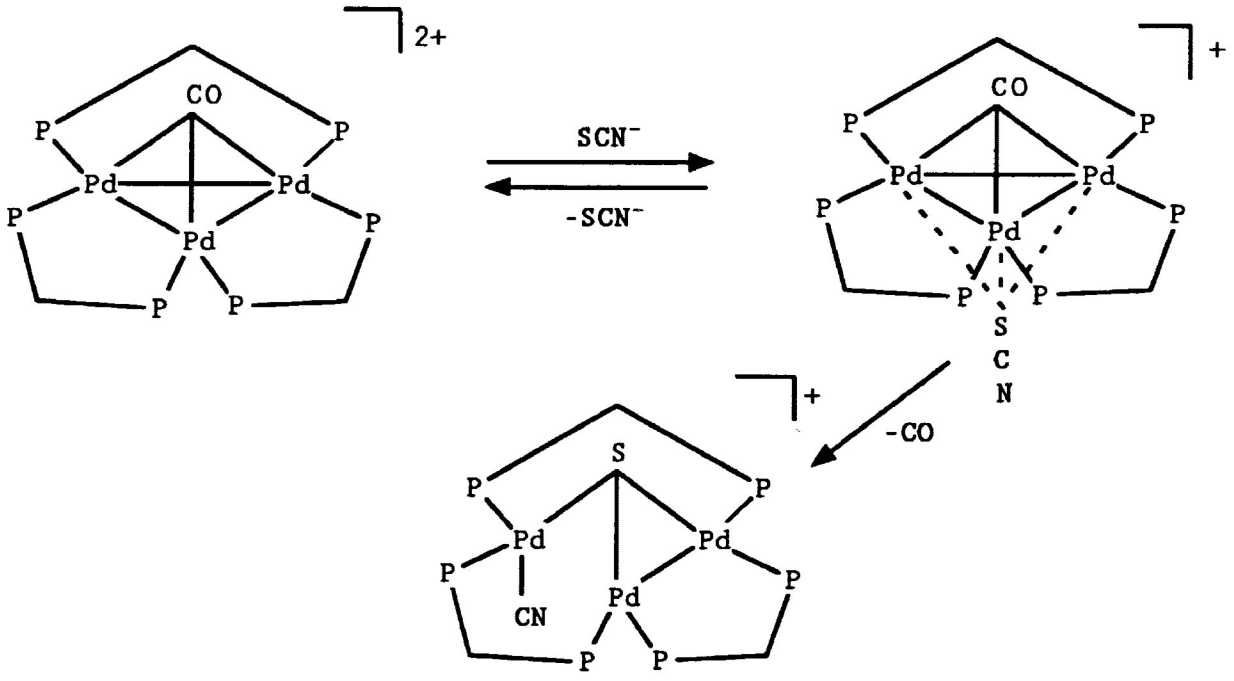
X=Cl, Br, I or CF_3COO

Scheme 20.

Reactions of 50 with various anions.

the possible coordination of various anions to the triangular Pd_3 unit in **50**. Essentially, they found that halide may reversibly add to **50** along with anions such as CF_3COO^-.

However, in the case where X=SCN, they found that the thiocyanate ligand does, in fact, cap the basic Pd_3 unit, but it further reacts with the cation, cleaving metal-metal bonds and expelling CO (see Scheme 21). The final product has been confirmed by X-ray analysis.

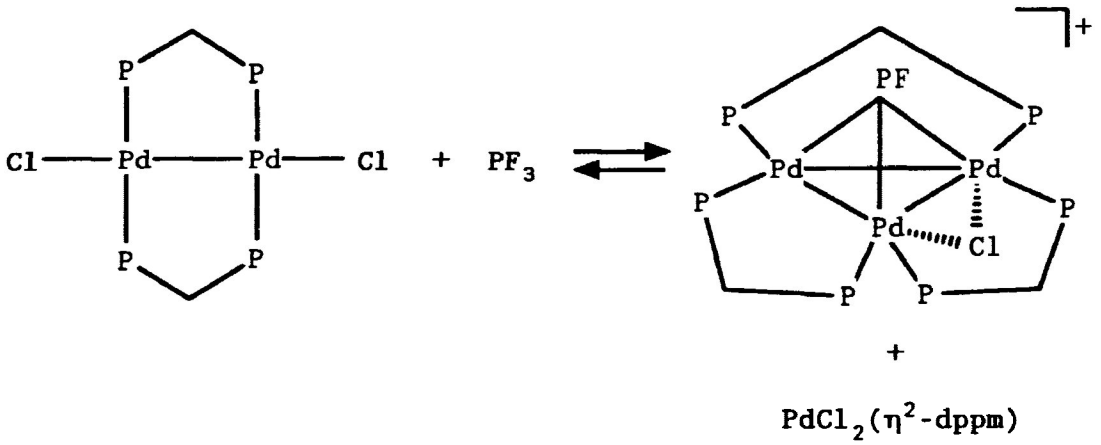


Scheme 21.

Reactions of 50 with SCN^-.

In their attempts to monitor the reversible

insertion of PF_3 into the Pd-Pd bond of **43**, Balch et al.[76] found that **43** disproportionates in the presence of PF_3 to produce the trimeric $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)]^+$, which contains a Pd_3 unit capped by PF_3 (see Scheme 22). The structure of this trimeric species has been confirmed by X-ray crystallography.



Scheme 22.

Formation of $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)]^+$.

Finally, in their attempts to synthesize methylene-bridged palladium complexes, Nakamura et al.[77] had isolated in their work the palladium tetramer $Pd_4(\mu\text{-dppm})_2(\mu\text{-}Cl)_2(\mu\text{-}C_3H_5)_2$, the structure of which was also confirmed by X-ray analysis.

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RESEARCH PROPOSAL

From the preceding introduction, it is obvious that the method devised by the Holah and Hughes group, which involves reductions of various metal salts (such as those of cobalt and nickel) in the presence of dppm or dppm/CO, leads to a wide variety of monomeric and dimeric complexes in various oxidation states. As mentioned earlier, the more general route to synthesizing metal-carbonyl-dppm complexes usually involves reacting metal carbonyls with phosphines. However, since some metal carbonyls are not always readily available, such as in the case of palladium, extending the method devised by Holah and Hughes to include palladium seemed like a good opportunity to uncover new routes to synthesizing palladium complexes containing CO.

The basic premise of this project, therefore, is to investigate reactions involving reduction of palladium salts in the presence of dppm and CO. Since it was found with Co(II) and Ni(II) that the reaction outcomes greatly depend on the reactant ratios, reaction times and rate of addition of reducing agent, careful attention will be given to the conditions under which

the reaction is conducted. As well, because $NaBH_4$ proved to be an adequate reducing agent in reactions involving cobalt and nickel, it, too, will be used as the reducing agent in these reactions.

Some of the reasons surrounding the extension of this method to include palladium consist of the following:

1. Because palladium carbonyls are unknown, it is impossible, then, to synthesize palladium-CO-dppm complexes using the more general method of reacting metal carbonyls with phosphines. Thus, reductions of palladium salts in the presence of CO and phosphines may lead to new routes to synthesizing palladium-CO-dppm complexes.

2. It is well known that coordinatively unsaturated palladium complexes (such as palladium clusters in low oxidation states) have the ability to catalyze a variety of reactions since they mimic those reactions that take place on metal (palladium) surfaces. Therefore, it is hoped that this method of reducing palladium salts in the presence of dppm and CO may lead to new synthetic routes to palladium cluster complexes. Dppm has been known to stabilize clusters against fragmentation and, thus, may serve as a useful ligand in these reactions.

Although this method has been found to be useful in synthesizing heterobimetallic systems, this will not be investigated. However, since a wide variety of heterobinuclear complexes containing palladium are known, this method may serve as a viable route to producing such compounds.

EXPERIMENTAL

Reagents and Solvents

The $NaBH_4$ used was obtained from the Aldrich Chemical Company, Inc. and was stored under dry conditions. Dppm and K_2PdCl_6 (also Aldrich) and $PdCl_2$ (from Alfa) were used without further purification. CP grade carbon monoxide and K grade nitrogen gases were purchased from Canadian Liquid Air, Ltd. $PdBr_2(COD)$ was prepared by the method cited in the literature,[1] as was $Pd_2(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$[2] and $Pd_2(\mu\text{-dppm})_2Cl_2$.[2] All solvents were reagent or ACS grade and were degassed prior to use with N_2.

Physical Measurements

All samples were protected from atmospheric oxygen. ^1H, ^{13}C and ^{31}P spectra, recorded at 200 MHz, 50.3 MHz and 81 MHz respectively, were obtained using a Bruker AC-E 200 NMR spectrometer, equipped with a variable temperature controller (BVT-1000S). For ^1H and ^{13}C spectra, Me_4Si (assigned a δ=0 value) was used as an

internal reference with the downfield shifts taken as positive values. For ^{31}P measurements, external 85% H_3PO_4 was the reference. Deuterated solvents provided the lock signal or in the cases where non-deuterated solvents were used, a co-axial D_2O insert provided the lock.

Infrared spectra (Nujol mulls) were recorded using a Beckman IR-4250 or a Bruker IFS 66 (for FTIR) spectrophotometer.

Elemental analyses (C, H and N) were obtained in our laboratories using a Control Equipment Corporation model 240XA analyzer with V_2O_5 as a combustion aid. Commercial analyses for Pd, Cl and P were performed at Galbraith Laboratories, Inc.

To check for the presence of solvent, either coordinated or trapped in the molecular lattice, a combination of ^1H NMR and mass spectrometry (acquired using a Hitachi-Perkin Elmer RMU-7 spectrometer) was used.

Scanning Electron Microscope Energy Dispersive Spectrometer data were obtained using an Hitachi model 570 SEM equipped with a Tracor Northern 5502 Energy Dispersive X-ray spectrometer.

To establish the presence of sodium halide in samples, X-ray fluorescence spectra were measured on a Philips PN 1352 X-ray system.

X-ray powder diffraction data were collected using a Philips P.W. 1050 diffractometer equipped with a P.W. 1010 generator.

The X-ray crystal structure of **3** was solved at the University of Minnesota-Duluth by Dr. V. Magnuson using data acquired at the University of Minnesota at Minneapolis. Dr. Magnuson is currently solving the crystal structure of **4a** (again, using data acquired at the University of Minnesota, Minneapolis) as of the time of writing this thesis. A data set has been collected.

Melting points were recorded using a Gallenkamp melting point apparatus and are uncorrected.

Molecular weight determinations were done using a Wescor 5500 Vapor Pressure osmometer.

Syntheses of Compounds

The reactions were carried out in a fumehood under N_2 or CO atmospheres. In a typical synthesis, a mixture of K_2PdCl_6 and dppm dissolved in EtOH and benzene or toluene respectively was contained within a 100 mL three-necked flask. Carbon monoxide was passed at a rate of approximately 30 bubbles per minute for 15 minutes. The reducing agent, $NaBH_4$, dissolved or suspended in EtOH, was added in various amounts and over

varying times to the reaction mixture. The work-up of these solutions or suspensions was carried out in a glovebox under nitrogen. The fact that the reactivity of $NaBH_4$ changes over a period of time caused severe problems in some of the syntheses (in terms of reproducibilty). Therefore, the amount of $NaBH_4$ had to be adjusted accordingly. The experiments described below were carried out many times and the quoted amounts of $NaBH_4$ represent typical values.

1. Synthesis of $Pd_2(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$, 1.

Through an orange solution of K_2PdCl_6 (0.42g, 1.1 mmol) and dppm (0.46g, 1.2 mmol) in 1:1 toluene and ethanol (30.0 mL), CO was passed at a rate of 20 bubbles per minute. $NaBH_4$ (0.08g, 2.1 mmol) in ethanol (15.0 mL) was added dropwise over 3 minutes to the stirred solution. The orange reaction mixture became a deep, dark green. CO was passed through the solution for another 20 minutes and the orange solid which precipitated, was filtered off, washed with hexane (20.0 mL) and dried under vacuum. Spectral data: $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 18.9 (s), which agrees with the reported[3] shift, $^{31}P\{^1H\}$ NMR (CH_2Cl_2), δ 19.1 (s); IR, ν_{CO} 1705 (m) cm^{-1}, again, in agreement with the reported[4] stretch, ν_{CO} 1704 cm^{-1}. Anal. calc. for **1**

($C_{51}H_{44}O_1Cl_2P_4Pd_2$): C, 56.7; H, 4.61. Found: C, 55.5; H, 4.19.

2. Synthesis of $Pd_2(\mu\text{-dppm})_3$, 2.

Through a stirred solution containing K_2PdCl_6 (0.42g, 1.1 mmol) and dppm (0.46g, 1.2 mmol) in toluene (15.0 mL) and ethanol (15.0 mL), carbon monoxide was passed over a period of 15 minutes. $NaBH_4$ (0.16g, 4.1 mmol) in ethanol (15.0 mL), degassed with N_2, was added to the reaction mixture in one portion. The result was a dark green solution which was filtered and left in the glovebox for 24 hours during which orange, needle-like crystals formed. They were filtered off, washed with hexane (20.0 mL) and dried under vacuum for 30 minutes. Spectral data: $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 14.8 (s). This shift agrees with the reported chemical shift for this compound.[4]

3. Synthesis of $Pd_6(\mu\text{-dppm})_3(\mu\text{-CO})_6$, 3.

3.1 This particular method of synthesizing **3** involves a direct reduction of Pd(IV) by $NaBH_4$. CO was bubbled through a solution of K_2PdCl_6 (0.42g, 1.1 mmol) and dppm (0.46g, 1.2 mmol) in 1:1 toluene and ethanol (30.0 mL) for 15 minutes until all of the suspended

solid was dissolved. The solution was continuously stirred and $NaBH_4$ (0.62g, 16.4 mmol) was added dropwise over 2 minutes. The reaction mixture was filtered and the filtrate was left for about 24 hours during which small, black crystals appeared. These were filtered off, washed with hexane (20.0 mL) and dried under vacuum for 10 minutes. Spectral data: $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 11.0 (s); ^1H NMR, δ 2.91 (m, br, P-CH_2-P); IR, ν_{CO} 1876 (s,sh), 1854 (m), 1841 (s,sh), 1826 (m) and 1818 (m) cm^{-1}. Anal. calc. for **3** ($C_{81}H_{66}O_6P_6Pd_6$): C, 49.7; H, 3.40. Found: C, 49.3; H, 3.66. The best yield obtained for **3** was 78.3%. The melting point of **3** was found to be 185° C.

3.2 Another route to synthesizing **3** is to react the unknown compound **5a**, which will be discussed later, with CO. The unknown **5a** (0.13g) was dissolved in CH_2Cl_2 (20.0 mL) giving a reddish brown solution. CO was bubbled slowly through the solution (15 bubbles per minute) until the solution was evaporated to dryness. The brown solid obtained was dissolved in CH_2Cl_2 (10.0 mL) and the solution was filtered. Hexane (20.0 mL) was carefully layered on the top of the filtrate and the entire mixture was then set aside. After 48 hours, black crystals (0.05g) were obtained, which were washed with hexane (30.0 mL) and dried under vacuum for 10

minutes. From this crop, a suitable crystal was chosen for an X-ray structure determination.

3.3 A third method of synthesizing **3** involves the reaction of the unknown **5a** with $NaBH_4$. Compound **5a** (0.13g) was dissolved in CH_2Cl_2 (10.0 mL) giving a reddish-brown solution. $NaBH_4$ (0.08g, 0.21 mmol) in ethanol (3.00 mL) was added dropwise to the solution over a period of one minute; the resulting solution was a greenish-brown. The reaction mixture was filtered and hexane (20.0 mL) was layered over the top of the filtrate. Within 48 hours, small, black crystals (0.03g) appeared. They were filtered off, washed with hexane (30.0 mL) and dried under vacuum for 10 minutes.

4. Synthesis and reactions involving compounds 4a and 4b tentatively formulated as $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})X_3]X$ or $Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})(\mu_3\text{-X})X_3$ (X=Cl for 4a; X=Br for 4b).

Syntheses of 4a.

Two methods were explored in synthesizing **4a**:

4.1 K_2PdCl_6 (0.42g, 1.1 mmol) and dppm (0.46g, 1.2 mmol) were dissolved in a 1:1 toluene-ethanol mixture

(30.0 mL). CO was passed through the stirred orange solution for 15 minutes and then $NaBH_4$ (0.10g, 2.6 mmol) in ethanol (15.0 mL) was added dropwise over 2 minutes. The reaction mixture was then filtered and either hexane or diethyl ether (300 to 500 mL) was added to the brown filtrate; the entire mixture was then set aside. Within 24 hours a brown solid settled on the bottom of the flask, along with small brown crystals on the inner surface of the flask. After filtration, both the solid and the crop of crystals were dissolved in acetone (15.0 mL) to which 50.0 mL of diethyl ether were added. Alternatively, the brown solid and crystals may also be recrystallized from CH_2Cl_2 and hexane or acetone and hexane (15.0 mL and 50.0 mL, respectively, in either case). The precipitate obtained from the recrystallization was filtered off and and dried under high vacuum pumping at 10^{-6} Torr for 2 hours. Spectral data: $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ -9.7; ^1H NMR (CD_2Cl_2), AB doublet of doublets pattern, δ 4.73 (d), 4.36 (d), J_{HH} 12.2 Hz [P-C(H^a)(H^b)-P]; ^{13}C NMR (CD_2Cl_2), multiplet (P-C-P), δ 51.3. IR: ν_{CO} 1817 (w, sh) cm^{-1}. The presence of ethanol (carried through from the original reaction solvent) in the crystal lattice was confirmed by ^1H NMR. Even after high vacuum pumping at 10^{-6} Torr for 2 hours, the samples remained contaminated with solvent, which varied from sample to sample, typically

between 2 to 6 moles per trimeric unit (see Results and Discussion section). Hence, analyses found for **4a** varied between 50 - 57% for carbon and 3.7 - 4.5% for hydrogen. One sample, recrystallized from 10.0 mL acetone and 50 mL of diethyl ether, and pumped under high vacuum (10^{-6} Torr) for 2 hours, gave the following analyses: Cl, 7.18; Pd, 16.40; P, 10.43 -- a ratio of 4:3:6. Another sample prepared in the exact same way gave: C, 55.06 (58.63, 57.44); H, 4.16 (4.42, 4.19), the various values being attributed to different degrees of solvation in different crystals. The ^{1}H NMR of this sample showed it to contain approximately 1 mole of diethyl ether per trimeric unit. On this basis, the proposed empirical formula is $Pd_3P_6C_{76}H_{66}OCl_4.1(CH_3CH_2)_2O$. Analysis calculated for this compound: Pd, 17.9; P, 10.39; Cl, 7.94; C, 55.47; H, 4.43. The best yield obtained for **4a** was 0.18g or 25.15%. SEM/EDS analysis confirmed the presence of halogen in **4a**. The melting point and molecular weight of **4a** were determined to be 206° C and 1142 $gmol^{-1}$, respectively. Given the presence of solvent in the compound, the measured molecular weight is undoubtedly low.

It should be noted here that a crystal structure of **4a** is pending. The method used to obtain the X-ray quality crystal differs slightly from the general procedure discussed above. Basically, after performing

the general reaction, 300 mL of hexane were added to the filtrate. Successive additions of hexane (30.0 mL), approximately every third day over a 3 week period, produced suitable crystals for X-ray analysis.

4.2 The second method of preparing compound **4a** is as follows. K_2PdCl_6 (0.42g, 1.1 mmol) and dppm (0.46g, 1.2 mmol) were refluxed in a 1:1 benzene and ethanol mixture (40.0 mL). CO was bubbled through the stirred solution at a rate of about 10 bubbles per minute. $NaBH_4$ (0.10g, 2.6 mmol) in ethanol (15.0 mL) was added to the solution over a period of 2 minutes while CO was continuously passed through the solution. The heating was stopped and CO was bubbled for another 30 minutes. The reaction mixture was filtered and hexane (500 mL) was added to the filtrate. After 24 hours, the flask contained small, brown crystals on the side mixed with a brown precipitate on the bottom. The crystals were scraped from the flask, along with a small amount of the solid, and filtered off leaving behind the brown solid stuck to the inside of the flask; the crystals were washed with hexane (20.0 mL). The remaining solid was dissolved in 10.0 mL of acetone to which 50.0 mL of diethyl ether were added. The precipitate was then filtered off and washed with hexane. Recrystallization from acetone (10.0 mL) and hexane (30.0 mL) was

performed twice, followed by recrystallization from a mixture of CH_2Cl_2 (10.0 mL) and $(CH_3CH_2)_2O$ (30.0 mL). The compound (**4a**) was dried under vacuum for 2 hours. The yield from this synthesis typically ranged from 0.08g to 0.1g (11.2 to 14.0%).

Synthesis of 4b

4.3 The bromide analog of **4a** was synthesized using the following method. Through a yellow, refluxing mixture of $PdBr_2(COD)$ (0.21g, 0.56 mmol) and dppm (0.23g, 0.6 mmol) in 1:1 benzene and ethanol (30.0 mL), CO was passed at an average rate of 20 bubbles per minute for about 15 minutes. $NaBH_4$ (0.04g, 1.01 mmol) in ethanol (8.0 mL) was added dropwise over 2 minutes, during which time the reaction mixture changed colour from yellow to brown. The rest of the procedure was exactly the same as described in synthesis 4.1. Spectral data: $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ -9.4; ^1H NMR (CD_2Cl_2), AB doublet of doublets pattern, δ 4.45 (d), 4.76 (d), J_{HH} 13.6 Hz [P-C(H^a)(H^b)-P]. IR: ν_{CO} 1818 (w, sh) cm^{-1}. Evidence of ethanol trapped in the crystal lattice came from the ^1H NMR of **4b**. Analyses found for **4b**: C, 51.9 to 54.85; H, 4.07 to 4.22. Scanning electron microscopic EDS data suggest an approximate Pd:P:Br ratio of 3:6:1, but SEM/EDS data

should be treated with caution unless an ideal crystal surface is used

4.4 Treatment of 4a with CO.

Through a brown solution containing compound **4a** (0.059g) in CH_2Cl_2 (10.0 mL), CO was bubbled for 1.5 hours. No visible change in colour was observed. The $^{31}P\{^1H\}$ NMR showed only a singlet with a shift corresponding to **4a**.

4.5. Treatment of 4a with CO and dppm.

To the resulting solution from reaction **5** (discussed later), dppm (0.03g) was added in toluene (5.0 mL) and CO was passed for a further 30 minutes. No visible change in colour was observed. The $^{31}P\{^1H\}$ NMR showed two singlets, one corresponding to **4a** and the other corresponding to free dppm (δ -22.0).

4.6. Treatment of 4a with N_2.

Compound **4a** (0.05g) was stirred in CH_2Cl_2 (20.0 mL) and N_2 was bubbled through the solution for one hour. No apparent change in colour was observed and the $^{31}P\{^1H\}$ NMR of the solution showed only a singlet

corresponding to **4a**.

4.7. Treatment of 4a with CO and $NaBH_4$.

To the reaction mixture described in procedure 2.8, a solution of $NaBH_4$ (0.16g, 4.1 mmol) in ethanol (15.0 mL) was added over a period of 30 minutes. There was no noticeable change in the colour of the reaction mixture. However, the $^{31}P\{^1H\}$ NMR of the reaction mixture showed a broad, unresolved multiplet centred at δ 13.6 (compound **5a**, discussed later).

4.8. Spiking experiment of 4a with 4b.

Compound **4a** was mixed with compound **4b** in CD_2Cl_2 (1.0 mL). The $^{31}P\{^1H\}$ NMR of the mixture showed two singlets, one at δ -9.3, the other at δ -9.6. Thus, at least some of the halogen in each of the complexes is covalently bonded.

5. Synthesis of the unknown compounds 5a and 5b (a=Cl, b=Br).

5.1 One method of preparing **5a** involved a straight reduction of K_2PdCl_6 by $NaBH_4$ in the presence of dppm and CO. CO was passed through an orange solution

containing K_2PdCl_6 (0.42g, 1.1 mmol) and dppm (0.46, 1.2 mmol) in a stirred 1:1 toluene-ethanol (30.0 mL) mixture for 15 minutes. After this time, no visual change in colour was observed. $NaBH_4$ (0.16g, 4.1 mmol) in ethanol (15.0 mL) through which N_2 was bubbled, was added dropwise to the reaction mixture over 2 minutes. The colour of the reaction mixture changed from orange to beige and finally, to brown. The solution was then filtered, leaving some unreacted $NaBH_4$ and some NaCl on the filter frit. The filtrate obtained was left overnight under N_2 at room temperature. The next day, small, deep reddish-brown crystals were filtered off. The crystals were washed with ethanol (10.0 mL), followed by 3 successive washings with de-ionized water (10.0 mL), ethanol (10.0 mL) and finally, hexane (20.0 mL). The crystals were then dried under vacuum for about 10 minutes. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): a broad, unresolved multiplet between δ 5 and δ 20, centred at δ 13.6. $^{31}P\{^1H\}$ NMR (CD_2Cl_2; low temperature (233 K): three separate regions at around δ 25, 15 and 0 (see Spectrum 10). Solid state ^{31}P CP MAS NMR shows a similar pattern to that of the low temperature (233 K) $^{31}P\{^1H\}$ NMR except that the shifts are somewhat different (see Spectrum 11). ^1H NMR (CD_2Cl_2): δ 3.3 (m, br), 3.9 (m, br). At low temperatures these multiplets did not resolve. ^{13}C NMR was attempted.

However, due to the instability and low solubility of the compound, the results were inconclusive. IR: ν_{CO} 1854 (s, sh); 1839 (s, sh); 1760 (m); 1747 (m); 1715 (shoulder). Mass spectrometry provided evidence pertaining to solvents present in the crystal lattice: peaks corresponding to toluene were detected at m/e 92(100) and 77(20). The IR spectrum showed the probable presence of ethanol since a broad OH shoulder was observed at around 3500 cm^{-1}. This was confirmed by the ^1H NMR of **5a** which showed the presence of ethanol. Attempts at recrystallizing **5a** (from CH_2Cl_2/hexane or CH_2Cl_2/diethyl ether) to produce unsolvated X-ray quality crystals were unsuccessful, again due to its low solubility and instability in solution. Analyses found for **5a**: C, 55.82; H, 4.06; Pd, 22.18; P, 10.42. Scanning electron microscopic energy dispersive data indicated the presence of halogen in **5a**. Based on this evidence and the analysis of **5a**, the tentative empirical formula of **5a** was determined to be $Pd_5(dppm)_4(CO)_6Cl_2$. Analysis calculated for **5a**: C, 55.18; H, 3.81; Pd, 23.0; P, 10.75; O, 7.26. The melting point of **5a** was determined to be 187°C. The best yield recorded was 0.26g. Finally, it is important to note that **5a** is very unstable, but its stability is increased slightly when the reaction is carried out in an ethanol-toluene mixture rather than

ethanol-benzene.

5.2 Attempts at synthesizing **5a** from **4a** were performed. Compound **4a** (0.11g) was dissolved in THF (10.0 mL) and CO was passed through the stirred solution for 15 minutes. $NaBH_4$ (0.02g, 0.47 mmol) in ethanol (5.0 mL) was added dropwise to the brown mixture over a period of 2 minutes. During this time no change in colour was observed but the $^{31}P\{^1H\}$ NMR showed that the sole product of this reaction is **5a**.

Synthesis of 5b.

5.3 Successful attempts at synthesizing the bromide analog of **5a** from $PdBr_2(COD)$ were also made. $PdBr_2(COD)$ (0.21g, 0.56 mmol) and dppm (0.23g, 0.6 mmol) were dissolved in a 1:1 ethanol-toluene mixture (30.0 mL) which was stirred while CO gas was passed through the mixture for 15 minutes. $NaBH_4$ (0.04g, 1.01 mmol) in ethanol (8.0 mL) was added dropwise over a period of 2 minutes. A change in colour was observed from yellow to brown. The reaction was filtered and the filtrate left overnight in the glovebox. Twenty-four hours later, small black crystals appeared. They were filtered off, washed with hexane (30.0 mL) and dried under vacuum for about 5 minutes. Typical yields in

these reactions were very low.

6. Attempted reaction of compound 4a with 3.

Since **4a** and **3** are the sole decomposition products of **5a**, the reverse of this decomposition was attempted. Thus, compound **4a** (0.08g) was dissolved in CH_2Cl_2 (10.0 mL). Compound **3** (0.08g, 0.04 mmol) was dissolved in CH_2Cl_2 (10.0 mL). These two solutions were mixed together and left under N_2 for 1 month. The $^{31}P\{^1H\}$ NMR of this solution was checked periodically and generally it was found that the singlets corresponding to **4a** and **3** disappeared with a concurrent appearance of a singlet at δ 24.1, compound **6**, to be discussed next.

7. Analysis of compound 6.

Compound **6**, a by-product that frequently appeared in these reactions was isolated and analyzed. The $^{31}P\{^1H\}$ NMR (CH_2Cl_2) showed a singlet at δ 24.1; the ^1H NMR spectrum was uninformative. The molecular weight was found to be 442 $gmol^{-1}$. Scanning electron microscopy energy dispersive data showed that **6** contained virtually no palladium. The IR of **6** showed a strong band at 1190 cm^{-1}. Analysis found: C, 66.4; H, 5.20. Based on this evidence (and reaction 8,

discussed below), compound **6** was determined to be dppm dioxide.

8. Synthesis of the dioxide of dppm, 7.

To a sample of dppm (0.05g, 0.13 mmol) dissolved in hot ethanol (10.0 mL), 20 drops of 32% H_2O_2 were added. A white solid was recovered and analyzed. The $^{31}P\{^1H\}$ NMR of the solid in $CDCl_3$ showed a singlet at δ 23.0, which agrees with the value cited in the literature.[3]

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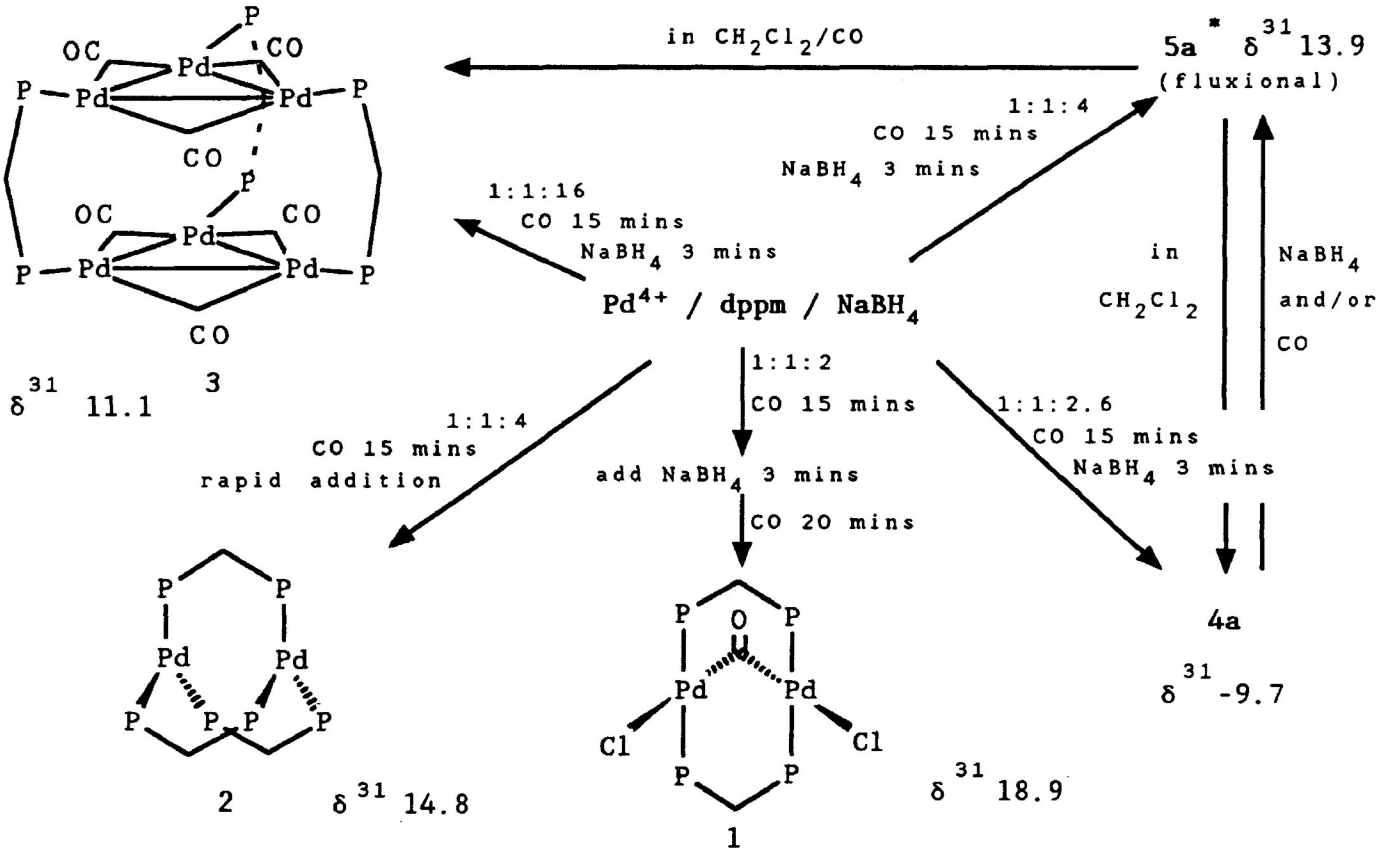
RESULTS AND DISCUSSION

Introduction

Phosphine substituted metal carbonyl complexes possess unique structural and chemical properties.[1] As mentioned in chapter 1, the general route for preparing such compounds involves reacting metal carbonyls with the appropriate ligand.[2] Other methods include electrochemical techniques,[3] or by appropriate input of thermal or photochemical energy into a suitable reaction mixture.[4,5,6] The fact that $Pd(CO)_4$ is unknown and therefore not available as a precursor for the synthesis of palladium-carbonyl-phosphine complexes provided a perfect opportunity for applying the simple one-step synthesis of metal-carbonyl-phosphine complexes devised by the Holah and Hughes group.[7]

The reductions of palladium ions with $NaBH_4$ in the presence of dppm and CO led to the formation of any one or more of five different complexes, depending on the conditions, and the inter-relationships of these reactions and products are represented in Schemes 23 and 24. The five complexes include the known $Pd_2(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$,[8] **1**, and $Pd_2(\mu\text{-dppm})_3$,[9,10] **2**,

along with three new palladium complexes containing dppm and CO, which will be discussed later in more detail. Briefly, one of these new complexes is the zero oxidation state $Pd_6(\mu\text{-dppm})_3(\mu\text{-CO})_6$, complex **3**,



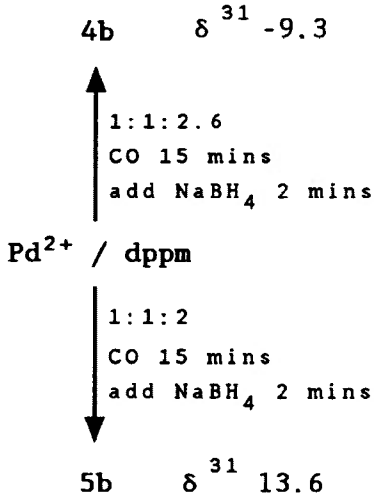
* generally, the reaction mixture is contaminated with other products, including **3**, **4a** and **8**.

Scheme 23.

Synthesis of compounds 1, 2, 3, 4a and 5a using K_2PdCl_6.

which has been fully characterized spectroscopically and crystallographically. Complex **3** is the end product of

a reduction reaction. The complexes **4** and **5** have not yet been fully identified, but much structural information has been obtained. A crystal of **4** suitable for X-ray analysis has recently been obtained. Dppm dioxide, **6**, appeared in all of the reactions as a minor product.



Scheme 24.

Synthesis of 4b and 5b using $PdBr_2$(COD).

All of these complexes will be discussed according to the sequence given in Chapter 2 (the Experimental Section).

1. Synthesis of $Pd_2(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$, 1.

Compound **1** was previously prepared by passing CO

through a CH_2Cl_2 solution containing $Pd_2(\mu\text{-dppm})_2Cl_2$.[8] This method is somewhat tedious since it involves three reaction steps: the synthesis of $[Pd(CO)Cl]_n$; synthesis of $Pd_2(\mu\text{-dppm})_2Cl_2$ from $[Pd(CO)Cl]_n$; and, finally, addition of CO to $Pd_2(\mu\text{-dppm})_2Cl_2$. The simpler one-step route to synthesizing **1** described here gives very good yields (up to 90%). The $^{31}P\{^1H\}$ NMR of **1** was recorded in $CDCl_3$ and its phosphorus resonance occurred at δ 18.9 when referenced to $H_3PO_4/CDCl_3$. This shift agrees with that reported for an authentic sample by Schreiner et al.[11] The infrared stretching frequency occurs at 1705 cm^{-1} which also agrees with the value reported by Balch and Benner.[8] The structure of **1** is thought to be an A-frame type structure[8,12] based on its NMR shift and IR data. This is supported by the fact that dppm is a very flexible ligand and that insertion of CO into a metal-metal bond converts side by side dimers into A-frame complexes.

Further identification of **1** was carried out in two ways. First, since CO addition to give **1** is readily reversed[8,12] to produce $Pd_2(\mu\text{-dppm})_2Cl_2$, a solution of **1** in $CDCl_3$ was monitored over a period of one week. The $^{31}P\{^1H\}$ NMR resonance at δ 18.9 decreased in area while a new singlet at δ -2.5 appeared; this new singlet was assigned to the known $Pd_2(\mu\text{-dppm})_2Cl_2$, **9**, as its $^{31}P\{^1H\}$ NMR shift agrees with the shift reported by Hunt and

Balch.[13] However, to be absolutely certain about the structure of **1**, another experiment was carried out. First, the compound $Pd_2(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$ was prepared by the method described by Benner and Balch.[8] A spiking experiment was carried out and the respective $^{31}P\{^1H\}$ NMR shifts of **1** and $Pd_2(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2$ did, in fact, coincide in $CDCl_3$ solution.

Compound **1** is stable in the solid state under an atmosphere of N_2, but decomposes in solution to yield **9**, as proven by $^{31}P\{^1H\}$ NMR spectroscopy.

2. Synthesis of $Pd_2(\mu\text{-dppm})_3$, 2.

Complex **2** was previously made by reacting $(PPh_3)_2PdCl_2$ with dppm in hot ethanol and then subsequently reducing the mixture with anhydrous hydrazine, as described by Stern and Maples.[10] The elucidation of this structure was based on a complete microanalysis. Kirss and Eisenberg[9] also obtained compound **2** by reacting an unidentified hydride $Pd_2H_x(dppm)_2$ with dppm in benzene solution. The identity of this compound, given below, was finally established by a single crystal X-ray structure determination. The compound consists of two trigonally coordinated Pd(0) atoms bridged by three dppm ligands. The Pd-Pd distance of 2.959 Å indicated the absence of a

metal-metal bond when compared to the Pd-Pd distances found in $Pd_2(\mu\text{-dppm})_2Br_2$ which is 2.699 Å.[13]

The Pd salt/dppm/$NaBH_4$/CO route to this compound described herein involves a virtually instantaneous reduction of Pd(IV) ions by BH_4^- (added in on portion) in the presence of CO and dppm. The resulting product (formed in roughly 60% yield) is a highly crystalline orange compound, for which the $^{31}P\{^1H\}$ NMR spectrum was recorded (in $CDCl_3$). The recorded shift at δ 14.1 agrees well with the value of δ 14.6 reported by Hunt and Balch.[13]

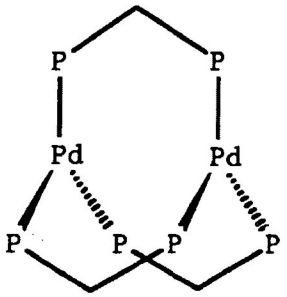


Figure 8. $Pd_2(\mu\text{-dppm})_3$, 2.

In the early stages of the identification of this complex, the infrared spectrum showed no stretching frequencies in the carbonyl region of the spectrum. This was a little surprising given the ease with which Pd-dppm-CO complexes are formed under only slightly different conditions (see Scheme 23). However, it appears that the course of the reaction depends greatly

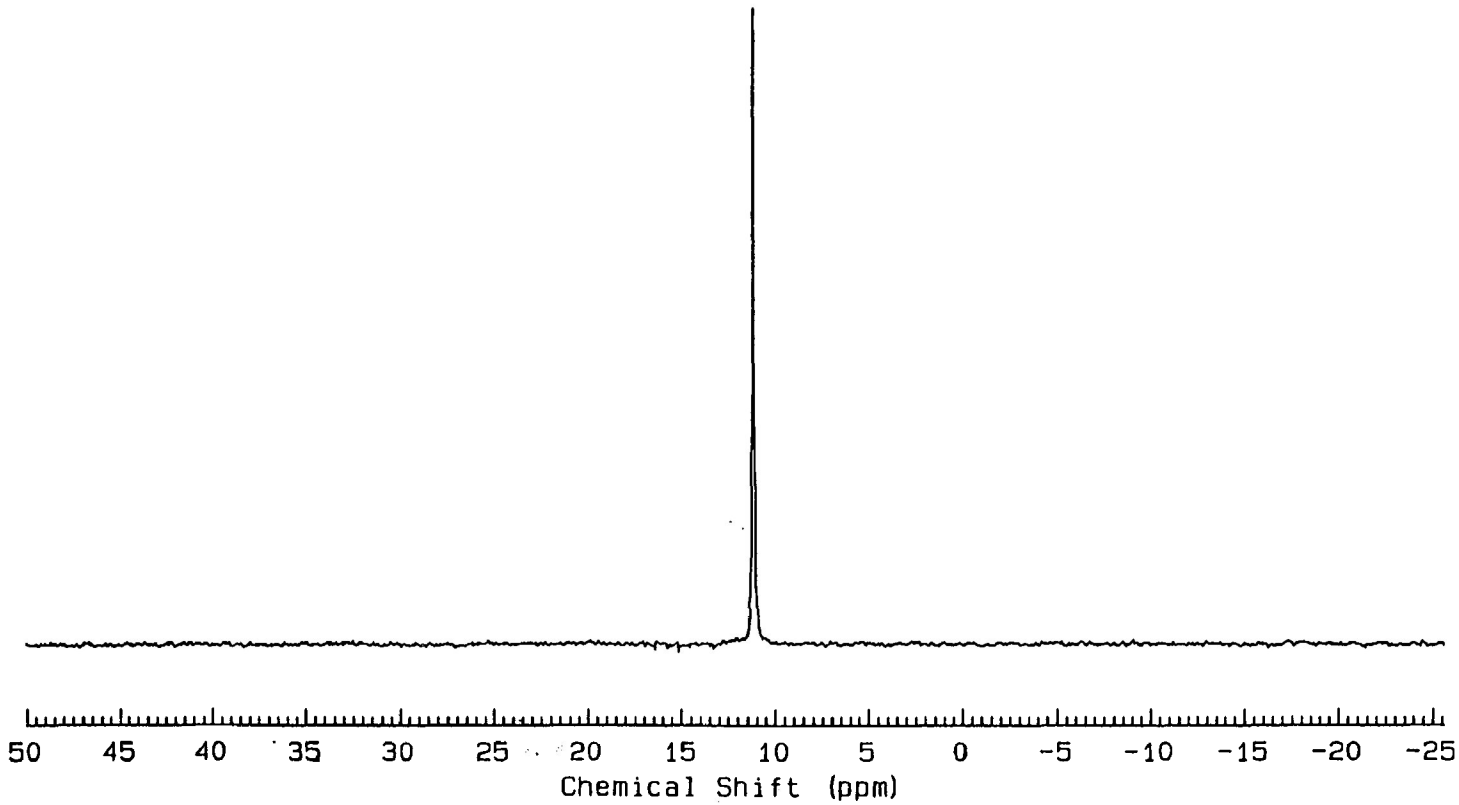
upon the time of addition of BH_4^- and the reactant ratios. In this case where reduction is rapid, it is possible that the phosphine is a better σ donor than CO and thus, would bind to the metal before CO.

3. Synthesis of $Pd_6(\mu\text{-dppm})_3(\mu_3\text{-CO})_6$, 3.

The novel $Pd_6(\mu\text{-dppm})_3(\mu_3\text{-CO})_6$ complex, **3**, may be prepared by two different methods (see Experimental Section). Briefly, when CO is passed through a CH_2Cl_2 solution of the as yet unidentified compound **5** (discussed later), two products are obtained: a black crystalline compound, **3**, as well as compound **4a**, which will be discussed shortly. The other method is the direct reduction of Pd(IV) by $NaBH_4$ (in the presence of dppm and CO) in the ratio 1:16 -- under these conditions, it is the only isolable product.

The NMR spectra of **3** are quite simple. The $^{31}P\{^1H\}$ NMR (see Spectrum 1) shows a sharp singlet at δ 11.0, indicating that **3** is a symmetrical species (with respect to the phosphorus atoms) which most likely contains bridging dppm. This singlet remains unresolved and unbroadened at low temperatures (233 K) showing that **3** is non-fluxional. The proton NMR of **3** shows a broad unresolved signal at δ 3.55 which corresponds to the protons of the coordinated dppm

Spectrum 1. $^{31}P\{^{1}H\}$ NMR of $Pd_6(\mu\text{-dppm})_3(\mu\text{-CO})_6$, 3, in CH_2Cl_2.



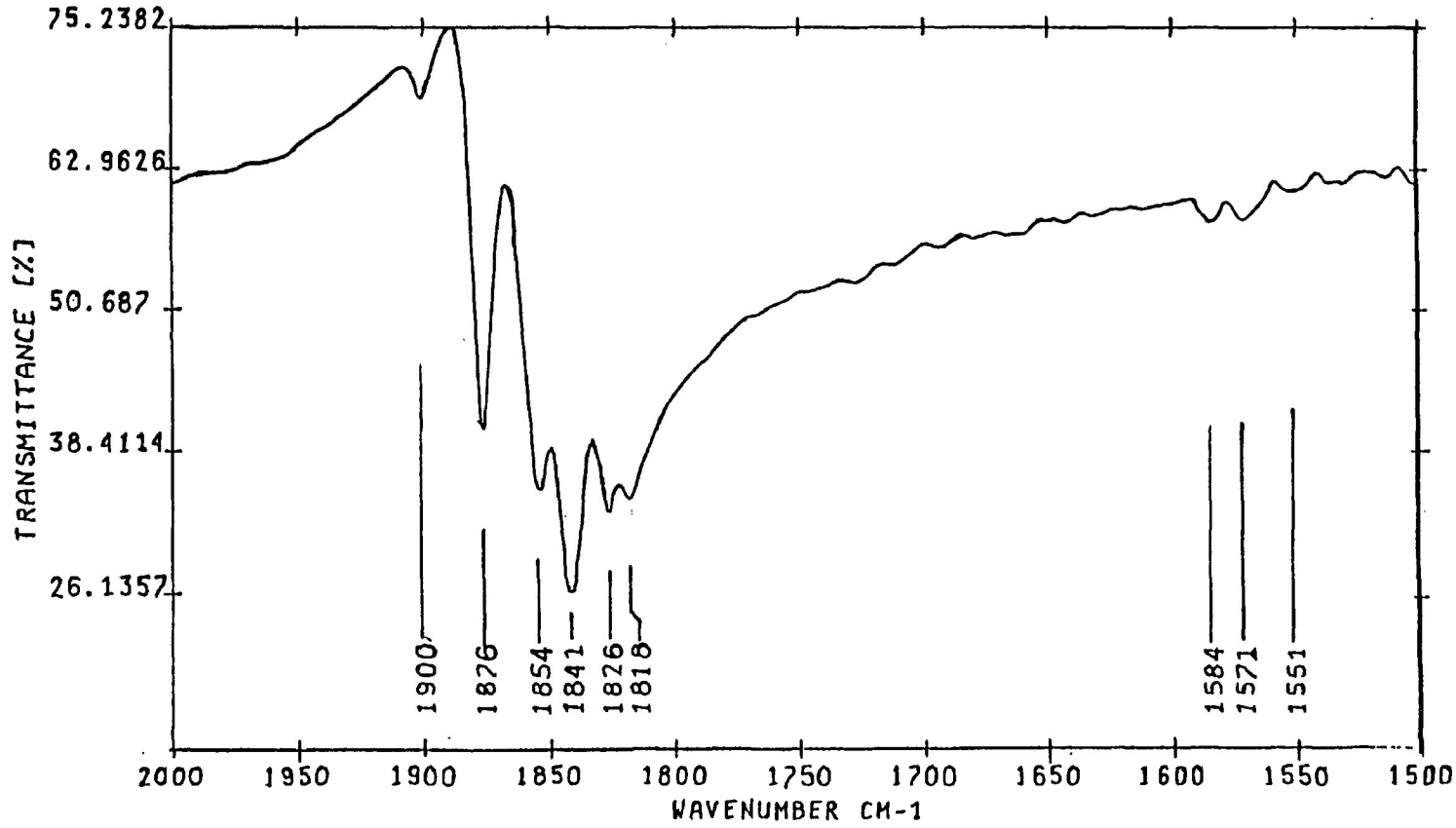
ligands in **3**.

The IR spectrum of **3**, in contrast, is quite complex (see Spectrum 2). Several CO absorption bands were detected at 1899 (weak and sharp), 1877, 1854, 1843, 1827, 1818 (all strong and sharp) cm^{-1}. It was originally surmised that these absorptions corresponded to terminally bound CO since these generally occur at higher wavenumbers.[14] However, in what will be discussed in more detail later, the X-ray crystal structure of **3** showed that the CO ligands, in fact, each edge-bridge two palladium centres in a Pd_3 triangle.

The combustion analysis obtained for **3** was in excellent agreement with the empirical formulation $Pd_2(CO)_2(dppm)$.

The hexameric nature of **3** was revealed by an X-ray crystal structure determination. The structure shows **3** to be a palladium hexamer consisting of two palladium trimers face-to-face to one another, linked apex to apex by dppm ligands. The faces of the planes of the two palladium trimers are parallel (slightly twisted) with the overall molecular geometry approximating D_{3h} symmetry, with a mirror plane lying between the two trimer units. The Pd-Pd distances [2.658(3) - 2.695(3) Å] are comparable to those found[18] in the complex $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ [2.576(1) - 2.610(2) Å], as well with 2.699 Å found in $Pd_2(\mu\text{-dppm})_2Br_2$.[15] The details of

Spectrum 2. IR of $Pd_6(\mu\text{-dppm})_3(\mu\text{-CO})_6$, 3.



the structure analysis are presented in Table I, and refined bond angles and distances are presented in Table II. Table III shows distances (Å) to the least squares plane. The ORTEP drawing of **3** is presented in Figure 9; Figure 10 presents the side view of **3**; and, finally, the view down the principle axis of rotation is presented in Figure 11.

Knowing the crystal structure of **3**, the complexity of its IR spectrum may easily be explained in terms of the CO ligands being in slightly different environments, as well as the symmetrical and asymmetrical stretches of the six CO ligands.

While compound **3** has long term stability in the solid state for about 3 months, some decomposition occurs over time. Thus, examination of the $^{31}P\{^{1}H\}$ NMR spectrum after about 3 months shows the presence of dppm dioxide, **6**, and two other unidentified decomposition products with signals at δ 14 and 15 (singlets). Presumably the dppm dioxide arises from slow oxygen contamination.

Finally, **3** was found to be soluble in non-polar, aromatic solvents, as well as in CH_2Cl_2. It is slightly soluble in ethanol and insoluble in CH_3CN.

Table I: Summary of X-ray Structure Data

formula:	$Pd_6P_6O_6C_{81}$
crystal system:	orthorhombic
space group:	P $na2_1$
cell parameters:	
a	39.836(13) Å
b	15.587(4) Å
c	12.165(4) Å
Z:	4
radiation:	MoK_α (λ = 0.7093 Å)
observed reflections:	5649
least squares number of variables:	457
R_f	7.7
R_w	10.3
disordered solvent not included:	CH_2Cl_2

Table II: Bond Distances and Angles for $Pd_6(\mu_2\text{-dppm})_3(\mu_2\text{-CO})_6$.

	Angstroms (Å)		Angstroms (Å)
Pd1-Pd2	2.678(2)	Pd4-Pd5	2.722(3)
Pd2-Pd3	2.695(3)	Pd5-Pd6	2.697(3)
Pd1-Pd3	2.658(3)	Pd4-Pd6	2.724(3)
Pd1-P1	2.304(6)	Pd4-P4	2.357(6)
Pd2-P2	2.304(6)	Pd5-P5	2.299(6)
Pd3-P3	2.306(6)	Pd6-P6	2.317(7)
Pd1-C12	1.968(23)	Pd4-C45	2.117(22)
Pd1-C13	2.003(23)	Pd4-C46	2.067(24)
Pd2-C12	2.132(23)	Pd5-C45	2.028(21)
Pd2-C23	1.995(21)	Pd5-C56	2.020(30)
Pd3-C13	2.006(22)	Pd6-C46	2.072(23)
Pd3-C23	2.052(21)	Pd6-C56	2.070(30)
C12-O12	1.20(3)	C45-O45	1.13(3)
C13-O13	1.24(3)	C46-O46	1.19(3)
C23-O23	1.19(3)	C56-O56	1.21(3)
P1-Cp14	1.889(23)	P4-Cp14	1.87(3)
P2-Cp25	1.85(3)	P5-Cp25	1.801(24)
P3-Cp36	1.82(3)	P6-Cp36	1.889(25)
	Degrees		**Degrees**
Pd2-Pd1-Pd3	60.67(7)	Pd6-Pd5-P5	145.76(17)
Pd2-Pd1-P1	149.94(18)	Pd6-Pd5-C45	108.2(6)
Pd2-Pd1-C12	51.9(7)	Pd6-Pd5-C56	49.7(7)
Pd2-Pd1-C13	109.1(6)	P5-Pd5-C45	103.5(6)
Pd3-Pd1-P1	144.21(18)	P5-Pd5-C56	96.1(7)
Pd3-Pd1-C12	112.3(7)	C45-Pd5-C56	149.1(9)
Pd3-Pd1-C13	48.5(6)	Pd4-Pd6-Pd5	60.27(7)
P1-Pd1-C12	99.5(7)	Pd4-Pd6-P6	150.22(18)
P1-Pd1-C13	98.5(7)	Pd4-Pd6-C46	48.8(7)
C12-Pd1-C13	160.7(9)	Pd4-Pd6-C56	107.8(7)
Pd1-Pd2-Pd3	59.30(7)	Pd5-Pd6-P6	149.01(19)
Pd1-Pd2-P2	146.86(18)	Pd5-Pd6-C46	106.6(7)
Pd1-Pd2-C12	46.6(6)	Pd5-Pd6-C56	48.0(7)
Pd1-Pd2-C23	108.4(6)	P6-Pd6-C46	101.9(7)
Pd3-Pd2-P2	153.79(18)	P6-Pd6-C56	101.1(7)
Pd3-Pd2-C12	105.6(6)	C46-Pd6-C56	146.9(10)
Pd3-Pd2-C23	49.1(6)	Pd1-P1-Cp14	113.8(8)
P2-Pd2-C12	100.6(6)	Pd2-P2-Cp25	108.9(8)
P2-Pd2-C23	104.8(6)	Pd3-P3-Cp36	105.3(8)
C12-Pd2-C23	153.5(9)	Pd4-P4-Cp14	110.4(7)
Pd1-Pd3-Pd2	60.03(7)	Pd5-P5-Cp25	114.3(8)
Pd1-Pd3-P3	161.12(17)	Pd6-P6-Cp36	118.5(8)
Pd1-Pd3-C13	48.4(7)	Pd1-C12-Pd2	81.5(9)
Pd1-Pd3-C23	107.3(6)	Pd1-C12-O12	140.4(21)
Pd2-Pd3-P3	138.79(17)	Pd2-C12-O12	131.7(17)
Pd2-Pd3-C13	108.3(7)	Pd1-C13-Pd3	83.1(9)

Table II (continued)

	Degrees		Degrees
Pd2-Pd3-C23	47.4(6)	Pd1-C13-O13	138.1(18)
P3-Pd3-C13	112.7(7)	Pd3-C13-O13	138.5(19)
P3-Pd3-C23	91.6(6)	Pd2-C23-Pd3	83.5(8)
C13-Pd3-C23	155.7(9)	Pd2-C23-O23	140.1(18)
Pd5-Pd4-Pd6	59.38(7)	Pd3-C23-O23	136.1(18)
Pd5-Pd4-P4	147.24(17)	Pd4-C45-Pd5	82.0(8)
Pd5-Pd4-C45	47.6(6)	Pd4-C45-O45	134.7(17)
Pd5-Pd4-C46	105.9(6)	Pd5-C45-O45	140.2(18)
Pd6-Pd4-P4	147.78(18)	Pd4-C46-Pd6	82.3(9)
Pd6-Pd4-C45	104.6(6)	Pd4-C46-O46	136.6(19)
Pd6-Pd4-C46	48.9(6)	Pd6-C46-O46	138.8(20)

Table III: Distances (Å) to the Least-Squares Planes

(1) Plane #1:

(i) Equation of plane:

16.04(4)X + 1.712(19)Y + 11.055(6)Z = 2.658(7)

(ii) Distances (Å) to the plane from atoms IN the plane:

Pd1 - 0.000(3)	Pd2 - 0.000(3)	Pd3 - 0.000(4)

(iii) Distances (Å) to the plane from atoms OUT of the plane:

P1 - -0.543(7)	P2 - 0.042(8)	P3 - 0.050(8)
O12 - -0.725(22)	O13 - 0.119(19)	O23 - -0.102(21)
C12 - -0.23(3)	C13 - 0.102(23)	C23 - -0.083

(2) Plane #2:

(i) Equation of plane:

14.61(5)X + 1.153(20)Y + 11.281(6)Z = 5.202(8)

(ii) Distances (Å) to the plane from atoms IN the plane:

Pd4 - 0.000(3)	Pd5 - 0.000(3)	Pd6 - 0.0003

(iii) Distances (Å) to the plane from atoms OUT of the plane:

P4 - 0.564(8)	P5 - 0.154(8)	P6 - 0.156(8)
O45 - 1.142(18)	O46 - 1.110(22)	O56 - 0.629(21)
C45 - 0.541(23)	C46 - 0.557(24)	C56 - 0.25(3)

(3) Dihedral angle between Planes 1 and 2: 3.09(10)°

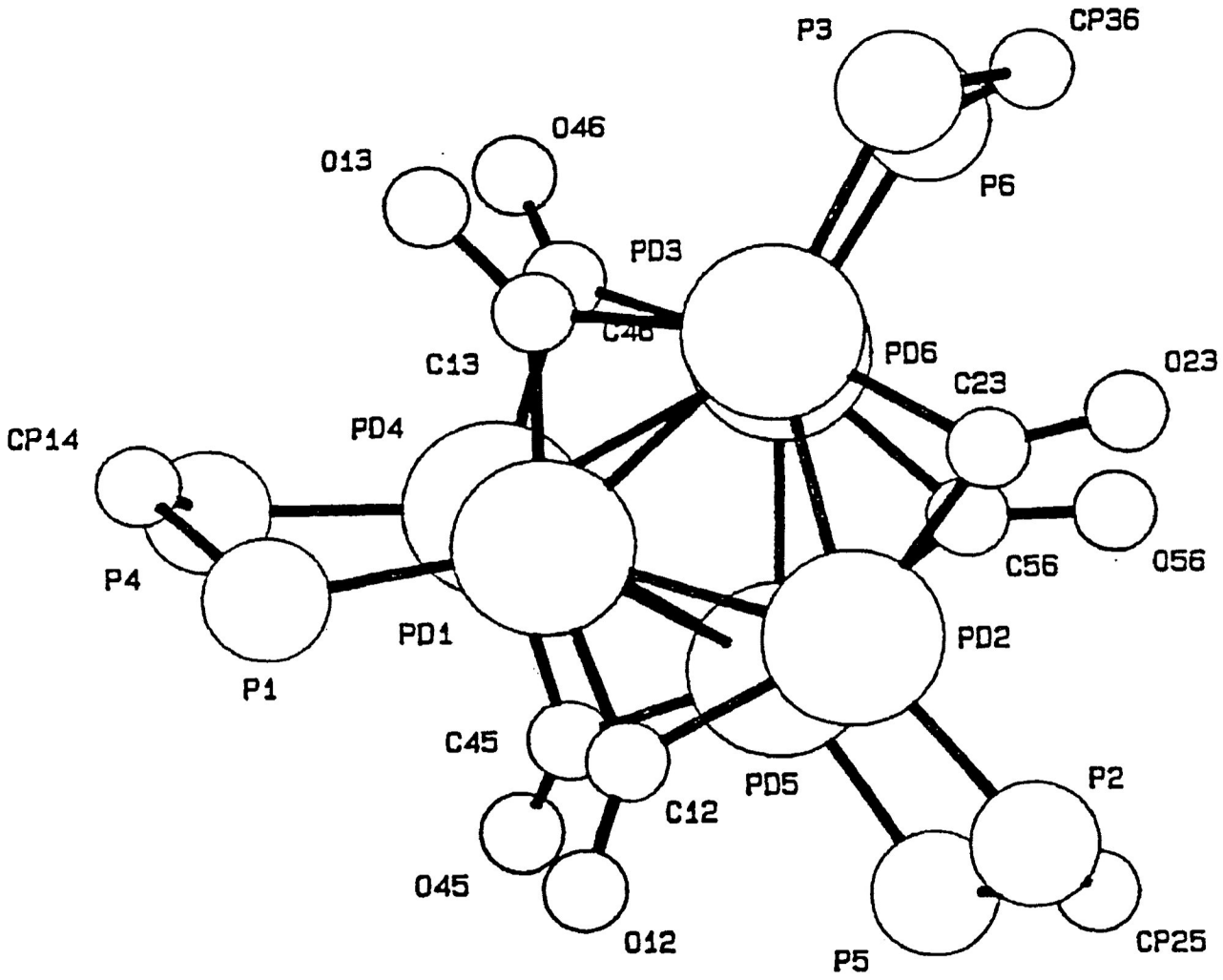


Figure 9. ORTEP drawing of $Pd_6(\mu\text{-dppm})_3(\mu\text{-CO})_6$, 3.

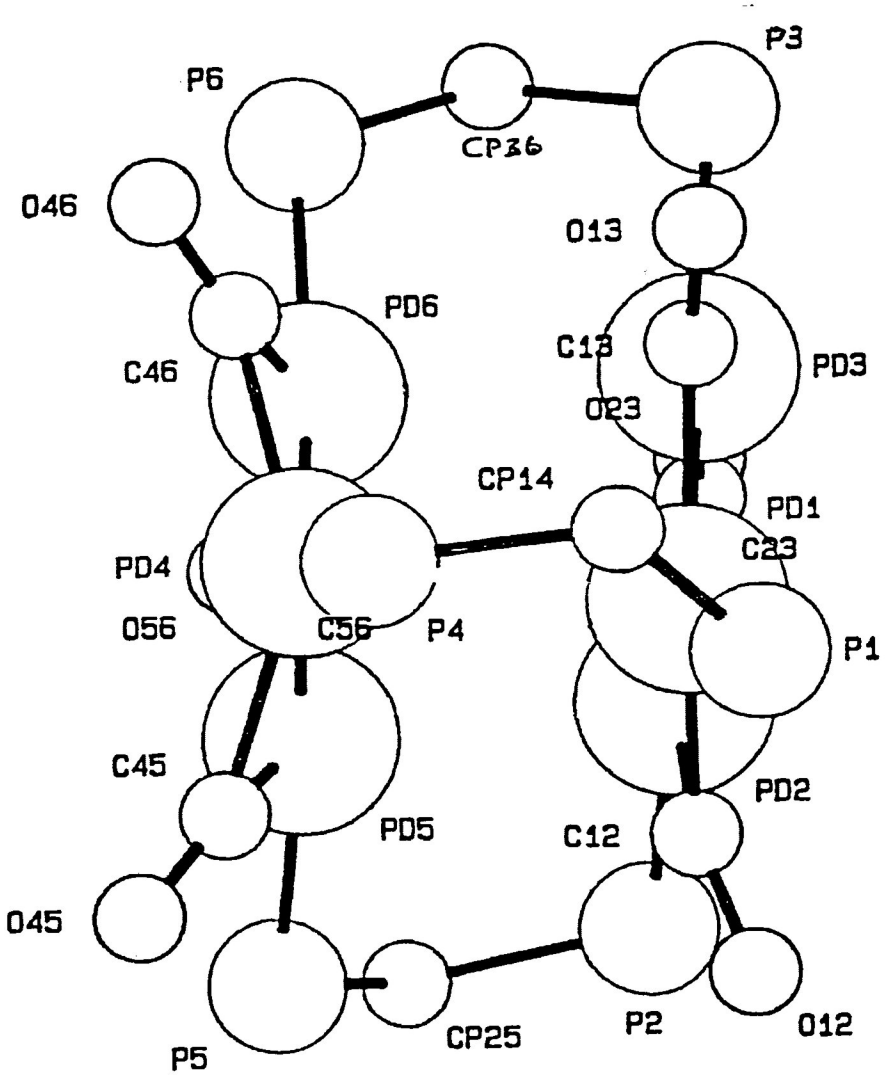


Figure 10. ORTEP drawing of $Pd_6(\mu\text{-dppm})_3(\mu\text{-CO})_6$, 3, from the side.

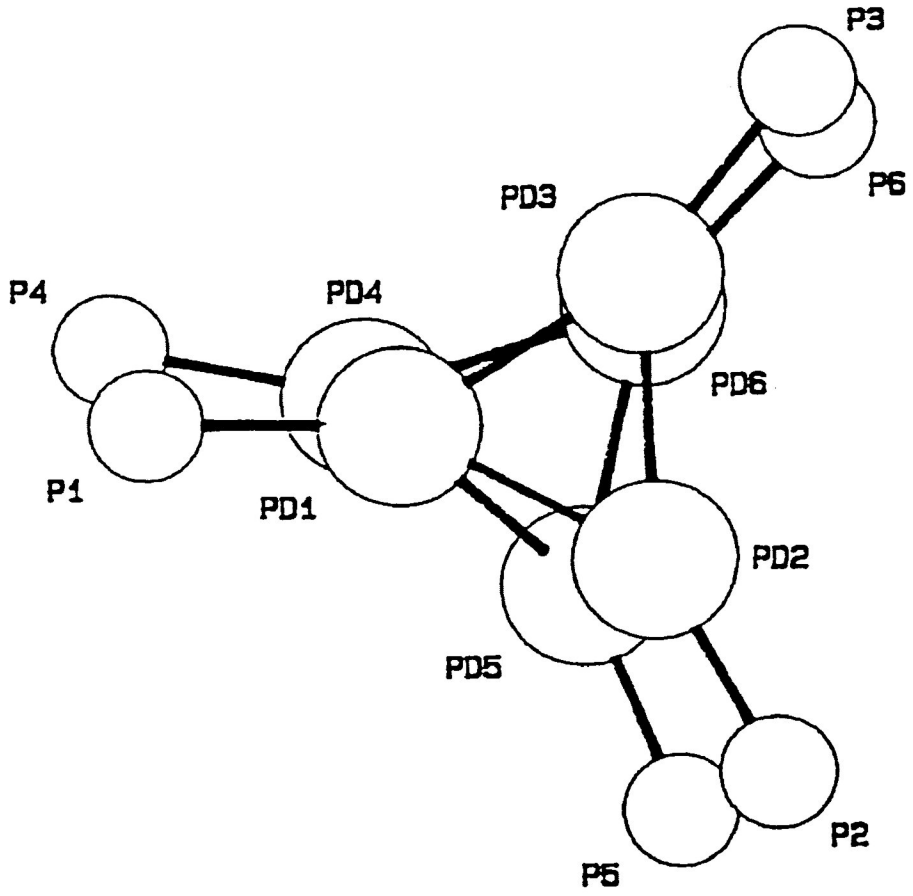


Figure 11. ORTEP drawing of $Pd_6(\mu\text{-dppm})_3(\mu\text{-CO})_6$, 3, down the principal axis of rotation.

4. Discussion of compounds 4a and 4b, tentatively identified as the ionic $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})X_3]X$, or $Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})(\mu_3\text{-X})X_3$ (X=Cl for 4a; X=Br for 4b).

These not yet fully characterized Pd-CO-dppm complexes can be prepared either by *in-situ* reductions of Pd(IV) (as the hexachloropalladate ion) with $NaBH_4$ under reflux (2 hours) in the presence of dppm and CO (for **4a**), or by similar reactions using $PdBr_2(COD)$ (for **4b**). The compound **4a** may also be prepared at room temperature by varying the amount of $NaBH_4$ (see Experimental Section). At room temperatures, the reactions lead in sequence to **4a**, **5a**, and then **3**.

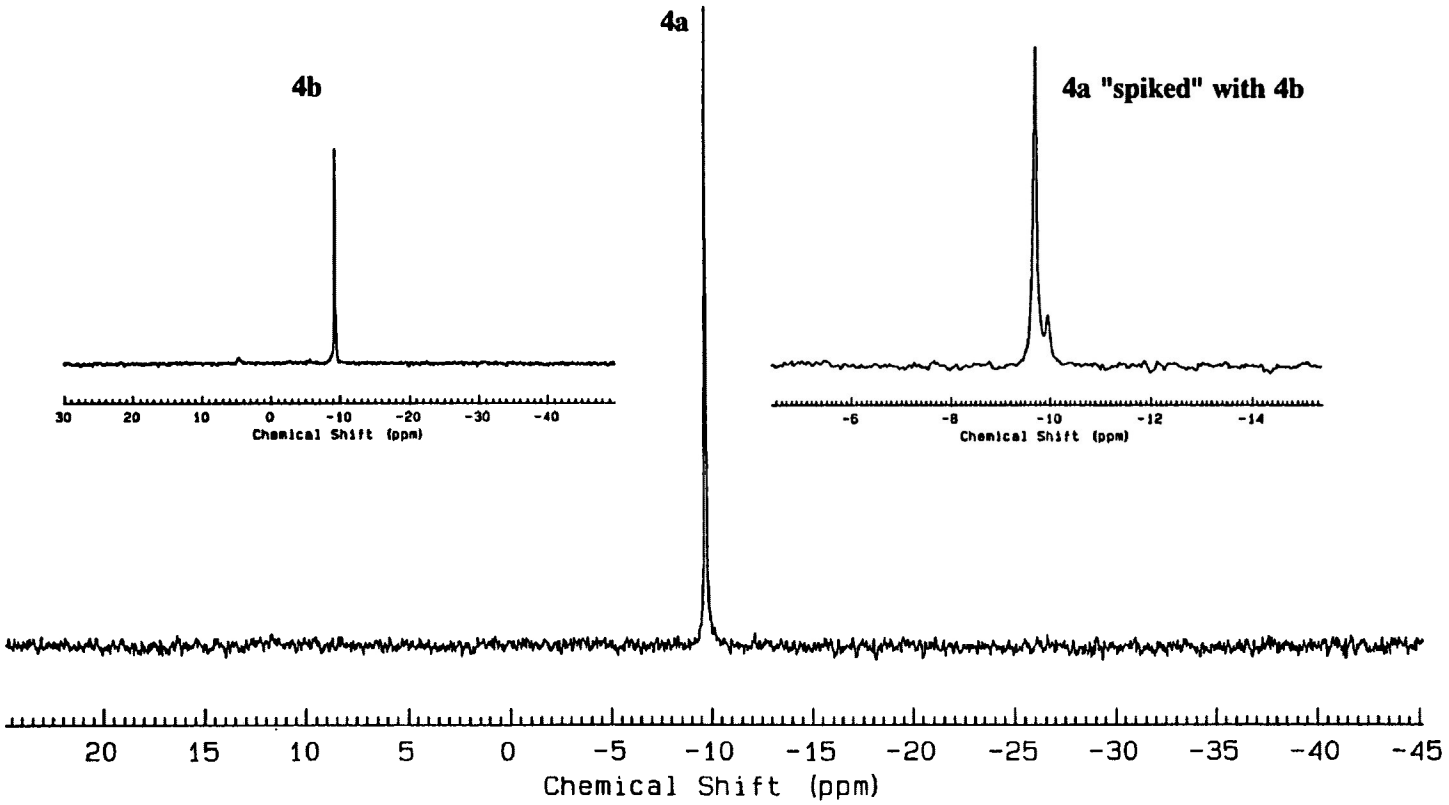
Combustion analyses were obtained for several different samples of **4a**. All varied in carbon content between 52 and 57%, while the hydrogen content varied between 3.7 and 4.5%. Although some samples were recrystallized twice from CH_2Cl_2-hexane and once from acetone-hexane, as well as being pumped under reduced pressure (10^{-6} Torr) for several hours, close examination of the ^1H NMR spectrum of the recrystallized and pumped products revealed that solvent was still present in the lattice. One sample that was recrystallized and pumped gave an analysis of Cl, 7.18; Pd, 16.40; and P, 10.43, (ie.) a Cl:Pd:P ratio of 4:3:6.

Another sample prepared and treated in a similar manner gave variable carbon and hydrogen analyses (see Experimental Section). The ^{1}H NMR of the second sample showed it to contain approximately 1 mole of diethyl ether per trimeric unit. Based on these analyses, it would appear, then, that **4a** has an empirical formula of $Pd_3P_6C_{76}H_{66}OCl_4.1(CH_3CH_2)_2O$, although the solvent content varies greatly from sample to sample and even among different crystals in a sample.

The $^{31}P\{^{1}H\}$ NMR of the crude reaction filtrate obtained from the direct reaction noted above shows only two resonances: a singlet at δ -8.7, which is assigned to the unknown compound **4a**; and another singlet at δ 27.9 due to the dioxide of dppm. The $^{31}P\{^{1}H\}$ NMR of pure **4a** in CD_2Cl_2 shows a singlet at δ -9.7 (Spectrum 3). A "spiking" experiment carried out by adding **4a** to the solution of **4b** showed that each have slightly different shifts (see also Spectrum 3).

No significant changes are observed in the $^{31}P\{^{1}H\}$ NMR when the temperature is lowered to 233 K. Based on this information, it can be speculated that these complexes are highly symmetrical (with respect to the phosphorus atoms), non-fluxional, diamagnetic molecules. However, since **4a** and **4b** contain four halides per three three palladium atoms and since there is no evidence for

Spectrum 3. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) of 4a, 4b and 4a "spiked" with 4b



the presence of hydride, the Pd atoms cannot be in the same formal oxidation state. This Pd non-equivalence is not apparent in the $^{31}P\{^{1}H\}$ NMR spectra, and thus there must be electronic non-equivalence or delocalization amongst the Pd atoms in **4a** and **4b**.

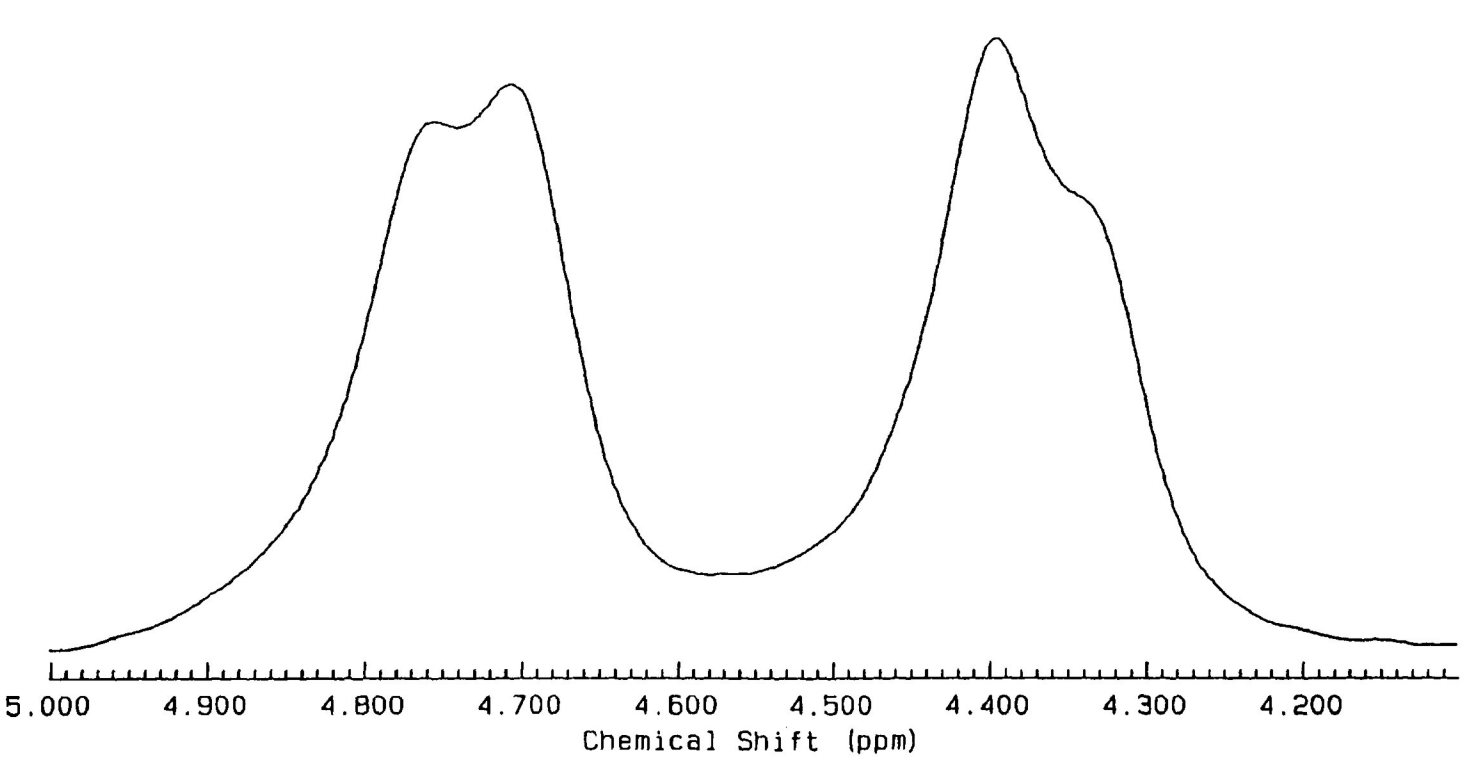
It was thought initially that **4a** and **4b** may be ionic because there are only very slight differences in their respective ^{31}P shifts. The slight difference could be due to strong ion-pairing in solution rather than the effect of coordinated halogen. Coordinated halogen in such circumstances is known to result in shift differences which are usually significantly larger than those observed here. Thus, Hunt and Balch[13] report $Pd_2(\mu\text{-dppm})_2Cl_2$ and $Pd_2(\mu\text{-dppm})_2Br_2$ as having ^{31}P resonances at δ -2.5 and -4.71 respectively. However, the "spiking" experiment in which **4b** is added to **4a** strongly suggests that at least some of the halogen is, indeed, coordinated to the two species since although close ion-pairing could give rise to slightly different shifts for **4a** and **4b** in separate solutions, mixing of the solutions should put the two phosphorus containing ions into a common environment with respect to the halide ions if all halogen is ionic. Under these conditions, only one ^{31}P signal should be observed for the mixture.

Since for dppm-bridged Pd(I) dimers, resonances

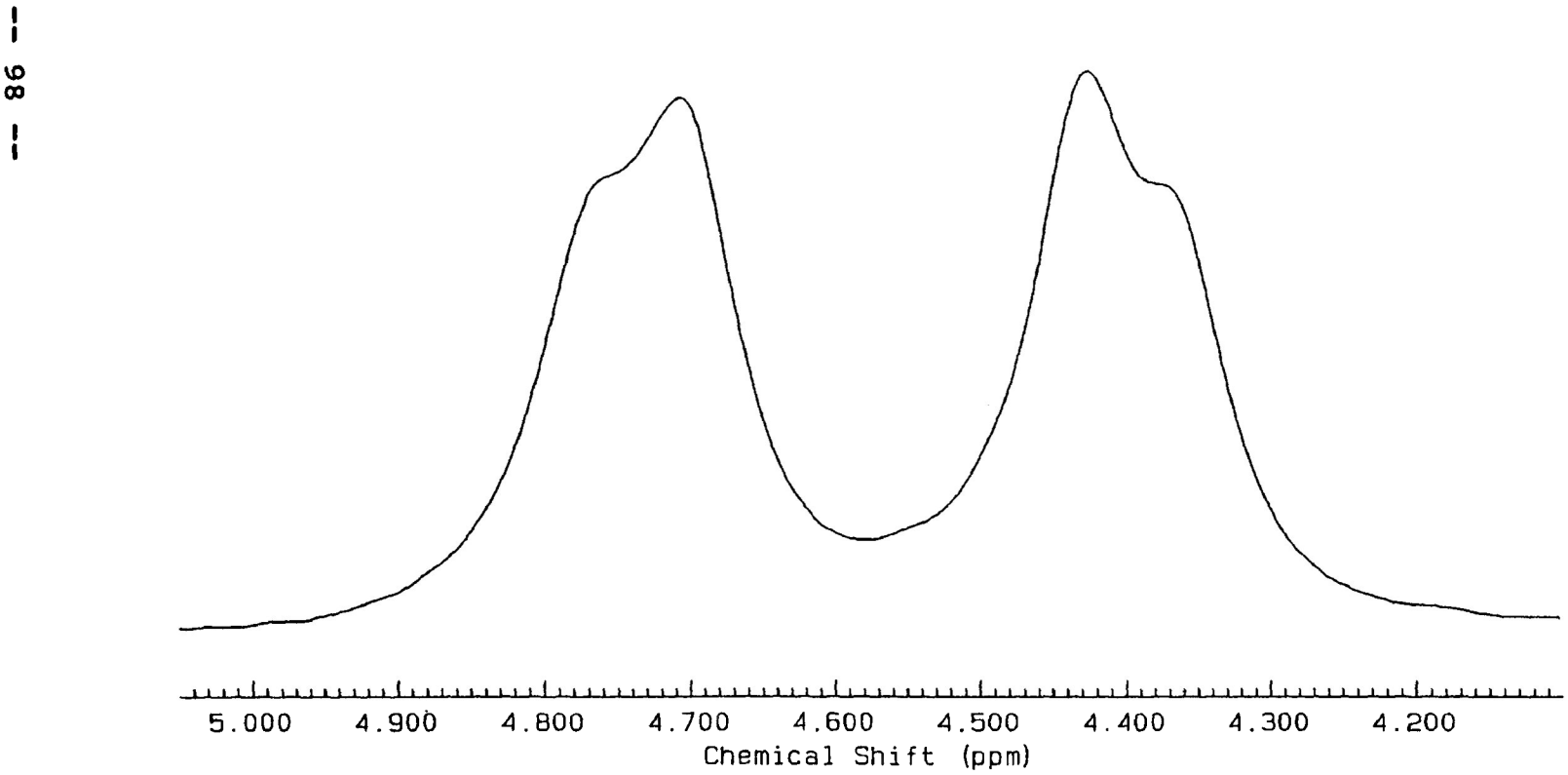
frequently occur[13] in the region between δ -1.5 to -10.5, a preliminary supposition was that the compounds **4a** and **4b** could be Pd(I) dimers. However, the palladium trimer[14] $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$, which contains edge-bridged dppm, has a shift of δ -11.7. The shift at δ -9.7 for **4a** and the fact that **4a** contains 3 palladium atoms as the empirical Pd structural unit appears to suggest that **4a** may also contain the basic trimeric moiety with edge-bridged dppm.

The proton NMR spectra of **4a** and **4b** in CD_2Cl_2 are almost identical and they both show the down-field multiplet centred at δ 6.9 due to the phenyl protons. The dppm methylene resonances of both of these compounds appear as two broadened doublets of doublets indicating non-equivalence of the two methylene protons in each dppm ligand. The doublet of doublets for **4a** (see Spectrum 4) are centred at δ 4.73 and 4.37 and the principal coupling constant for each doublet was found to be 12.2 Hz. The bromide analog, **4b** (see Spectrum 5) had the doublet of doublets centred at δ 4.74 and 4.04 with a signal separation somewhat lower than that of **4a**. The coupling constant for each broadened doublet in **4b** was determined to be 11.8 Hz. These data are similar to those reported by Colton, Farthing and McCormic,[15] who give corresponding values for $Pd_2(\mu\text{-dam})_2Cl_2$ and $Pd_2(\mu\text{-dam})_2Br_2$. In these complexes the coordinated

Spectrum 4. ^1H NMR of 4a in CD_2Cl_2.



Spectrum 5. ^{1}H NMR of 4b in CD_2Cl_2.

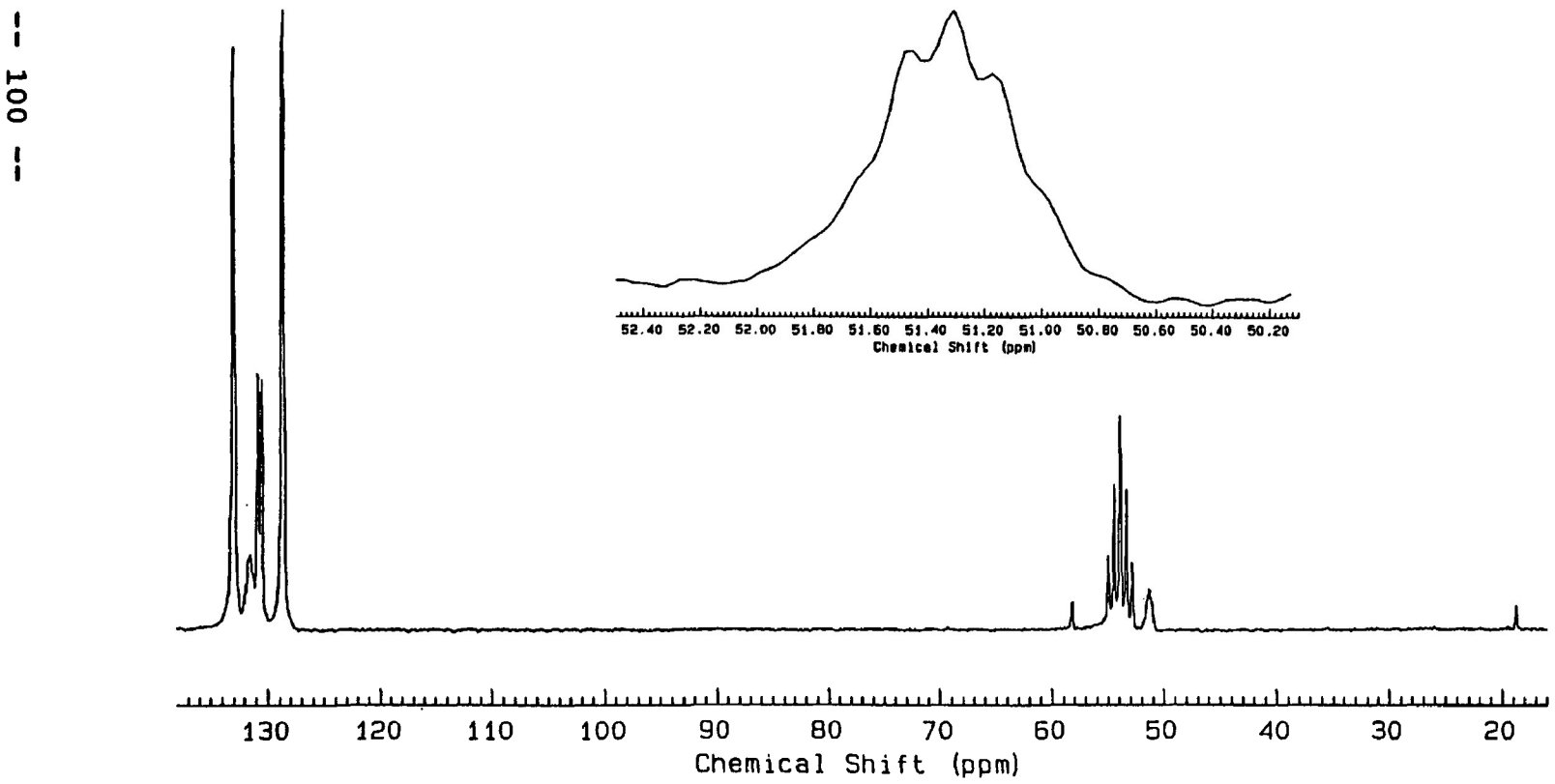


halide appears to have no bearing on the shifts corresponding to the methylene protons for the bridging ligand since their shifts are also similar (such as the case for **4a** and **4b**).

The non-equivalence of the protons could arise in a variety of ways. Thus, Balch et al.[16] rationalize the inequivalence of the methylene protons in various palladium complexes in terms of an A-frame type of structure. Cradle-type structures with bridging dppm ligands on the same side of the molecule would also produce inequivalent methylene protons. On the other hand, a μ_3-CO capped trimeric unit would also produce proton non-equivalence, as would numerous other possible structures.

The ^{13}C NMR (see Spectrum 6) of **4a** in deuterated dichloromethane at room temperature shows the expected aromatic signals, the CD_2Cl_2 signal at δ 53.4, residual ethanol of recrystallization at δ 18.8 (CH_3) and 58.2 (CH_2) and what appears to be a quintet at δ 51.4 due to the methylene carbon of coordinated dppm.[17] Closer examination of the quintet reveals both line broadening and peak areas which are not quite what would be expected of a true quintet. It is therefore probably a poorly resolved second order spectrum arising from coupling of the methylene carbon with both the adjacent phosphorus atoms in the ligand and the chemically

Spectrum 6. ^{13}C NMR of 4a in CD_2Cl_2.



identical phosphorus atoms in nearby ligands. The multiplet is centred at δ 51.4 with a line separation of 8.4 Hz, which is comparable with similar couplings oberved for some tertiary phosphines.[18]

The ^{13}C NMR gives a strong indication that the methylene carbons in the dppm ligands present in the structure are equivalent.

The FTIR spectra of compounds **4a** and **4b** are fairly simple and almost identical. Compound **4a** has a strong, sharp CO stretch at 1817 cm^{-1} and an unresolved shoulder at around 1810 cm^{-1}, while **4b** has a strong and sharp absorption band at 1819 cm^{-1}, again, with a shoulder at around 1810 cm^{-1}. The small differences in stretching frequencies of **4a** and **4b** may be attributed either to an ionic compound experiencing strong ion-pairing, or to similar structures in which the coordinated halogen is different.

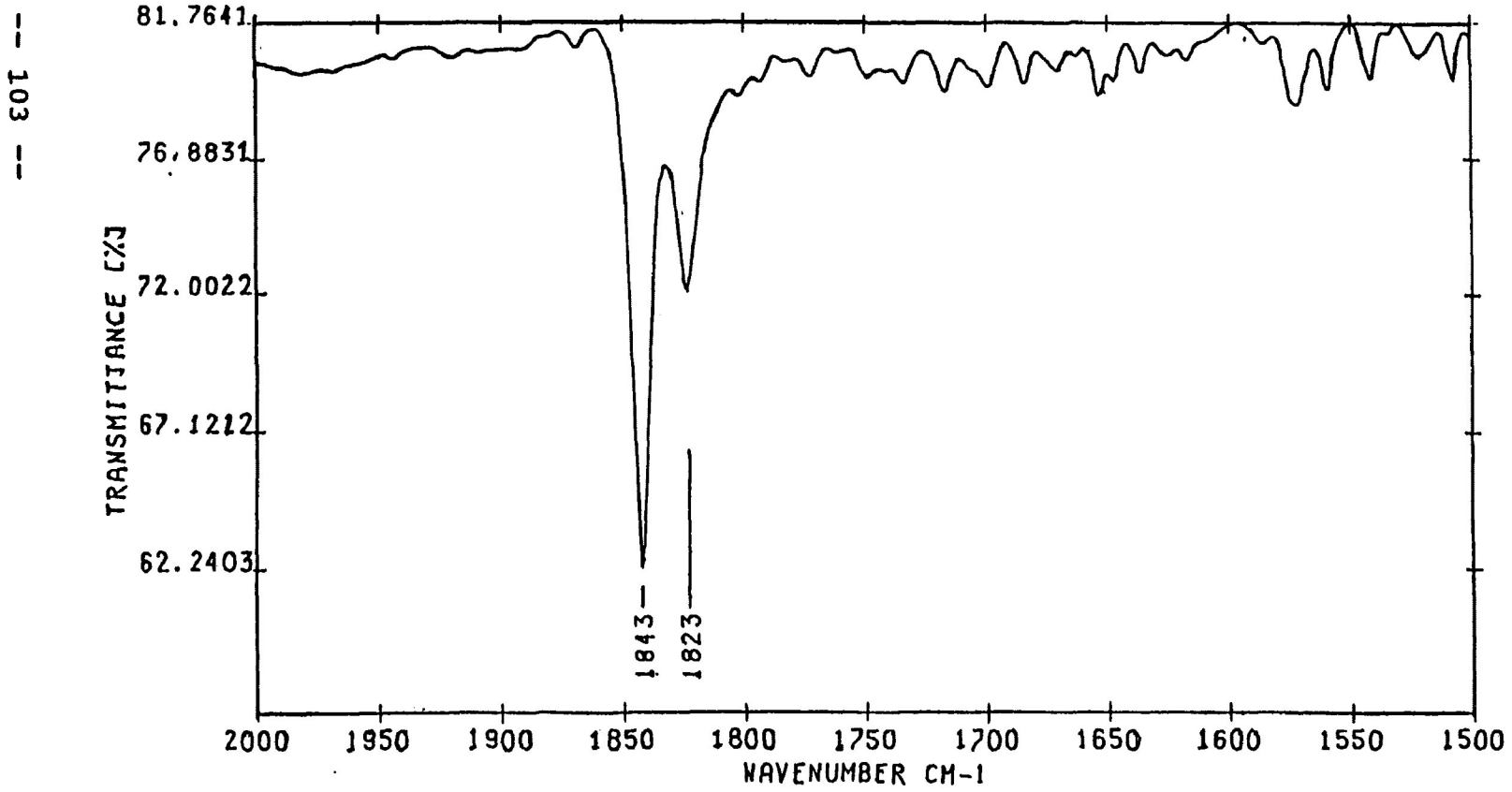
Because there is essentially only one CO stretching frequency present in each spectrum, **4a** and **4b** are thought to be highly symmetrical molecules, containing possibly only one CO group. However, whether the CO is terminal, bridging or triply bridging in **4a** and **4b** is still not known. A ^{13}CO exchange experiment may be performed followed by a ^{13}C NMR study of the product which would establish how many adjacent phosphorus atoms are present (see Suggestions for Further Work later in

this thesis).

Balch and Benner[8] list a number of Pd(I) complexes with bridging CO groups having vibrational frequencies ranging from 1705 cm^{-1} to 1723 cm^{-1}. The terminal stretching frequency for CO in $[Pd(CO)Cl]_n$ lies at 1976 cm^{-1} and in $Pd(CO)Cl_2(PhCN)$, the terminal stretch lies at 1947 cm^{-1}. These are generally regarded as very low for terminal carbonyl ligands since the degree of π back-bonding is lower for Pd(II) when compared to Pt(II). The vibrational stretching frequency of triply bridging CO in the complex $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ occurs at 1820 cm^{-1}, as reported by Puddephatt et al.[14] Since this frequency is virtually identical to that observed for **4a** and **4b**, a μ_3-CO palladium trimeric structure is a possibility.

It is interesting to note that recrystallization of **4a** and **4b** from CH_2Cl_2-hexane followed by prolonged (7 hours) pumping at 10^{-6} Torr resulted in changes in their respective IR spectra, which are shown for **4a** in Spectrum 7. Two new carbonyl vibrational frequencies occur at 1843 (sharp, strong) and 1823 (sharp, medium) cm^{-1} (the situation is similar for **4b**). However, there appears to be no change in molecular structure since when the recrystallized compounds **4a** and **4b** were redissolved in CH_2Cl_2 for solution $^{31}P\{^1H\}$ NMR studies, no changes in the ^{31}P shift were detected. From these

Spectrum 7. IR of 4a after pumping at 10^{-6} Torr for 7 hrs.



observations, two questions may be raised:

(1) are **4a** and **4b** formed in the reaction as kinetically preferred isomers which in solution rearrange to thermodynamically preferred isomers?, or

(2) are the changes observed in the IR spectra a result of occlusion of certain solvent molecules in the lattice during crystallization, which are removed by prolonged pumping, resulting in changes in the solid phase (lattice structure) of the compound and a subsequent loss of symmetry?

To answer the first question, the $^{31}P\{^{1}H\}$ NMR (see Spectrum 3) and ^{1}H NMR spectra (see Spectrum 4) of **4a** were monitored over a range of temperatures, specifically from 298 K to 213 K. No changes were observed in either the $^{31}P\{^{1}H\}$ NMR or ^{1}H NMR within this range of temperatures. On the basis of this observation, the first explanation seems less likely. It is known that solvent (ethanol) of crystallization is present and it is probable that some is removed by pumping. Pumping (10^{-6} Torr) for only 2 hours causes no change. Only prolonged pumping is effective.

The IR spectrum between 600-200 cm^{-1} of **4a** and **4b** was examined for Pd-Cl vibrations; however, no

vibrations which could be clearly assigned as such, were observed.

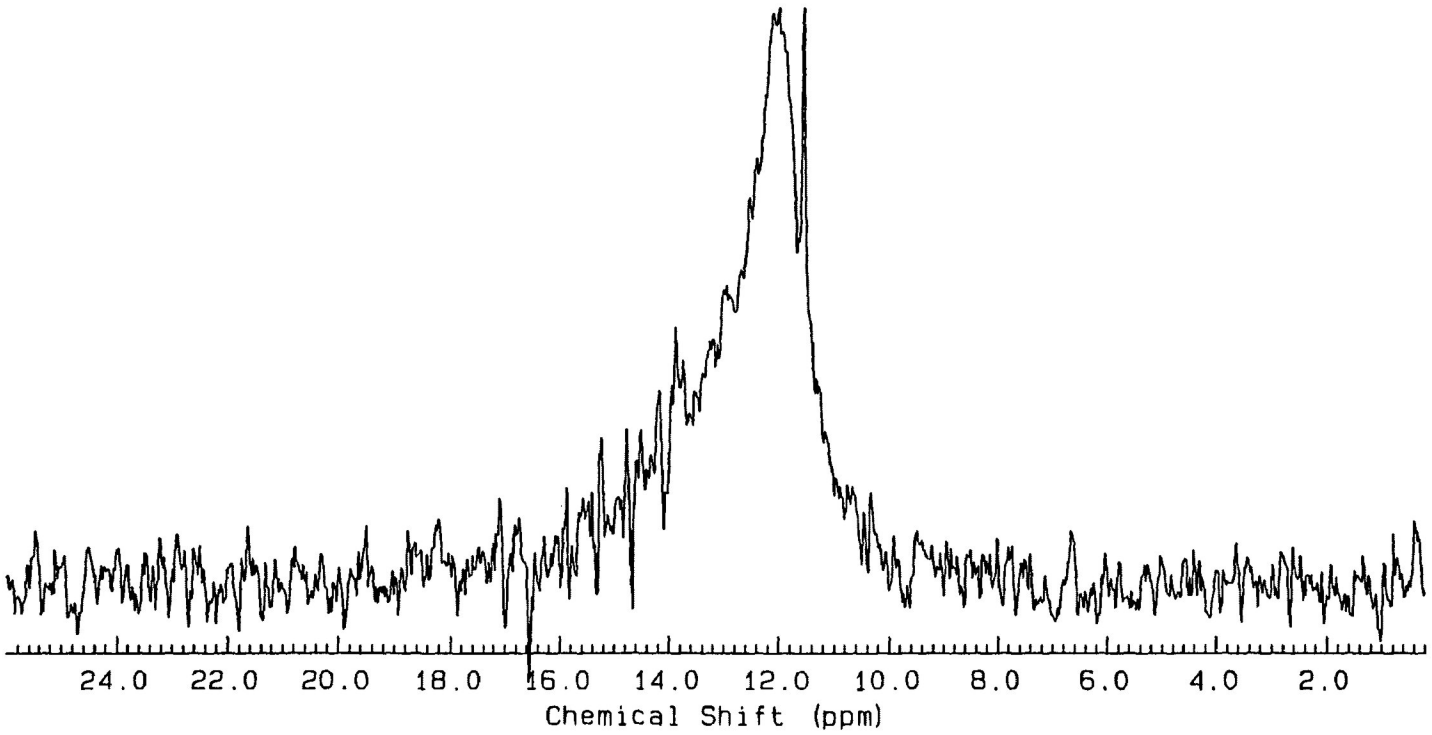
It is known that compound **4a** is a diamagnetic molecule, possibly with metal-metal bonds, or bridging chlorides. In order to determine whether or not **4a** contains Pd-Pd bonds, CO was bubbled through a solution of anhydrous THF containing **4a** in hopes of detecting a CO insertion into Pd-Pd bonds. There appeared to be no changes in the ^{31}P spectrum of the solution after passing CO. Calderazzo et al.[19] had observed a reduction of $PdCl_2$ by CO and, thus, it was thought that if **4a** is in an oxidation state greater than 0, by passing CO through a solution containing **4a**, a reduction of palladium may be observed.

Since a reduction of palladium by CO was not observed, other attempts at reducing the palladium in **4a** were tried. Compound **4a** was treated with $NaBH_4$ under CO yielding unkown compound **5a** (see later discussion) and the dioxide of dppm, as shown in Spectrum 8. This gives two important pieces of information:

(1) It confirms that at least some of the Pd atoms in **4a** are in a higher oxidation state than 0, and

(2) **4a** is a precursor of the unknown compound **5a** (which will be further elaborated on later).

Spectrum 8. $^{31}P\{^{1}H\}$ NMR of the reaction solution after 4a is treated with $NaBH_4$ under CO yielding unknown compound 5a.



Many attempts at growing X-ray quality crystals have been tried. Only very recently, after much time and effort have suitable crystals been grown. An X-ray crystal structure of **4a** should be available shortly as a good data set has now been acquired.

Compounds **4a** and **4b** are stable for several weeks in the solid state under an inert atmosphere of N_2, as proven by $^{31}P\{^1H\}$ NMR spectroscopy. However, exposure of the solid to the atmosphere results in decomposition. In the $^{31}P\{^1H\}$ NMR spectrum of a sample of **4a** exposed to air, an additional peak is observed at δ -54.3 (in CH_2Cl_2) which is attributed to the known compound $Pd(\eta^2\text{-dppm})Cl_2$.[20,21] Such an observation can either be assigned to the decomposition of compound **4a** or oxidation of Pd(I) to Pd(II) with molecular oxygen.

Complexes **4a** and **4b** are both soluble in aliphatic polar solvents such as CH_3CN, ethanol or chlorinated hydrocarbon solvents, but only sparingly soluble in aromatic hydrocarbon solvents.

Attempts at precipitating and recrystallizing **4a** and **4b** as their BPh_4^- or PF_6^- salts were unsuccessful, even though these compounds may be ionic. However, the failure to observe an ionic exchange does not necessarily indicate that **4a** or **4b** are not ionic. The compounds may simply prefer to crystallize with Cl^- or Br^- as opposed to BPh_4^- or PF_6^- due to the size and

energies of the preferred anion.

The melting point of **4a** was determined to be 206°C.

A typical reaction would have a yield of about 0.18g or 25.15% based on the formula for **4a** discussed above.

In summary, the shift of **4a** at δ -9.7 would seem to indicate that dppm is bridging two metal centres joined by a metal-metal bond. The ^{1}H and ^{13}C NMR shows that the methylene protons and methylene carbon of each dppm ligand are non-equivalent and equivalent, respectively. As well, the IR spectrum of **4a** gives a sharp band at 1819 cm^{-1}, which is comparable to palladium trimeric compounds containing a triply bridged CO ligand; furthermore, combustion analyses obtained for **4a** give a Pd:Cl:P ratio of 3:4:6 which would also seem to suggest that **4a** contains a trimeric arrangement of palladium atoms. Venanzi *et al.*[22] have successfully reduced platinum compounds with $NaBH_4$ in the presence of CO and bulky phosphines to produce a variety of compounds containing the basic platinum trimeric unit. It is quite possible, then, that reductions of palladium salts by $NaBH_4$ in the presence of dppm and CO may also produce compounds containing the basic palladium trimeric unit. Also, **4a** and **4b** have similar but not identical structures.

Based on all of this information, it appears that

4a may have one of a variety of possible structures, two of which include the 46 and 48 electron systems shown in Figures 12 and 13. This is not unreasonable since Pd(II) acetate is a 48 electron trimeric system.

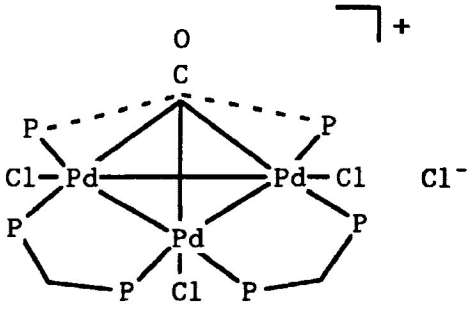


Figure 12.
Possible structure of complex 4a.

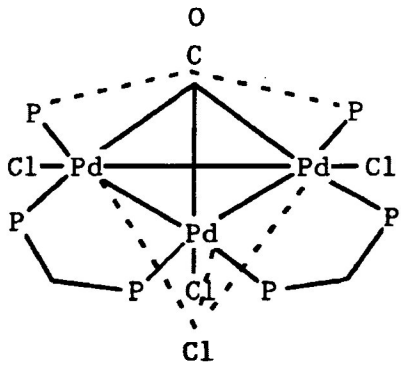


Figure 13.
Alternative possible structure of complex 4a.

Thus, it is believed that the vertices of the palladium trimeric unit are edged bridged by dppm in **4a** since the phosphorus shift corresponds to other palladium-CO-dppm trimers which also contain edge-bridged dppm.[14] The methylene protons (according to the ^{1}H NMR spectrum of **4a**) are non-equivalent and, thus, must be in different environments. This would seem to be the case if CO triply bridges each palladium in the complex, which appears to be the case according to the IR of **4a** which is very similar to trimeric palladium-CO-dppm compounds containing a μ_3-CO ligand.[14]

The SEM/EDS measurements also indicate that **4a** contains chloride, and this is further confirmed by the chemical analyses obtained for **4a**. Furthermore, the analyses calculated for either of these possible structures (Pd, 17.9; P, 10.39; Cl, 7.94; C, 55.7; H, 4.80) are in very close agreement with those obtained for **4a** when it is solvated with approximately 1 mole of diethyl ether per trimeric unit (see Experimental Section). It is thought that most, if not all, of the chloride is coordinated in **4a** due to the results of the spiking experiment with the bromide analog, **4b**. The inability of **4a** to exchange with PF_6^- and BPh_4^- does not necessarily mean that the compound is not ionic; hence, the structure in Figure 12 has also been proposed as a possibility. A triply bridged chloride (as in Figure 13) probably would not be visible in the far infrared, or, at least, would absorb at a very low wavenumber. Finally, treatment of **4a** with $NaBH_4$ yields **5a**, which would seem to indicate indirectly, as would be expected with a Pd_3Cl_4 unit, that some reduction has occurred. Compound **4b** would also have possible structures similar to those proposed for **4a** for the same reasons, the only difference being the nature of the halogen.

5. Attempted characterization of the unknown compounds 5a and 5b.

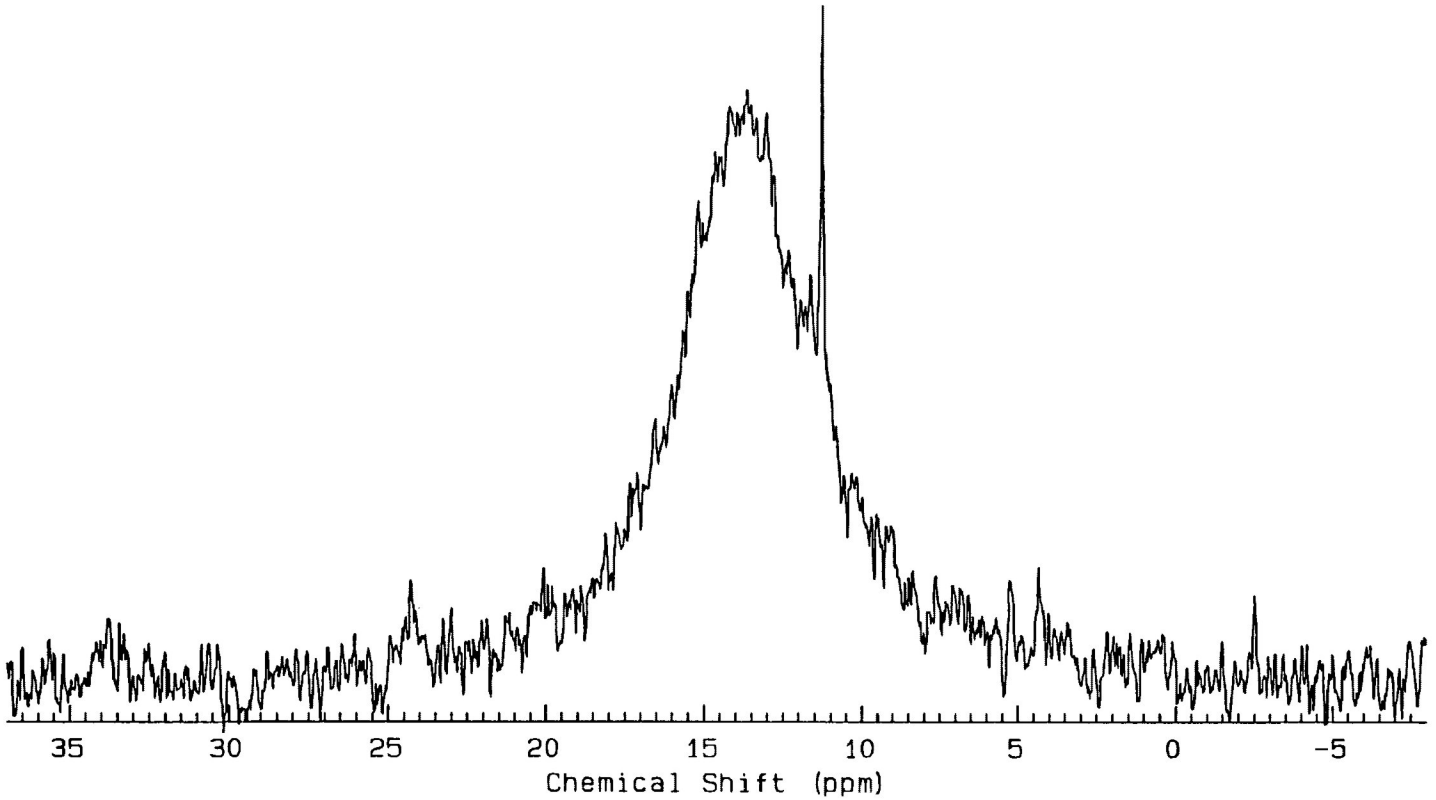
Generally, compounds **5a** and **5b** may be synthesized via either of two methods.

The first method involves a direct reduction of Pd(IV) or Pd(II) salts in the presence of dppm and CO by $NaBH_4$. Important factors in this synthesis are the rate of addition and the amount of $NaBH_4$ used (see Experimental Section). Basically, **5a** and **5b** may be obtained directly from the reaction filtrate as clusters of small red crystals.

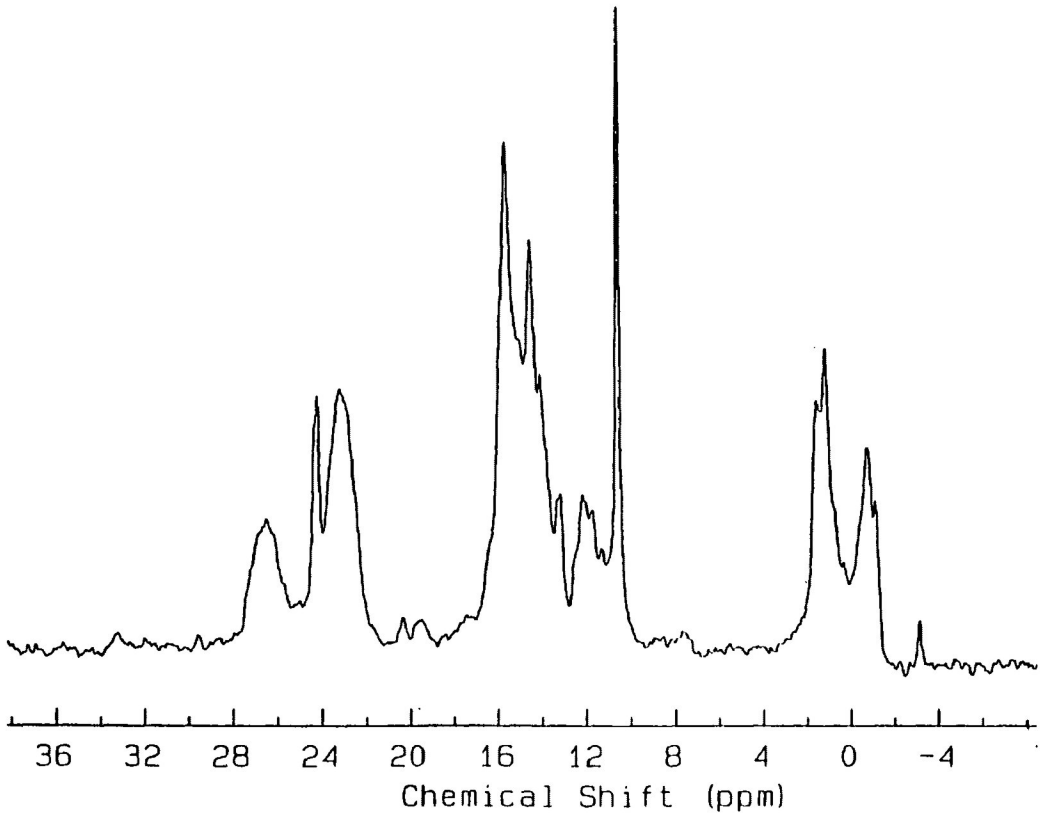
The second method involves the treatment of compound **4a** with $NaBH_4$ in the presence of CO, ultimately yielding **5a** or **5b**.

Combustion and SEM/EDS analyses were obtained for **5a** (see Experimental Section). Based on these analyses and the fact that the ^1H NMR indicated that **5a** was solvated, it would appear, then, that **5a** has the empirical formula $\mathbf{Pd_5(dppm)_4(CO)_6Cl_2}$. The room temperature $^{31}P\{^1H\}$ NMR spectrum shows a very broad unresolved signal centred at δ 13.6 (see Spectrum 9). The spectrum also shows small amounts of **3** and **4a** at δ 11.1 and -9.7 respectively. However, at lower temperatures (233 K), the broad signal resolves into three separate regions with signals around δ 25, 15 and 0 (see Spectrum 10). The region at δ 15 is about twice the area of either the δ 25 or 0 signals, which are approximately equal in area. Clearly, then, the system

Spectrum 9. $^{31}P\{^{1}H\}$ NMR of 5b in CH_2Cl_2.



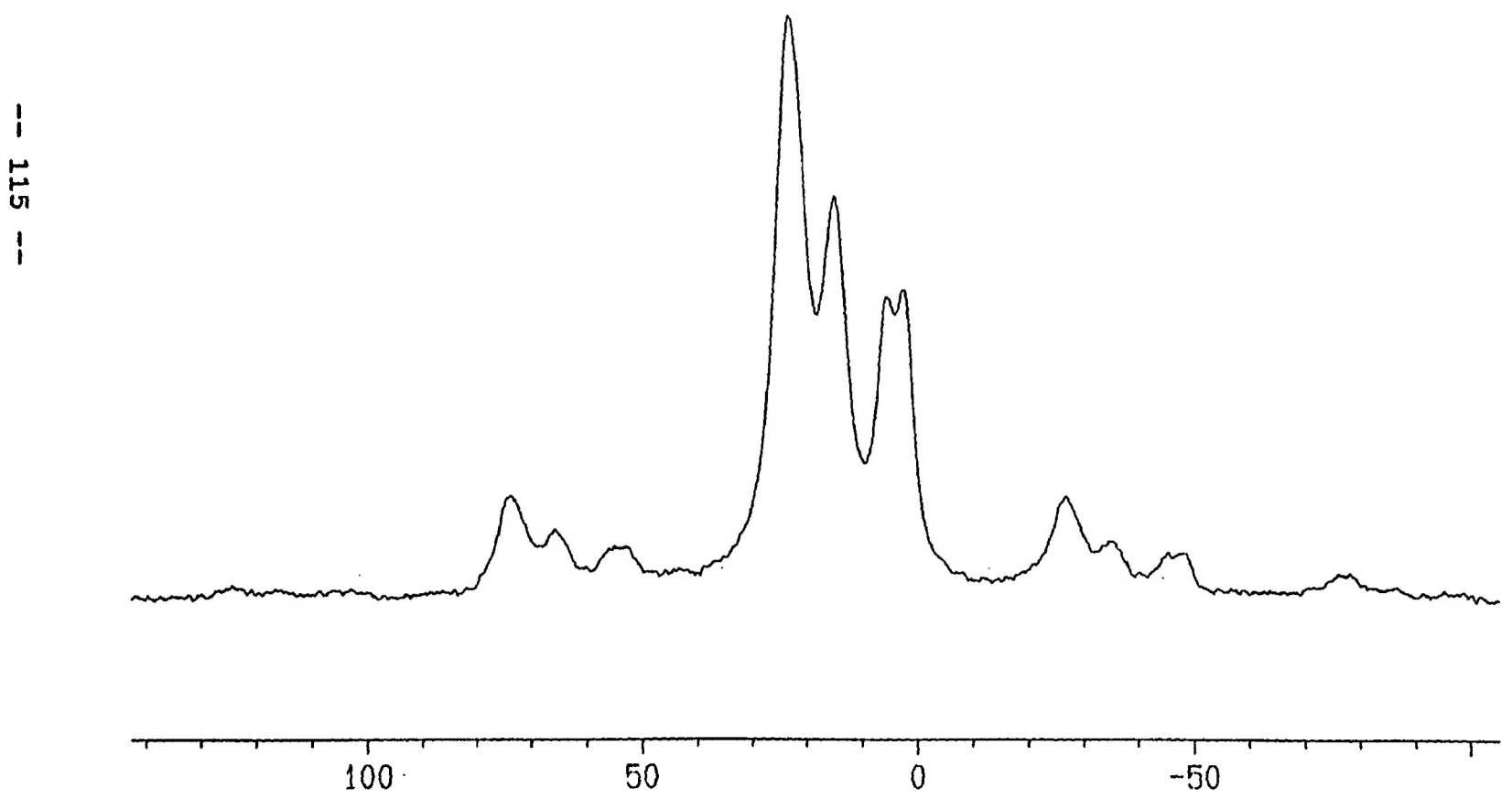
Spectrum 10. Low temperature (233 K) $^{31}P\{^{1}H\}$ NMR of 5a in CD_2Cl_2.



is fluxional at room temperature. The downfield signals at δ 25 and 15 could be attributed to bridging dppm. Thus, Wink, Creagon and Lee[23] report a chemical shift of about δ 22 for a Pd(I) dimer containing a metal-metal bond and bridged by dppm. However, Lloyd and Puddephatt[24] have reported a palladium trimeric system containing bridging dppm with a corresponding shift at around δ -9. Therefore, the third region centred at around δ 0 could also be attributed to bridging dppm.

Also, upon closer examination of Spectrum 10, the regions at δ 25 and 0 appear to be similar, but not the same, and thus, there are indications of an interaction between them. This is suggestive of monocoordinated dppm where the downfield shift corresponds to the coordinated phosphorus end, as one would expect. The upfield shift at around δ 0 may correspond to the free phosphorus end of the monocoordinated ligand, although one might expect the signal to be at somewhat higher field. This speculation is rationalized on the basis that for the ^{31}P CP MAS (see Spectrum 11) and the low temperature $^{31}P\{^{1}H\}$ NMR solution spectra, the flexibility of monocoordinated dppm is diminished and the monocoordinated dppm ligand is orientated such that the uncoordinated end is poised to coordinate in the fluxional process. It appears, then, that **5a**

Spectrum 11. ^{31}P CP-MAS NMR of compound 5a.



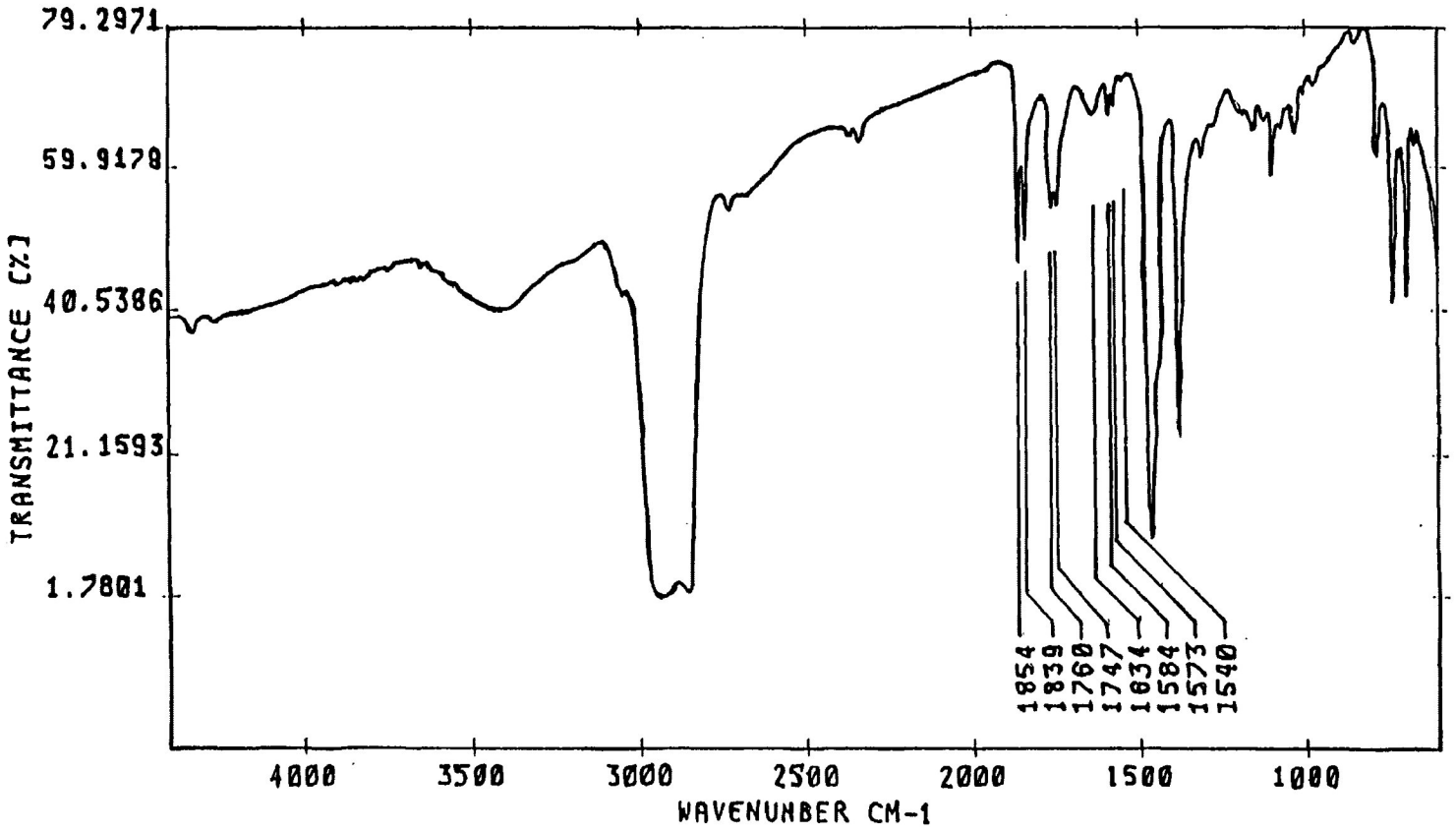
contains both bridging and possibly monocoordinated dppm in a fluxional structure. Above room temperature, the broad signal at δ 13.6 sharpens considerably and this is further evidence for a fluxional system.

The ^1H NMR spectrum of **5a** at room temperature and at 233 K shows two unresolved broad multiplets of almost equal area at δ 1.6 and 3.1. These multiplets are assigned to the methylene protons of dppm. The shift at δ 1.6 is suggestive of methylene protons in a monodentate dppm ligand. Thus, the situation could be similar to that of the methylene proton resonances of dppm in the complexes $Pt(1\text{-naphthyl})_2(\eta^1\text{-dppm})_2$ and $Pt(C_6H_4Me\text{-}O)_2(\eta^1\text{-dppm})_2$ which are at δ 1.97[25] and 2.23[3] respectively (both complex multiplets). The other multiplet at δ 3.1 in the ^1H NMR spectrum of **5a** is assigned to the methylene protons of a bridging dppm ligand, which has a similar shift to the methylene protons of the compound $Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2$.[26] The low temperature ^1H NMR of **5a** was recorded, but no further resolution of these multiplets was observed.

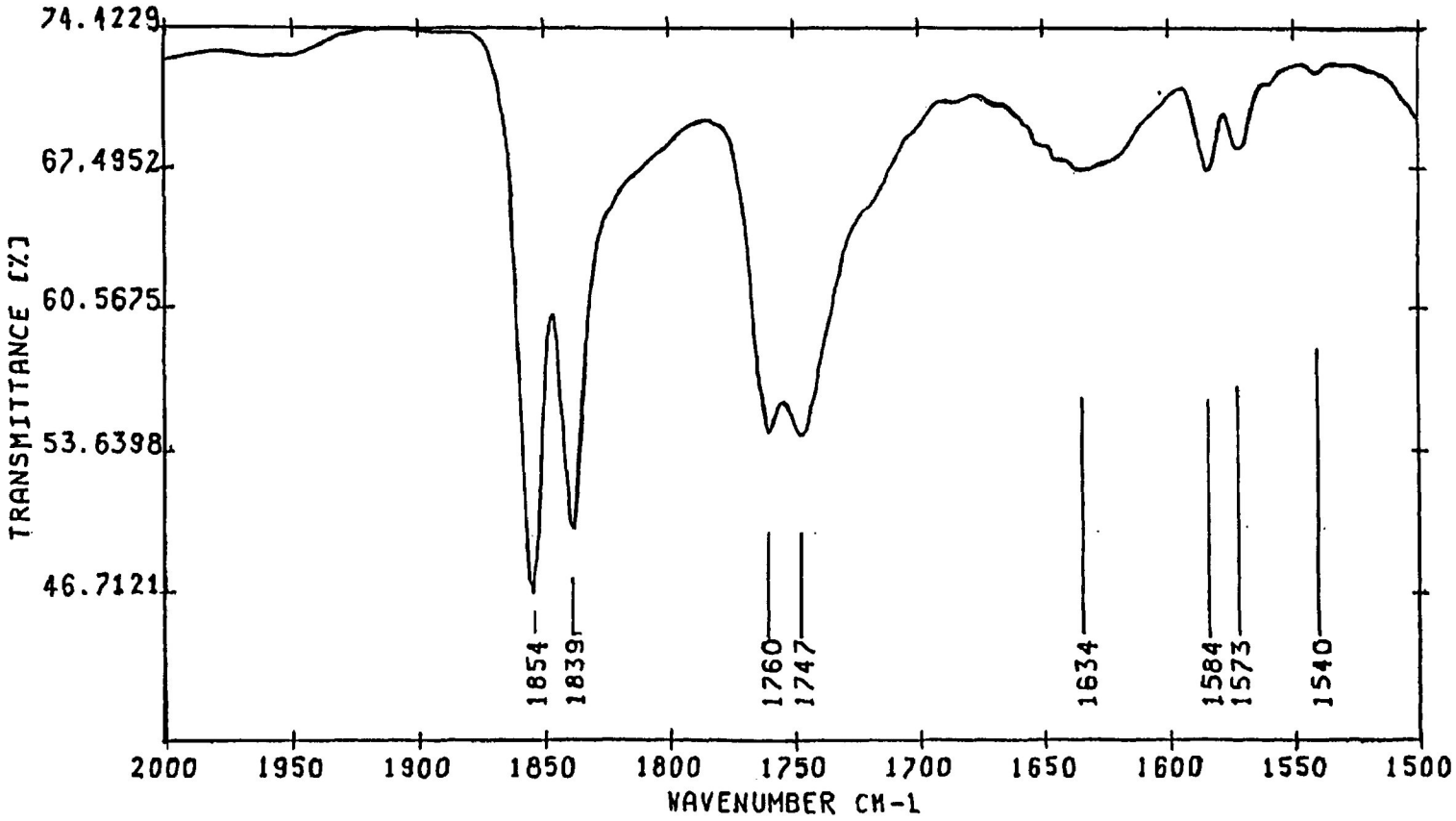
The low solubility of **5a** and its instability in solution made it difficult to record a ^{13}C NMR spectrum.

Several things may be said about the infrared spectrum obtained for **5a**. The absorptions at 1760, 1747 and 1715 cm^{-1} may be attributed to bridging carbonyls[27] (see Spectra 12a and 12b). However, while

Spectrum 12a. IR of unknown 5a between 4000 and 600 cm^{-1}



Spectrum 12b. IR of unknown 5a between 2000 and 1500 cm^{-1}



the absorptions at 1854 and 1839 cm^{-1} could be assigned to terminal CO,[31] it is thought that they too are more likely to be bridging. Thus, compound **3** has a series of absorptions ranging from 1876 to 1818 cm^{-1} which have been shown quite clearly (see Spectrum 2) by X-ray crystallography to be be bridging. Therefore it is difficult to determine whether the CO groups in compound **5a** are bridging or terminal.

As mentioned earlier, compound **5a** contains chloride. Typically, terminally bound metal halides absorb at very low frequencies,[29] but the region between 600 and 200 cm^{-1} appeared to be featureless as far as terminal halide is concerned. Chloride terminally coordinated to palladium would have absorptions in the range between 348 to 174 cm^{-1}.[29] Bridging halides typically would absorb at even lower frequencies and may not be observed within this region (absorptions below 200 cm^{-1} could not be measured). Also, it is quite possible that **5a** is ionic and, thus, palladium-halide absorptions would not be observed. It appears, then, that little can deduced from these spectra about the nature of the chloride present.

Attempted metathetical reactions of **5a** with BPh_4^- and PF_6^- gave inconclusive results suggesting that the chlorine may not be present as chloride ion.

A molecular weight determination by the vapour

pressure osmometric method could not be performed due to the instability and low solubility of **5a** in solution.

Attempts at growing a suitably sized crystal of **5a** from a variety of solvent mixtures were also unsuccessful. Only very small crystals could be obtained, usually as rosettes.

Other experiments have shown that this palladium-carbonyl-dppm-halide complex is stable in the solid state under an inert atmosphere of N_2 for 2-3 days. However, even the slightest exposure of **5a** to the atmosphere results in decomposition. Also, **5a** has never yet been obtained free from impurities. Thus, as can be seen in Spectrum 9, compound **5a** always appears to be contaminated with compound **3**, although the amount varies considerably from preparation to preparation. The difficulties in the purification of **5a** are largely due to its instability in solution and it should be noted again that even solutions of **5a** saturated with CO or N_2 decompose to give **3** and **4a** as the only products. If **5a** is suspended in CD_3OD and subsequently undergoes decomposition, compounds **3** and **4a** appear. Since **4a** is known to contain chloride, it is quite evident, then, that the chloride does not come from the solvent. Furthermore, this indirectly proves that halide is present in **5a**.

Taking into account all of the previously discussed

information, it appears that **5a** contains both bridging and monocoordinated dppm. Also, although it is difficult to determine if CO is bridging or terminal, it is thought that **5a** contains at least some bridging CO since its IR spectrum is similar to that of **3**. Combustion and SEM/EDS analyses suggest that **5a** contains, as an empirical unit, five palladium, six CO, four dppm and probably two halide atoms. Finally, as mentioned before, **5a** decomposes to yield compounds **4a** and **3**. Based on this final piece of evidence, it is thought that **5a** possibly contains a basic palladium trimeric unit since **3** contains 2 trimeric units while **4a** is thought to contain one trimer.

6. Characterization of Compound 6.

Compound **6** frequently appeared as a minor product of several different reactions that were previously discussed. For example, the synthesis of **4a** or **4b**, decomposition of **5a** or **5b**, synthesis of **3** by treating **5a** with $NaBH_4$, etc. As well, **6** may be obtained from an equilibrium reaction between **3** and **4a** over time.

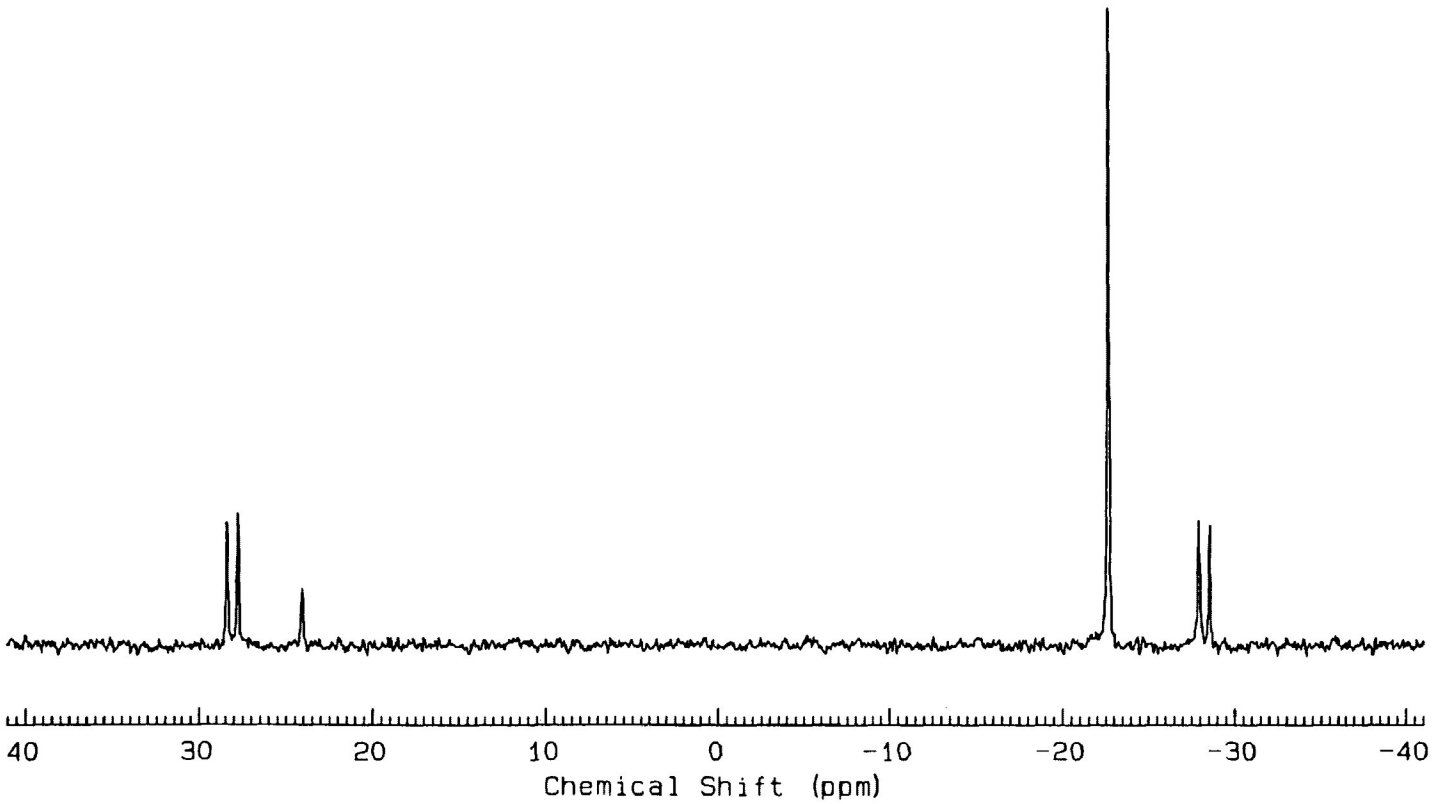
Originally it was thought that **6** was a symmetrically bridged palladium species as it shows a ^{31}P singlet at δ 27. However, SEM/EDS analysis revealed that **6** contained no palladium or halide.

Also, the combustion analysis of **6** revealed that it had a very high carbon content. Furthermore, the FTIR of **6** showed a strong absorption at around 1190 cm^{-1} which is due to a P=O absorption.[30]

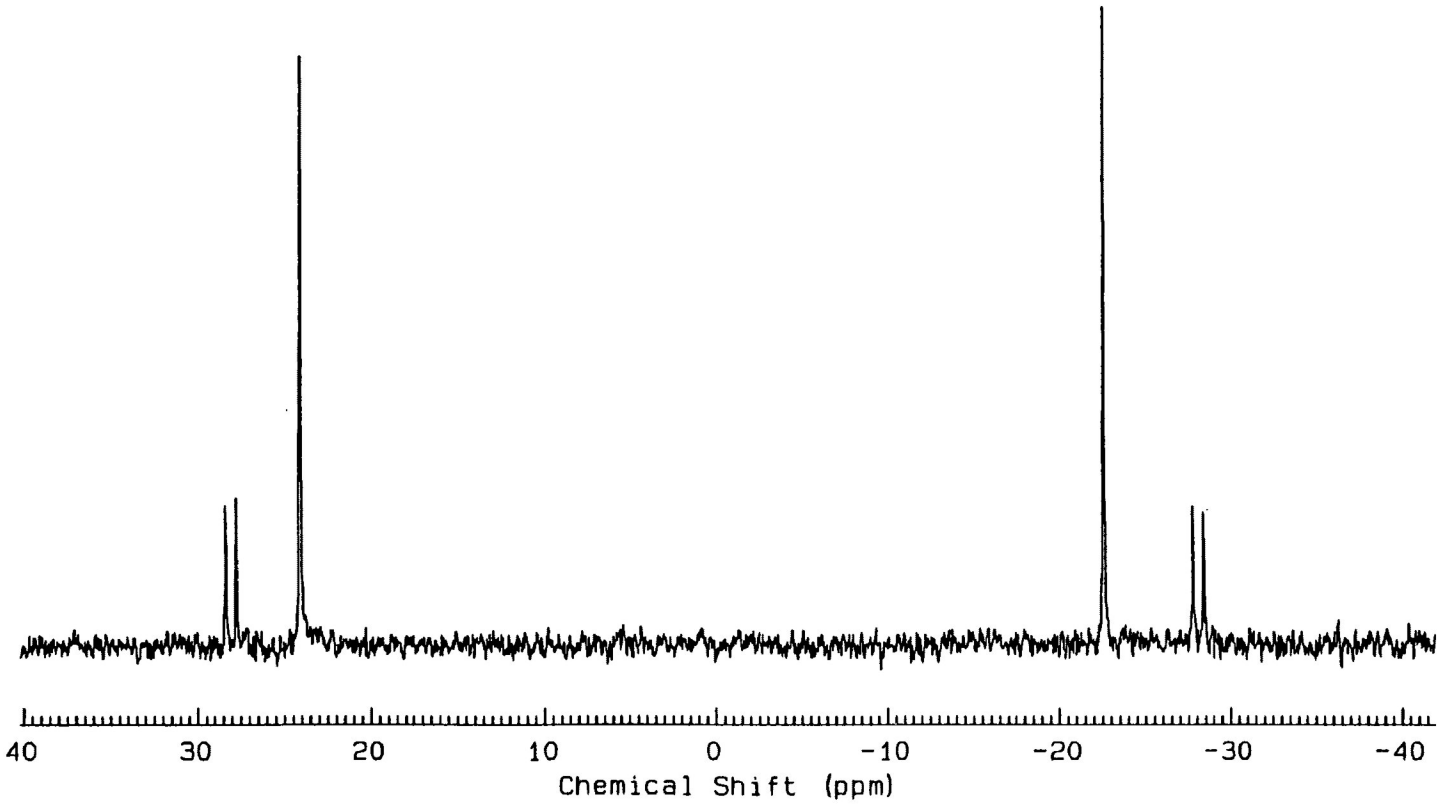
Taking into account the above information, it was thought that **6** was the dioxide of dppm. To confirm this, dppm was treated with H_2O_2. The $^{31}P\{^1H\}$ NMR of the white solid obtained from the reaction gave several signals (see Spectrum 13). The strong singlet at δ -22 corresponds to unreacted (unoxidized) dppm; the two doublets at around δ 28 and -28 are attributed to the monoxide of dppm; finally, a singlet at around δ 24 is due to the dioxide of dppm.[11] When this solution was spiked with a sample of compound **6**, the area under the signal at δ 24 increased dramatically (see Spectrum 14).

The molecular weight found for **6** confirmed it as the dioxide of dppm.

Spectrum 13. $^{31}P\{^{1}H\}$ NMR of dppm and the mono- and dioxides of dppm in CH_2Cl_2.



Spectrum 14. $^{31}P\{^{1}H\}$ NMR of dppm and the mono and dioxides of dppm (in CH_2Cl_2) "spiked" with compound 6.



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SUGGESTIONS FOR FURTHER WORK

Although it is quite evident that reductions of palladium salts by $NaBH_4$ in the presence of dppm and CO have proven to be a viable route to synthesizing palladium-CO-dppm complexes, there are still some related points that require further investigation:

(1) What are the 2 unidentified compounds (with singlets at δ 14 and 15) that appear as decomposition products of **3**?

(2) The chemistry of complex **3** was not investigated in this work. How would **3** react when treated with S^{2-}, halide, CO, etc.? What are, if any, the catalytic properties of **3**?

(3) Would a ^{13}CO exchange reaction with complex **4a** give any insight into its structure?

(4) Rapid addition of $NaBH_4$ to mixtures of Pd^{4+} and dppm saturated with CO yields $Pd_2(\mu\text{-dppm})_3$, **2**, at room temperature. What would happen if the rapid addition

occurred at low temperatures? That is, will palladium catalyze P-C bond cleavage in dppm at low temperatures?

(5) A variety of heterobimetallic compounds containing palladium are known. Is it possible to synthesize these compounds by reducing mixtures of palladium and other metal salts in the presence of dppm and CO? Is it possible to synthesize new heterobinuclear compounds using this method?

(6) $Pd(OAc)_2$ has been used as a precursor in various reactions involving the synthesis of palladium-CO-dppm compounds. What would happen if this palladium salt was used (instead of K_2PdCl_6) in the reactions involving reductions in the presence of dppm and CO?

(7) $NaBH_3CN$, a milder reducing agent than $NaBH_4$, may aid in the isolation of reaction intermediates leading to the formation of the palladium-CO-dppm complexes reported in this thesis. What would happen if the more active reducing agent, $LiBH_4$, were to be used?

(8) A conductance measurement of compound **4a** would prove whether or not it is ionic and, as well, give the ionic ratio of the complex.