REACTIONS OF Ni(II) WITH $NaBH_4$ AND $NaBH_3CN$ IN THE PRESENCE OF MONO-AND BIDENTATE PHOSPHINES UNDER CO ATMOSPHERE

BY

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DEDICATED

TO

MY PARENTS

AND

MY BROTHER MUBARAK

Abstract:

Phosphine-substituted carbonyl complexes of Ni have been prepared.

The reaction between $NiCl_2.6H_2O$, $NaBH_4$ or $NaBH_3CN$ and either PPh_3 or a series of phosphines of the type $Ph_2P-(CH_2)_n-PPh_2$ (n=1-5) and also *cis*-dppe under CO atmospheres have been studied under a range of experimental conditions. The important factors which affect the reaction pathways are; the ratio of metal: phosphine: $NaBH_4$ or $NaBH_3CN$, the rate of addition of reducing agent, the temperature and the duration of reaction.

Complexes with bridging and monocoordinated dppm were obtained, while with dppe, complexes with bridging, chelating and monocoordinated phosphine were obtained.

Hetero and homobimetallic complexes have been prepared from mono-coordinated *bis*-phosphine complexes and were characterized by a variety of spectroscopic methods, by X-ray powder diffraction and in one instance by a single crystal X-ray diffraction study.

The reactivity of the metal-metal bonded species $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ towards insertion and oxidative addition was studied.

Cleavage of a P-C bond in dppm has been observed under very mild conditions and leads to the production of a phosphido complex.

The other ligands dppp, dppb, dpppe and *cis*-dppe have produced several additional complexes for which preliminary data are reported.

The important factors influencing the reaction pathways, the difficulties encountered in the isolation of some of the complexes and the characterization of these phosphine substituted metal carbonyls are discussed in detail.

Acknowledgement:

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Abbreviations:

Me.	methyl.
Et.	ethyl.
Pr^i.	isopropyl.
Bu^n.	n-butyl.
Ph.	phenyl.
Cy.	cyclohexyl.
Ph.	phenyl.
MeOH.	methanol.
EtOH.	ethanol.
PPh_3.	triphenylphosphine.
dppm.	_bis_(diphenylphosphino)methane.
dppe.	1,2-_bis_(diphenylphosphino)ethane.
dppp.	1,3-_bis_(diphenylphosphino)propane.
dppb.	1,4-_bis_(diphenylphosphino)butane.
dpppe.	1,5-_bis_(diphenylphosphino)pentane.
cis- and _trans_-dppe.	1,2-_bis_(diphenylphosphino) ethylene
PCy_3.	tricyclohexyl phosphine.
$P(o\text{-tolyl})_3$.	tri-o-tolylphosphine.
THF.	Tetrahydrofuran.
Arphos.	$Ph_2P(CH_2)_2AsPh_2$.
tedip.	$(EtO)_2POP(OEt)_2$.
dmpm.	_bis_(dimethylphosphino)methane.

dpme.	1,1,1-tris(diphenylphosphino methyl)ethane.
dmpe.	1,2-bis(dimethylphosphino)ethane.
dmdepe.	$Me_2P(CH_2)_2PEt_2$.
dmdppe.	$Me_2P(CH_2)_2PPh_2$.
Cp.	cyclopentadienyl.
bipy.	2,2'-bipyridyl
COD.	1,5-cyclooctadiene.

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1. Introduction:

1.1. General Remarks:

The study of transition metal complexes where carbon monoxide groups are present as ligands has been, and still remains, one of the most active and productive areas of chemical research. Earlier work was mainly devoted to the synthesis and the study of binary metal carbonyl compounds, and it is interesting to note that the discovery of the first metal carbonyl, $Ni(CO)_4$, was made by Mond and coworkers as long ago as 1890.[1,2,3] Since then, numerous other binary metal carbonyls have been discovered. These compounds possess many interesting properties such as high volatility, high chemical reactivity and the ability to form numerous derivatives. In addition, carbon monoxide has the very important property of being able to stabilize metals in low positive, zero or even negative oxidation states. The reason for this is generally attributed to the synergic effect, which is the transfer of electron density from the carbon of the CO group to the empty metal d orbitals of appropriate symmetry, forming a σ bond and the back donation of the excess of electron density from the filled metal d orbitals to the π^* orbitals of the CO group thereby forming a π-bond.[1,2,4] This mechanism is considered to be crucial in removing negative charge from the metal atom.

A major consequence of the back donation of electron density from metal d orbitals to the π^* orbitals of the CO is the reduction of the CO bond order. Infrared spectroscopy is particularly convenient for detecting this phenomenon.

With few exceptions, all of these compounds obey the effective atomic number rule (EAN) by forming eighteen electron systems. Metal - metal bonding is common, particularly with di- and polynuclear complexes formed by metals with odd atomic number.

As a ligand, CO is very versatile and can coordinate in several different ways as shown in Fig.1 in which the terminal carbonyl is shown in (a), while (b),(c) and (d) represent CO groups bridging two or three metals respectively. The bridging can be unsymmetrical, as in (b), or symmetrical as in (c) or (d). Parts (e)-(k) show CO groups in which the oxygen of the CO ligand is also involved in bonding to one or

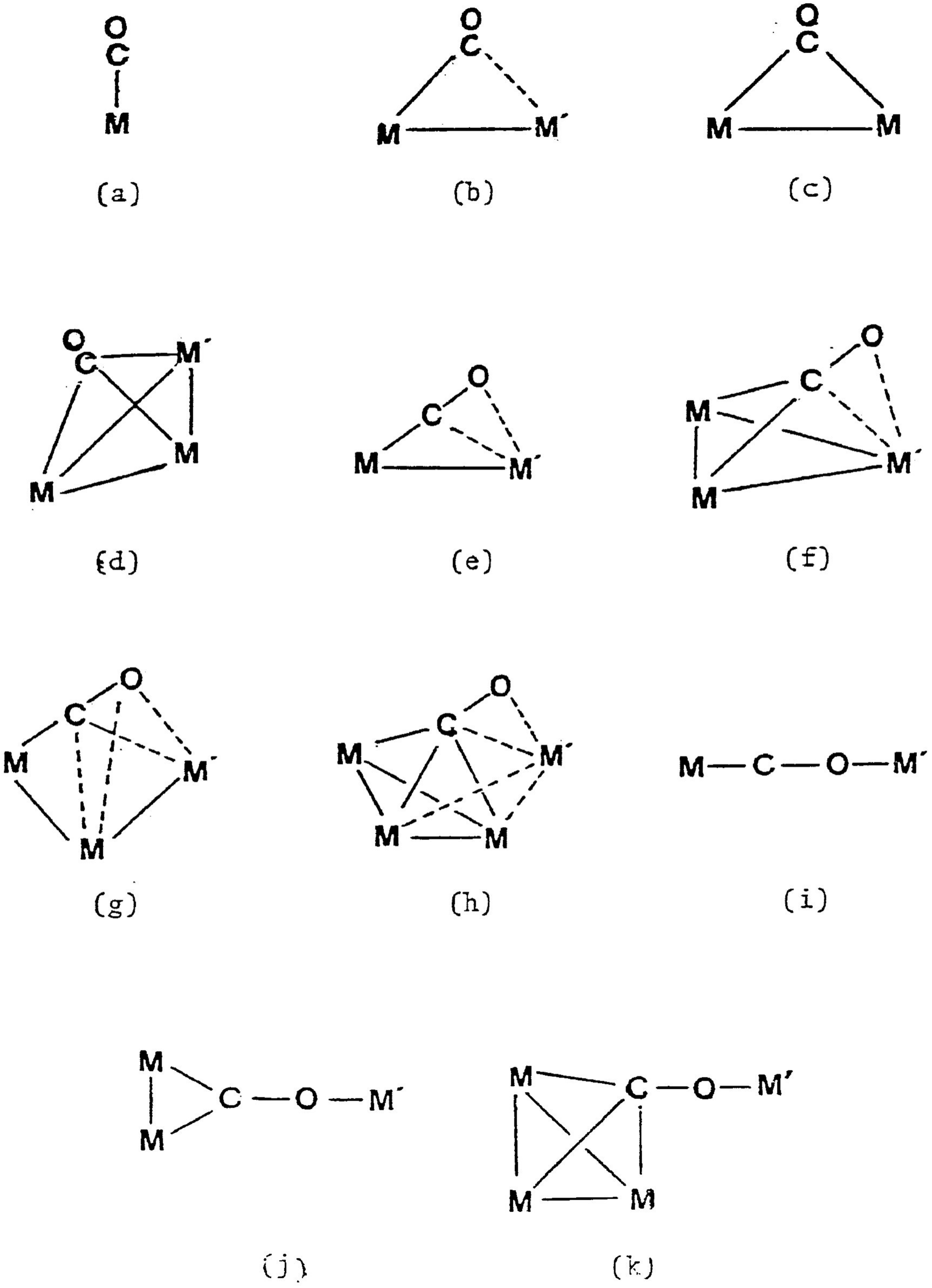


Fig. 1.

two metal centers.[4,5,6] This mainly occurs in substituted carbonyl derivatives or carbonyl anions. The last three examples, (i),(j) and (k) show essentially end-on arrays and these generally occur when strong oxygen acceptors such as $AlEt_3$ are available.[5,6]

Substitution reactions of the type shown in equation [1] are an important part of metal carbonyl chemistry and may occur (i) simply by mixing together the carbonyl and the appropriate ligand,[7] (ii) by the input of thermal or photochemical energy[8-10] or (iii) by electrochemical methods.[11]

$$M(CO)_x + yL \longrightarrow M(CO)_z L_y + (x-z)\, CO \qquad [1].$$

Examples of each method are listed in Table [1], which, for the sake of clarity, illustrates mostly phosphines as displacing ligands even though a wide range of ligands has been used for these reactions.

Phosphine ligands have played a significant role in the development of modern coordination chemistry and more recently in the development of homogeneous catalysis.[12,13] Many of these phosphine ligands are relatively easy to synthesize (some

Table [1].

Examples of substitution reactions in metal carbonys by phosphine ligands.

reactants		products	ref.
$Ni(CO)_4 + P(OEt)_3$	$\xrightarrow{}$	$Ni(CO)_3\{P(OEt)_3\}$	7
$Co_2(CO)_8 + 2PPh_3$	$\xrightarrow{}$	$Co_2(CO)_6(PPh_3)_2$	7a
$Ru_3(CO)_{12}$ + dppm	$\xrightarrow{\text{heat}}$	$Ru_3(CO)_{10}(dpp_m)$	8
$Cr(CO)_6$ + dppe	$\xrightarrow{\text{heat}}$	$Cr(CO)_4$(dppe)	10
$Cr(CO_6)$ + dmpe	$\xrightarrow{\text{heat}/h\nu}$	$Cr(CO)_2(dmpe)_2$	10b
$Ru_3(CO)_{12} + P(OMe)_3$	$\xrightarrow{h\nu}$	$Ru_3(CO)_{11}\{P(OMe)\}$	9
$Re_2(CO)_{10}$ + dppe	$\xrightarrow{h\nu}$	$Re_2(CO)_8$(dppe)	9b
$Mo(CO)_6 + PMe_3$	$\xrightarrow{\text{Al anode}}$	$Mo(CO)_5(PMe_3)$	11
$Mo(CO)_6$ + dmpe	$\xrightarrow{\text{Al anode}}$	$Mo(CO)_4$(dmpe)	11

are commercially available), and their steric and electronic features can be systematically varied by changing the substituents on the phosphorus atom(s) or by varying the backbone length between the phosphorus atoms[14],[15]. Details of the steric and electronic effects on transition metal complexes resulting from changing substituents on the phosphorus atom in phosphine ligands have been described elsewhere.[16]

The characterstics of phosphines as ligands are related to those of CO (and the isocyanides). The phosphorus atom has a pair of electrons which forms a strong metal-σ bond . In addition, it has empty 3d orbitals which can accept electron density from the metal[17,18] as shown in Fig.2. Potentially therefore, phosphines combine the properties of strong σ donors (as in amines) with those of good π- acceptors (such as CO) although the extent to which the synergic effect and π-bond formation occurs in metal phosphine complexes is a controversial matter.[18-21] The 3d orbitals on phosphorus are much too diffuse and high in energy to interact effectively with the more compact metal nd orbitals. Furthermore, if the metal is in a positive oxidation state then this π- interaction would be further diminished; the higher effective nuclear charge further

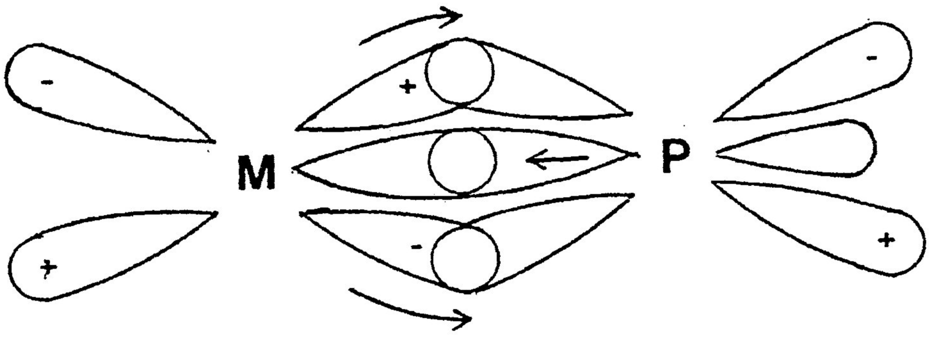


Fig. 2.

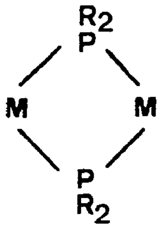
contracts the metal nd orbitals. Thus, electro negative substituents such as F or OPh on phosphorus would increase the effective nuclear charge on phosphorus and contract the 3d orbitals. Such an effect at the same time reduces the basicity of the lone pair on phosphorus. On the other hand, a substituent such as CH_3 on phosphorus would have the opposite effect. It has been shown[19] that the π-acceptor ability of phosphines increases in the following order, $P(t\text{-}Bu)_3 < PR_3 \sim PPh_3 < P(OR)_3 < PH_3 < P(OPh)_3 < PF_3$ while the σ donor ability is in the approximately reverse order.

In addition to monodentate ligands, phosphines occur as polydentate ligands[17] forming a large variety of structural products with metal ions. Of particular interest are bidentate ligands of the type $R_2P(CH_2)_nPR_2$ in the context of the work described later in this thesis. These bidentate ligands are often used[22] to stabilize two metal atoms by binding them together. In addition these ligands also allow isolation and characterization of intermediate products formed in these reactions.[23] Moreover, these bidentate phosphine ligands can coordinate through only one of the phosphorus atoms, leaving the other phosphorus atom dangling, resulting in the formation of reactive species. The potential of such complexes in forming homo and hetero-nuclear bimetallic complexes has recently been recognised[24]. The binuclear complexes formed using phosphines in which n=1 possess some particularly interesting properties such as the unusual coordination of small molecules,[25,26] the ability to initiate catalytic transformations[26,25] and often the formation of metal-metal bonds.[27,28] The well documented coordination modes for these ligands are shown in Fig.3.

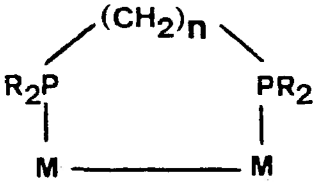
In catalytic systems, an important aspect is the control of the reactivity of the metal center(s). Thus, binuclear complexes provide better control of the reactivity of these systems, since the presence of two metal atoms may facilitate multi-electron redox reactions which could not be carried out by only a single metal atom.[29] Another novel method of changing reactivities of these catalytic systems is by having different metal atoms in the same molecule[30] which results in a different electron population on two metals in the same complex thus causing variable reactivities. The importance of such systems has been recognized only recently and is evident from the synthesis of a large number of such compounds in recent years.[31] More will be said later in the discussion section.

1. Monodentate $M\text{-}R_2P(CH_2)_nPR_2$

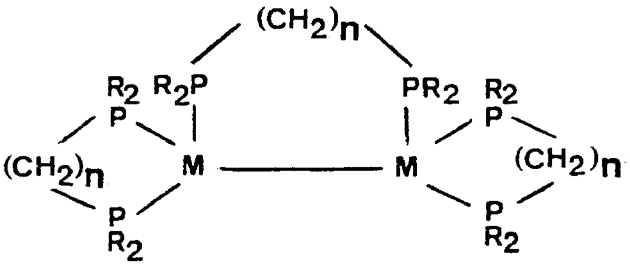
2. Chelating



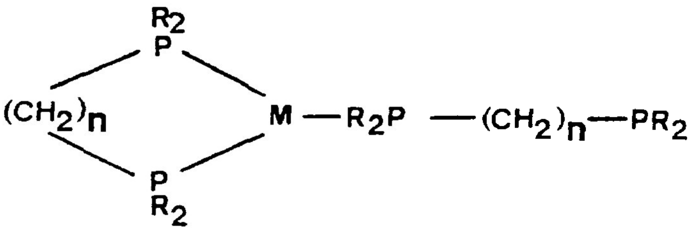
3. Bridging



4. Chelating-bridging



5. Chelating - monodentate



6. Bridging-monodentate

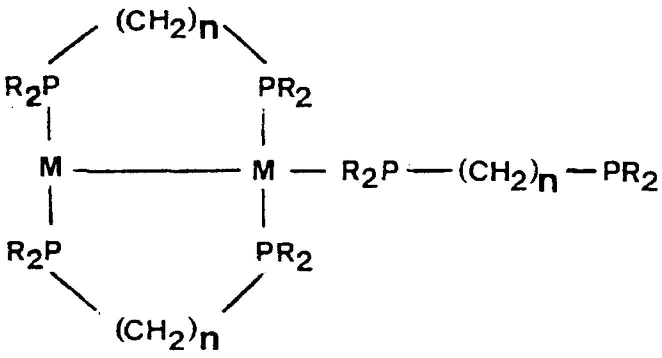


Fig. 3.

Since this thesis is mainly concerned with metal complexes containing carbon monoxide and phosphine ligands, the vast majority of which have been made according to equation [1], the main part of this introduction is organized into three sections. The first is a very brief survey of simple metal carbonyls followed by a survey of phosphine-substituted carbonyl complexes. The latter is further divided into three sections, dealing first with mono phosphines followed by bis phosphines and concluding with a discussion of bimetallic systems. Due to the vast number of such complexes in the literature, a discussion of these complexes will be restricted to some representative and interesting examples. The last section will briefly outline the objectives of the work to be described in this thesis.

1.2. Transition metal complexes containing only CO as ligands.

1.2.1. Ti, Zr and Hf:

No binary metal carbonyl has so far been reported for this triad .

1.2.2. V, Nb and Ta:

Dimeric species of the type $M_2(CO)_{12}$, without any structural details, have been reported for this triad.[32] $V(CO)_6$ is the only neutral, stable binary carbonyl isolated and characterized. It is an air-sensitive , paramagnetic solid with a single νco in the solution i.r. spectrum at 1973 cm^{-1} and has an octahedral structure.[33,34]

1.2.3. Cr, Mo and W:

All three metals form carbonyls (with closely related properties) of the type $M(CO)_6$, which are listed in the Table [2]. Studies on $Cr(CO)_6$ show a single νco in the i.r. spectrum at 2000 cm^{-1} in the gaseous phase[35] and a single resonance at δ 212.1 in the ^{13}C n.m.r spectrum[36] consistent with an octahedral structure. This has been confirmed by a variety of diffraction experiments.[37-41] Studies on $Mo(CO)_6$ and $W(CO)_6$ have shown similar results.

1.2.4. Mn, Tc and Re:

The simplest, structurally isomorphous,

Table [2].

Binary metal carbonyls:

complex	colour	methods of syntheses	ref.
$V(CO)_6$	blue-black	VCl_3,Na,CO,diglyme 160°C	2,94
$Cr(CO)_6$	Colourless	$CrCl_3$,Na,CO,diglyme naphthalene	2,94
$Mo(CO)_6$	Colourless	$MoCl_5$,Et_3Al,CO	2,94
$W(CO)_6$	Colourless	WCl_6,Et_3Al,CO	2,94
$Mn_2(CO)_{10}$	Yelow	$MnCl_2$,Ph_2CONa,CO, (200-700atms),200°C	2,94
$Tc_2(CO)_{10}$	Colourless	Tc_2O_7,CO,(300atms) 220°C	2,88
$Re_2(CO)_{10}$	Colourless	Re_2O_7,CO,250-270°C (200-250atms)	2,88
$Fe(CO)_5$	Yellow	Fe,S(Catalytst),CO	2,88
$Ru(CO)_5$	Colourless	$Ru(acac)_3$,CO,H_2, heptane or MeOH,150°C 200atms.	2,88
$Os(CO)_5$	Colourless	OsO_4,CO,heptane	2,88
$Fe_2(CO)_9$	Golden-Yellow	$Fe(CO)_5$,glacial acetic acid UV.	2,88
$Ru_2(CO)_9$	Orange-Brown		4,47
$Os_2(CO)_9$	Yellow-orange	$Os(CO)_5$,U.V.	
$Fe_3(CO)_{12}$	Black	$Fe(CO)_5$,Et_3N-H_2O,MeOH	2,88
$Ru_3(CO)_{12}$	Orange	$RuCl_3.3H_2O$,CO,MeOH	2,88
$Os_3(CO)_{12}$	Yellow	OsO_4,CO,MeOH	2,88
$Os_5(CO)_{16}$	Pink-Red	Vacuum Pyrolysis of	60,96

		$Os_3(CO)_{12}$, 210°C,12 hrs.	
$Os_5(CO)_{19}$	Orange	$Os_6(CO)_{18}$,CO,90 atms., heptane, heat.	62,63
$Os_6(CO)_{18}$	Dark-Brown	Vacuum Pyrolysis of $Os_3(CO)_{12}$ 210°C	60,96
$Os_6(CO)_{20}$	Purple	$Os_6(CO)_{18}$, CO, heat	63
$Os_7(CO)_{21}$	Orange-Brown	Vacuum Pyrolysis of $Os_3(CO)_{12}$, 210°C	60,96
$Os_8(CO)_{23}$	Orange-Yellow	Vacuum Pyrolysis of $Os_3(CO)_{12}$	60,96
$Co_2(CO)_8$	Orange red	(i) $CoCO_3$,CO,H_2,Petroleum ether, 150-160°C (ii) $CoCl_2$, Li,Naphthalene, CO.	88,94
$Rh_2(CO)_8$	Orange	Rh, CO	2,88
$Ir_2(CO)_8$	Yellow-Green	$IrCl_3$,Cu,CO	2,88
$Co_4(CO)_{12}$	Black	$Co_2(CO)_8$,heat	88,94
$Rh_4(CO)_{12}$	Red	$[Rh(CO)_2Cl]_2$, CO,Hexane, $NaHCO_3$,20°C	88,94
$Ir_4(CO)_{12}$	Yellow	$IrCl_3.3H_2O$,CO,MeOH	88,94
$Co_6(CO)_{16}$	Black	(i) Oxidizing$[Co_6(CO)_{15}]^{2-}$, (ii) $K_2[Co_6(CO)_{15}]$;HgCl,NaCl	84
$Rh_6(CO)_{16}$	Black	$RhCl_3.3H_2O$,MeOH	88,94
$Ir_6(CO)_{16}$	(i)Red-Brown	$[Ir_6(CO)_{15}]^{2-}$,$2H^+$,CO, HOAc.	87,95
	(ii) Black	$[Ir_6(CO)_{15}][Me_4N]_2$, CF_3COOH	87
$Ni(CO)_4$	Colourless	Ni,CO.	88,94

metal carbonyls from this subgroup have the formula $M_2(CO)_{10}$ [M = Mn, Tc or Re] and are listed in Table [2]. The compounds consist of two metal-metal bonded $M(CO)_5$ units whose radial carbonyl groups are in a staggered conformation with D_{4d} symmetry, as shown by an X-ray diffraction study on $Mn_2(CO)_{10}$.[42-43] The equatorial carbonyls on each metal are slightly bent towards each other to minimize the steric repulsions of axial and equatorial groups on each metal.

1.2.5. Fe, Ru and Os:

There is a large variety of binary metal carbonyls known for these metals. The simplest compounds are $M(CO)_5$,$M_2(CO)_9$ and $M_3(CO)_{12}$ [M=Fe, Ru or Os]. In addition, many complex, high-nuclearity carbonyls, particularly of osmium, are known, which are also listed in Table [2].

The simplest $M(CO)_5$ carbonyls have some common features. For example, they are colourless, volatile liquids (except iron) and have two i.r active bands of A_2'' and E_1' symmetry consistent with a trigonal bipyramidal geometry with D_{3h} symmetry. X-ray diffraction studies on $Fe(CO)_5$ confirm this and show that the axial and equatorial Fe-C lengths are essentially equal.[44]

The structure of $Fe_2(CO)_9$ shows the molecule to have approximately D_{3h} symmetry with the carbonyl carbon atoms in a distorted octahedral array around the iron atoms. Three CO ligands bridge the two metal centers, each iron atom has three terminal CO groups and an Fe-Fe bond completes the 18 electron count on each iron atom.[45] Detailed i.r. and Raman studies are consistent with the assigned structure [46] shown in Fig 5. The structure <u>2</u>, as shown in Fig 5, of $Os_2(CO)_9$ and $Ru_2(CO)_9$ is different from that of $Fe_2(CO)_9$,[47] and follows the general tendency that carbonyl ligands prefer terminal coordination positions with second and third row transition metals.[48]

Structural differences are also observed for the $M_3(CO)_{12}$ compounds in that $Fe_3(CO)_{12}$ consists of a triangle of iron atoms, two of which have three terminal carbonyls and are bridged by two by CO ligands in an asymmetric fashion. The remaining iron atom has only four terminal CO groups as shown[49-50] in Fig.5. In contrast, the structures of $Ru_3(CO)_{12}$[51-52] and $Os_3(CO)_{12}$[53] consist of triangular cluster of D_{3h} symmetry with only terminal CO groups in Fig.7.[54,67] There are six equatorial CO groups in the M_3 plane and six axial

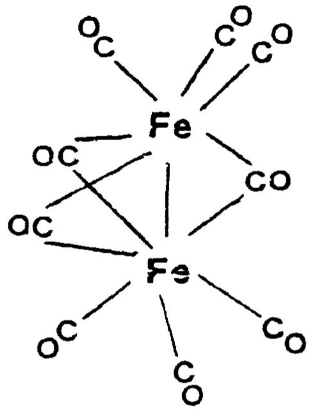


Fig. 4.

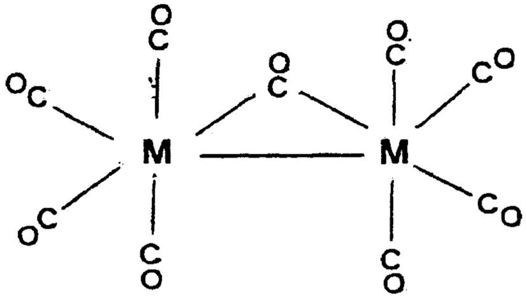
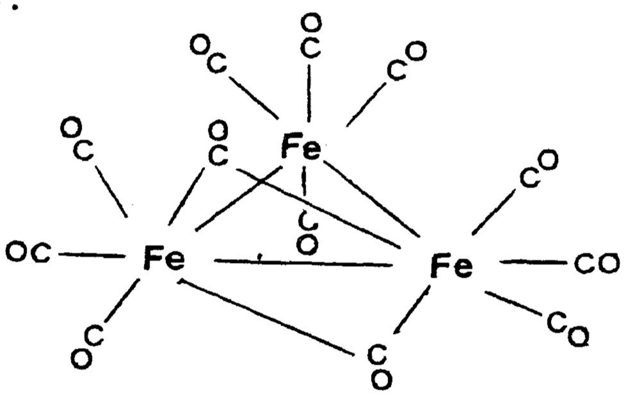


Fig. 5.



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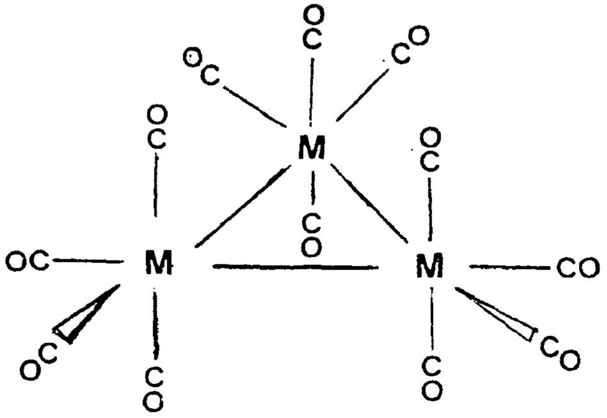


Fig. 7.

groups, with the axial M-C bonds being longer then the equatorial M-C bond.

In solution, ^{13}C n.m.r. studies show that the molecule is fluxional.[55-57] Structural differences between $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $OS_3(CO)_{12}$ have been rationalized in terms of the size of the cavity formed by the polyhedron from twelve CO groups. The Ru_3 and Os_3 triangles fit within the cubo octahedron found in these molecules while the icosahedron found for $Fe_3(CO)_{12}$ is only sufficient for the Fe_3 cluster.[58-59]

Several high-nuclearity clusters of osmium have also been prepared and characterized, including $Os_5(CO)_{16}$,[61] $Os_5(CO)_{19}$,[62] $Os_6(CO)_{18}$,[64,65] $Os_6(CO)_{20}$,[63] $Os_7(CO)_{21}$[64,66] and $Os_8(CO)_{23}$.[60,64]

$Os_5(CO)_{16}$ and $Os_5(CO)_{19}$ present the first examples of two binary carbonyls containing the same number of metal atoms from a particular element and having a different number of carbonyl ligands. The only other example in the literature is $Os_6(CO)_{18}$ and the complex $Os_6(CO)_{20}$ of unknown structure.[63]

1.2.6. Co,Rh and Ir:

Binary metal carbonyls from this subgroup are listed in Table [2], and can be generallized by the formula $M_2(CO)_8$,$M_4(CO)_{12}$ and $M_6(CO)_{16}$ {M=Co,Rh and Ir}. Of the dinuclear compounds, $Co_2(CO)_8$ is the most stable and exists in three isomeric forms, as shown in Figure.8 a,b and c. In one form,a,there are two bridging carbonyls with a Co-Co bond length of 2.52Å. The other two nonbridging isomers b and c exist in equilibrium with the bridging form in solution.[68-69] Very recent high pressure ^{13}C n.m.r. studies confirm the fast intramoleculer site exchange process between the CO ligands[70] as suggested earlier.[71] All three forms have been identified by i.r. spectroscopy in an argon matrix and both i.r. and Raman studies show that the amounts of the non-bridged isomers increases with increasing temperature.[72] It is interesting to note that in this group, the much less stable compounds $Rh_2(CO)_8$ and $Ir_2(CO)_8$ have been assigned structures analogous to that of the bridging form of $Co_2(CO)_8$ on the basis of i.r.[73] and electronic spectral results.[74]

For the $M_4(CO)_{12}$ systems, $Co_4(CO)_{12}$[75] and $Rh_4(CO)_{12}$[76] have similar structures, based on a tetrahedron of metal atoms. One metal atom has three terminal CO ligands while the other three metal atoms

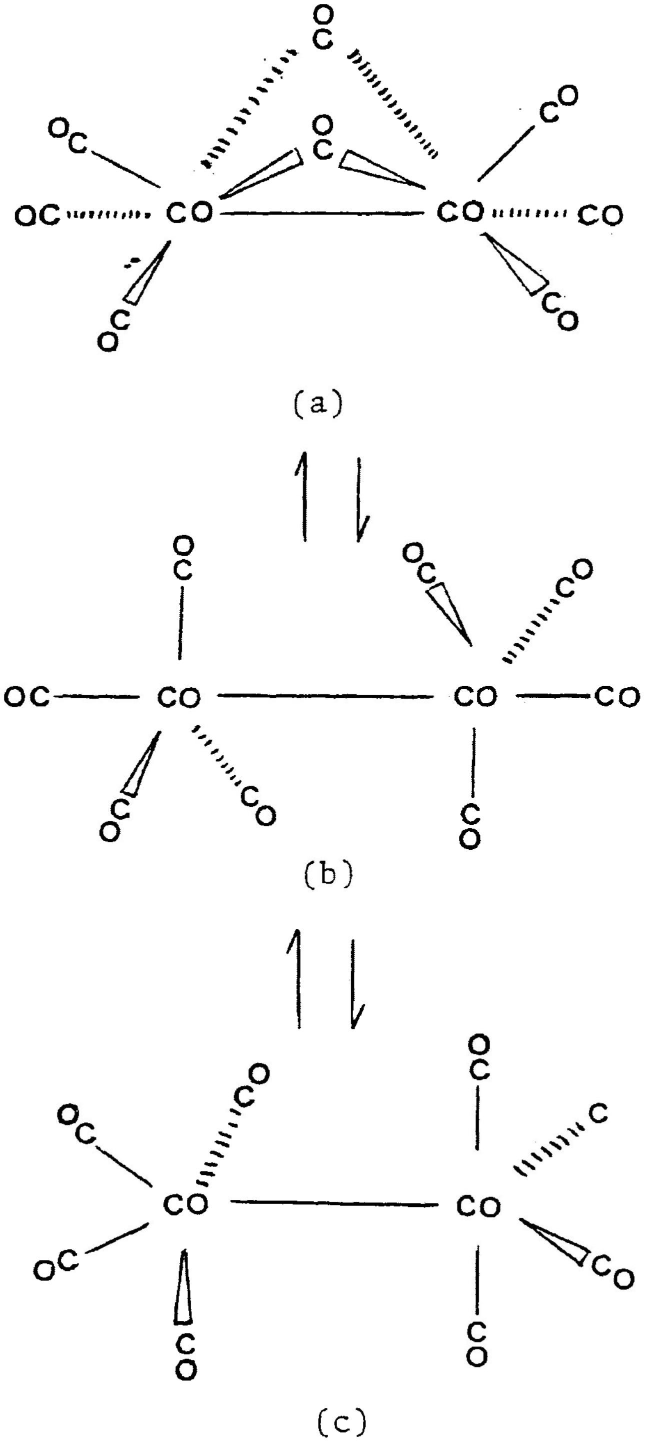


Fig. 8.

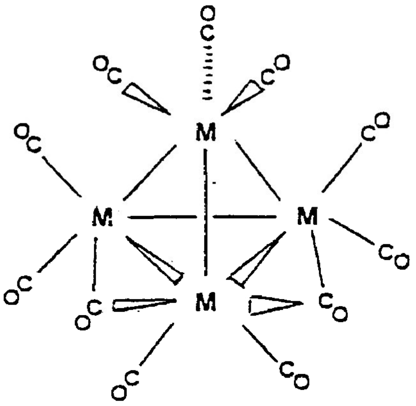


Fig. 9.

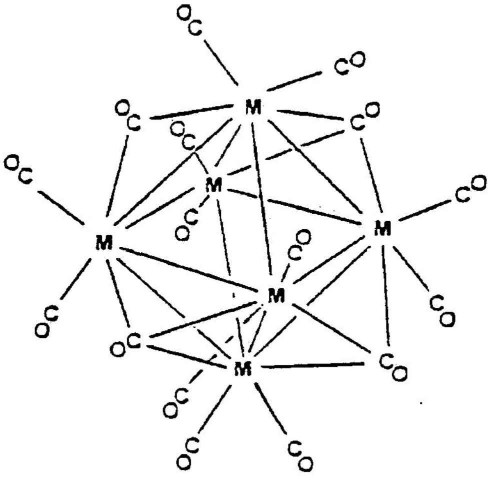


Fig. 11.

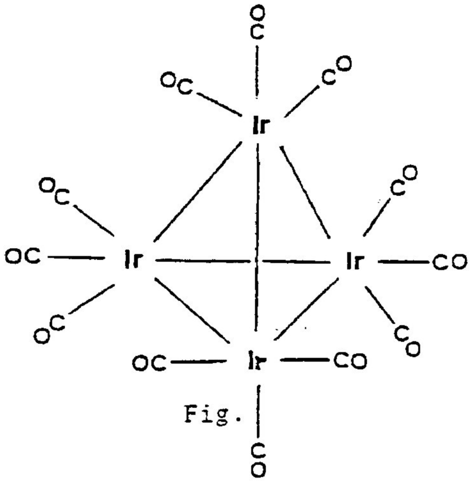


Fig. 10.

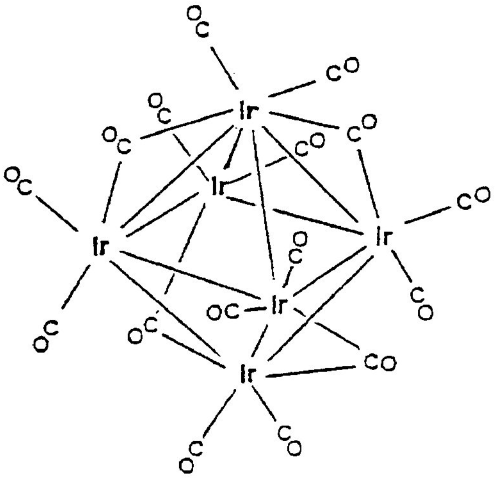


Fig. 12.

each have two terminal CO ligands. Three doubly bridging CO groups span three edges of the tetrahedron[81-83], as shown in Fig.9. In solution, ^{13}C n.m.r. studies show that the molecule(s) are fluxional.[77,78]

In contrast, $Ir_4(CO)_{12}$ has a different structure consisting of a regular tetrahedron of iridium atoms with all the carbonyl ligands terminally coordinated[79,80] as shown in Fig.10.

Turning now to the $M_6(CO)_{16}$ systems, $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$ have analogous structures based on an octahedron of six metal atoms, twelve terminal and four face-bridging carbonyl groups[84-86] as shown in Fig.11. Two isomeric forms of $Ir_6(CO)_{16}$ have been isolated. The red isomer is isostructural with $Rh_6(CO)_{16}$, described above, while a black isomer has (asymmetrically bonded) four edge-bridging carbonyl groups in addition to twelve CO groups[87] as shown in Fig.12. The Ir-Ir bond distance in both isomers is found to be essentially the same. Structural comparison of the two isomers shows that the set of four face-bridging carbonyls of the red isomer become edge-bridging in the black isomer.[87]

1.2.7. Ni,Pd and Pt.

From this subgroup, only nickel is known to form stable binary carbonyls. In fact $Ni(CO)_4$ is the first isolated binary carbonyl reported in 1890 by Mond and coworkers[1,2]. It is a colourless, volatile and extremely toxic liquid which decomposes at ~35°C. Gas-phase electron diffraction shows that the molecule has a tetrahedral geometry[88] and there is a net transfer of electron density from nickel to the CO groups, resulting in a small positive charge on nickel.[90] It has nine fundamental vibrations ($2A_1$, 2E, $4T_2$ and $1T_1$), eight of which are Raman-active (A_1, E and T_2), four are i.r. active (T_2) while one is inactive(T_1)[88,90,91]

Palladium is the most reluctant member of this triad to form carbonyl complexes while platinum shows behaviour intermediate between that of nickel and palladium[92]. This reluctance of palladium and platinum to form binary carbonyls has been rationalized in terms of the synergic effect involved in the bonding of metal carbonyls, which has σ and π components as discussed earlier. The ability of a metal to donate electron density to the π^* orbital of CO is closely related to its ionization potential. The first ionization potentials of nickel, palladium and platinum are 5.81, 8.33 and 8.20 eV respectively giving the π-back donation ability in the order of Ni>>Pt>Pd.[92,93] Parallel to this are the relative stabilities of zero valent metal carbonyl complexes which is best illustrated by metal-carbonyl force constants which are in the order $F_{Ni-C} > F_{Pt-C} > F_{Pd-C}$.[93] These trends are consistent with the observations that palladium is the most reluctant to form binary carbonyls from this subgroup.

1.3. Phosphine substituted transition metal carbonyl complexes.

1.3.1. Sc, Y and La:

No phosphine-substituted carbonyl complexes have been prepared from this triad so far.

1.3.2. Ti, Zr and Hf:

Only a few phosphine substituted carbonyl complexes have been prepared from this subgroup. They are listed in Table.[3].

Sikora et.al.[98] have reported that metallocene dicarbonyls from this subgroup readily undergo photochemically induced substitution reactions,

Table [3].

Phosphine substituted metal Carbonyl Complexes of Ti,Zr and Hf:

Complexes	Metal	Method of syntheses and comments		Ref
$MLX_2(PR_3)$	Ti,Hf	$D^{a,b}$	R=Me,Ph,MePh$_2$,F;X=Cp	97,98
$MLX_2(P-P)$	Zr;Hf	C,D^a	P-P=dppe,dmpe;X=Cp,C_4H_6	98,99
$ML_2X(P-P)_2$	Ti	E	P-P=dmpe;X=PF_3	101
$ML_3(P-P)_2$	Ti	C,F^c	P-P=dmpe;depe	97,98,101

Conditions:

A: ML + Y; B: MY + L; C: MXY + L. D: MLX + Y; E: MLY + X; F: MX + Y or L or both G: MLY + Y or L or both; H: MLY + R or X or both; I: MLXY; J: By some other methods; a= hν; b= heat or reflux; c= reducing agent used; d= CO releasing agent used or CO gas used; e= Z releasing agent used; L= CO; M= Metal; Y= Phosphine ligand.

These conditions also apply to Tables 4-9.

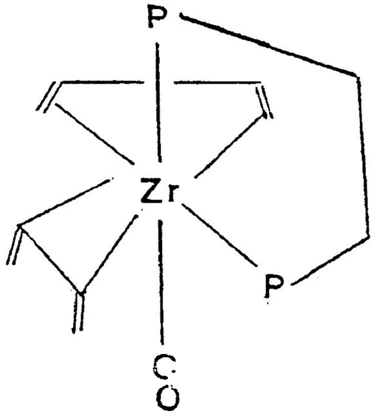


Fig. 13.

Zr and Hf derivatives being more photolabile than the Ti analogue. Thus, on photolysis of $Hf(CO)_2(Cp)_2$ in the presence of an excess of PPh_3 at $10^{\circ}C$, facile displacement of a CO ligand occurs over 4 hrs, resulting in the formation of a monocarbonyl complex characterized by elemental analysis, and i.r. and n.m.r. spectra as $Hf(CO)(Cp)_2(PPh_3)$. However, a similar reaction carried out under refluxing conditions does not proceed even after 21 hrs. It has also been noted that when the chelating ligand dppe is used under photochemical conditions, only the monosubstituted derivative, characterized as $Hf(CO)(Cp)_2(\eta^1$-dppe), is obtained.

Relatively recently, Wreford and coworkers[101] have reported the reduction of $TiCl_4.2THF$ with sodium amalgam in the presence of dmpe and 1000 Psig CO. This results in the formation of a red complex, formulated largely on the basis of analytical data as $[Ti(CO)_3(dmpe)_{1.5}]_n$. However, an X-ray diffraction study[100] later revealed that the molecule is a seven-coordinate, monomeric complex with a monocapped octahedral geometry, having significant distortion from the idealized geometry. In addition, this compound is reported as being non-rigid and it also undergoes a reversible dissociation of CO[100] as shown below.

$$\mathrm{Ti(CO)_3(dmpe)_2} \quad \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftharpoons\!=\!=\!=\!=\!=\!=\!=\!=}} \quad \mathrm{Ti(CO)_2(dmpe)_2} + \mathrm{CO}$$

On treatment with PF_3, this tricarbonyl complex can readily be converted into $Ti(CO)_2(PF_3)(dmpe)_2$ which has been characterized by i.r. and X-ray crystallography as a seven-coordinate complex with two chelating dmpe ligands.[101]

Reduction of $ZrCl_4(dmpe)_2$ in the presence of 1,3-butadiene with sodium amalgam produces purple crystals of an interesting diphosphine_bridged dimer $\{Zr(dmpe)(\eta^2-C_4H_6)_2\}_2dmpe$[77]. This complex was reacted with CO at $-78^\circ C$ to yield $Zr(CO)(dmpe)(\eta^2-C_4H_6)_2$ which has been characterized by spectroscopic data (i.r., ^{31}P and ^{13}C n.m.r.) as a seven-coordinated pentagonal bipyramidal structure with an approximately linear P-Zr-CO axis as shown in Fig13.

1.3.3. V, Nb and Ta:

Several phosphine substituted complexes have been prepared from this subgroup, and are listed in Table.4. These complexes can conveniently be generalized

Table [4].

Phosphine substituted metal carbonyl complexes of V,Nb and Ta:

Complexes	Metal	Method of syntheses and comments		Ref
$ML(Cp)X(PR_3)$	V	E^a	X=PhC≡CPh;R=Ph	102
$ML(C_5Me_5)XY(PR_3)_2$	Ta	C	X=Y=H;R=Me;X=Cl,Y=H	103
$ML_2Y(PR_3)_2$	V,Ta	D,C	$Y=C_5H_5,C_5Me_5$ $R=Me,Bu^n,Et_2Ph$	103,104
$ML_2(C_5Me_5)XY(PR_3)$	Ta	C	X=Cl,Y=H;R=Me	103
$ML_3(Cp)(PR_3)$	V,Nb	D^a	$R=H,Bu^n,Et_2Ph,Cy,Ph$	102,104 107
$ML_4(PR_3)_2$		A	$R=OMe,Ph,Ph_2H,PhH_2,$ Et,Pr,Cy	108, 126
$M_2L_4(Cp)_2(PR_3)$	V	D	R=Ph	104
$ML_4X(PR_3)$	V	H,D	$X=NO;R=Me,Me_2H,OMe$	123
$ML_5(PR_3)$	V	A	R=Ph	109,110 124
$[ML_5(PR_3)][NEt_4]$	V,Nb, Ta	$A^{a,c,e}$	$R=Et,Bu^n,Ph,OMe$	108,109 110,111 122
$ML_5Y(PR_3)$	V,Nb, Ta	A	$Y=SnPh_3,NO;R=Me_2H,$ Bu^n,Ph,OMe,OPh	111,112 123
$MLRX_2(P-P)$	Nb,Ta	C^a, D,E	$R=C_5H_5,C_5Me_5;X=Cl,Br,I$ P-P=dmpe	103,114
$ML_2(P-P)_2$	V	A^a	P-P=dppe,dmpe;	115,129
$ML_2R(P-P)$	V,Nb,	F^c	P-P=dppm,dppe,dmpe, $R=R'(p-C_6H_4NMe_2)_2,R'Ph_2$	103,114

			R´Me$_2$,R´(p-C$_6$H$_4$OMe)$_2$, C$_5$H$_5$,C$_5$Me$_5$; R´=C$_5$H$_4$CH	
	Ta		*cis*-dppee,dppp,arphos, dpppe	116,125 127,128
[ML$_2$(P-P)$_2$][Z]	Ta	C^c	P-P=dmpe; Z=Na	117
[ML$_2$(Cp)X(P-P)][Z]	Nb	G^e	X=H,Z=PF$_6$ P-P=dppe,dmpe	114
ML$_2$X(P-P)$_2$	V,Ta	C^b,H	X=2,H,Cl,Br,I,CN,Me, CF$_3$CO$_2$,PhPO$_2$H,NH$_2$SO$_3$,N$_3$, MeCO$_2$,EtCO; P-P=dmpe, dmdepe,dmdppe	119,129 117,118
ML$_4$(P-P)	V	A^b,J	P-P=dppm,dppe,dppp,dppb	115,124
[ML$_4$(P-P)][Z]	V,Nb, Ta	A^{a,e} J	P-P=dppm,dppe,dmpe,*cis*- dppee,dppp,dppb;Z=NEt$_4$	110,112 120,122 127
ML$_4$X(P-P)	V,Nb, Ta	A^a,H^a D	X=H,SnPh$_3$,NO;P-P=dppm, dppe,dmpe,dppp	106,112 111,113 121,123
ML$_5$X(P-P)	V	H,D	X=NO; P-P=dppm	123
ML$_3$R(P-P)	V,Nb	H^a	R=C$_5$H$_4$CHPh$_2$,C$_5$H$_4$CHMe$_2$ C$_5$H$_5$;P-P=dppm,dppe	125,127 126
M$_2$L$_6$(Cp)$_2$(P-P)	V	D^a	P-P=dppm	127

by the formula $[M(CO)_{6-n}Y_n]_x$ (n=1-5;x=1,2; Y=Phosphine). These complexes have been prepared either by the replacement of other ligands by phosphines or directly from the parent carbonyls $M(CO)_6$ and $[M(CO)_6]^-$, generally by thermal or by photolytic carbonyl displacement by phosphines.

Thus, Always and Barnett[105] reported that when a benzene solution of $V(CO)_4(Cp)$ is irradiated by U.V. light in the presence of PPh_3, the orange, monomeric complex $V(CO)_3(Cp)(PPh_3)$ is formed. Attempts to prepare disubstituted complexes were unsuccessful even after longer irradiation periods or from reactions in the presence of an excess of ligand, indicating that either $V(CO)_3(Cp)(PPh_3)$ is not photo-labile or the phosphorus ligand is being dissociated preferentially. This is actually observed when a CO saturated benzene solution of $V(CO)_3(Cp)(PPh_3)$ is photolyzed, resulting in the formation of $V(CO)_4(Cp)$. It has been suggested that the substitution reaction proceeds through the coordinatively unsaturated species $V(CO)_3(Cp)$ which may be stabilized by weak bonding interactions with solvent molecules. Furthermore, the species $V(CO)_3(Cp)$ is expected to recombine rapidly with CO, regenerating $V(CO)_4(Cp)$, and PPh_3 must compete with CO for the vacant coordination site on the intermediate $V(CO)_3(Cp)$.

However, further CO substitution can be achieved when this complex is treated with toluene under U.V. irradiation conditions, giving a highly substituted monocarbonyl complex[102] characterized as $V(CO)(Cp)(PhC{=}CPh)(PPh_3)$ which has the structure shown in Fig.14.

Earlier Fischer and Schneider[104] reported that when the dimeric species $V_2(CO)_5(Cp)_2$ is treated with PPh_3 over an extended period of time, a binuclear complex $V_2(CO)_4(Cp)_2(PPh_3)$ is obtained The i.r. spectrum shows both terminal and bridging CO groups, and the structure shown in Fig.15 has been suggested.

Relatively recently, Mayer and Bereaw[105] have reported that on treatment of $Ta(C_5Me_5)H_4(PMe_3)_2$ with CO in the presence of an excess of PMe_3 over an extended period, a brown complex $Ta(CO)(C_5Me_5)H_3(PMe_3)_2$ is formed. Similar reactions at elevated temperatures over shorter periods of time give the dicarbonyl complex $Ta(CO)_2(C_5Me_5)(PMe_3)_2$. I.r. and n.m.r. results suggest that this molecule has a "four-legged piano stool" type of structure as shown in Fig.16.

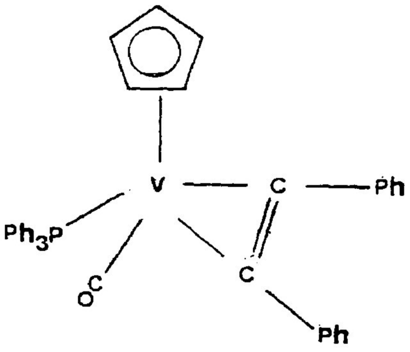


Fig. 14.

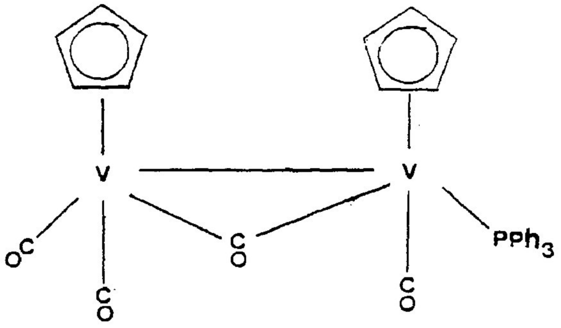


Fig. 15.

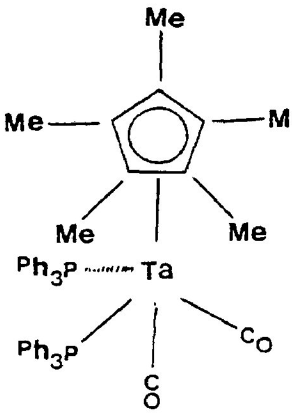


Fig. 16.

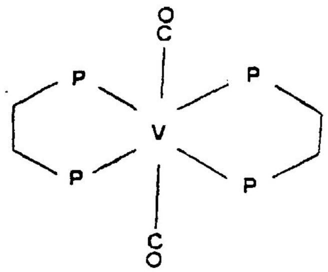


Fig. 17.

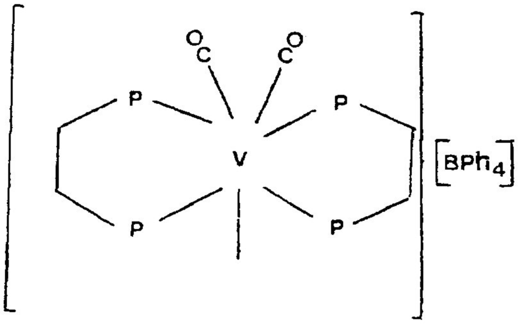


Fig. 18.

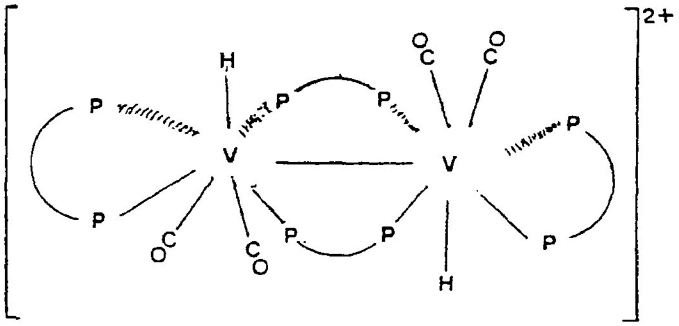


Fig. 19.

Ellis et.al.[109] have reported that when $V(CO)_6$ is treated with PPh_3 for a short period of time at low temperatures, the very heat, oxygen and solvent sensitive paramagnetic green compound $V(CO)_5(PPh_3)$ is obtained. This is the first neutral paramagnetic vanadium carbonyl derivative which has been reported. Further substitution by additional PPh_3 is a rather slow process. When attempts were made to isolate $V(CO)_5(PPh_3)$ by removing the solvent under reduced pressure, $V(CO)_4(PPh_3)_2$ was obtained.

Davison and Ellis[110] have reported that treatment of $[M(CO)_6]^-$ (M=V, Nb, Ta) with PR_3 ($R=Ph, Bu^n$), under photochemical conditions, gives $[M(CO)_5(PR_3)]^-$ complexes, isolated as NEt_4^+ salts. This direct substitution of donor molecules into the coordination sphere of metal carbonyl anions via photolysis is important particularly when the neutral metal carbonyl, the metal carbonyl halide or the hydride does not exist or has marginal stability.

Several bisphosphine complexes have also been prepared from this subgroup. Thus, when $Ta(C_5Me_5)H_4(dmpe)$ is treated with CO under U.V.

irradiation, it gives $Ta(CO)(C_5Me_5)H_2(dmpe)$.[103] Further photolysis at elevated temperatures over a one week period gives the red dicarbonyl complex, $Ta(CO)_2(C_5Me_5)(dmpe)$ in which the dmpe ligand is coordinated in a chelating fashion, as shown by n.m.r. results.[103]

However, when $Nb(Cp)Cl_4$ is treated with dmpe followed by the addition of $AlEtCl_2$, the violet $Nb(Cp)Cl_3(dmpe)$ complex is obtained,[114] which, when reduced with magnesium amalgam (Mg-Hg) in the presence of CO gas, gives the deep green, monocarbonyl complex $Nb(CO)(Cp)Cl_2(dmpe)$. When this complex is further treated with $Na[AlH_2(OCH_2CH_2OMe)_2]$ under a carbon monoxide atmosphere, the deep orange coloured $Nb(CO)_2(Cp)(dmpe)$ is formed. This complex can also be prepared by treating $Nb(Cp)Cl_3(dmpe)$ with Na-Hg in the presence of CO. The complex is a strong base and can readily be protonated by dilute HCl, giving the hydride containing cation, isolated as a PF_6 salt, $[Nb(CO)_2(Cp)H(dmpe)]PF_6$. In addition, when $Nb(CO)_2(Cp)(dmpe)$ is treated with MeI or benzyl bromide, dihalo complexes of the type $Nb(CO)(Cp)X_2(dmpe)$ (X=Br, I) were obtained.

Datta and Wreford[117] reported that the reduction of $TaCl_5$ with sodium amalgam in the presence of dmpe under a CO atmosphere produces the yellow anionic complex $[Ta(CO)_2(dmpe)_2]^-$, which, when treated with HCl, yields the apparently seven_coordinated complex $Ta(CO)_2Cl(dmpe)_2$. Spectroscopic evidence suggests a structure best described as a monocapped trigonal prism where the Cl is at the capping site. Br and CN analogues were also prepared similarly.

Photosubstitution has been the only practical method for the synthesis of substituted metal carbonyl anions of group V elements. Ellis and Faltynek[120] have suggested that the existence of stable triphenyl stannyl derivatives of such anions could provide a useful alternative route to substituted carbonyl anions which do not require photolysis. Thus, when $V(CO)_4(dppe)(SnPh_3)$ is treated with sodium amalgam followed by the addition of NEt_4Cl, a deep-red anionic complex $[V(CO)_4(dppe)][NEt_4]$ is isolated.

Acidification of this complex with $[Ph_4As][HCl_2]$ in benzene or interaction with tertiary butyl chloride in the presence of water, gives the neutral yellow hydride complex $V(CO)_4H(dppe)$[113] which, on decomposition, gives the neutral, paramagnetic $V(CO)_4(dppe)$ complex. This complex can also be prepared by treating $[V(CO)_4(dppe)][NEt_4]$ with $[C_7H_7][BF_4]$.[118]

The Nb analogue of $[V(CO)_4(dppe)][NEt_4]$ has been prepared[122] by treating $[Nb(CO)_4][NEt_4]$ with dppe under U.V. irradiation. Similar complexes with dppm, cis-dppee, dppp and dppb have also been prepared. However, when $Nb(CO)_4(Cp)$ is treated with dppm under similar conditions, it gives the dicarbonyl complex[128] $Nb(CO)_2(Cp)(dppm)$. The V analogue has also been prepared.[127]

Very recently Wells et.al.[129] have reported that when trans-$VCl_2(dmpe)_2$ is treated with sodium-amalgam under 5 atms of CO at -78°C, it gives the orange_red complex $V(CO)_2(dmpe)_2$. The structure of this 17 electron, paramagnetic, low spin species is shown in Fig.17. This complex reacts with $AgSO_3CF_3$ in acetonitrile forming a cationic complex characterized, as the BPh_4 salt, as $[V(CO)_2(MeCN)(dmpe)_2][BPh_4]$. X-ray analysis shows[129] that the molecule is pseudo octahedral, with two dmpe ligands occupying the equatorial sites. One axial site is occupied by the MeCN and the other accommodates the two carbonyls as shown in Fig.18.

In contrast, when trans-$V(CO)_2(dmpe)_2$ is treated with RX (R=H, K, Na;X=Cl, $MeCO_2$, $EtCO_2$, CF_3CO_2, $PhPO_2H$, N_3, CN, NH_2SO_3), it gives neutral V(I) complexes of the type cis-$V(CO)_2X(dmpe)_2$. However, when trans-$[V(CO)_2(dmpe)_2]$ is treated with tetrafluoroboric acid at low temperatures, an orange cationic complex with empirical formula $[V_2(CO)_4H_2(dmpe)_4]^{2+}$ is formed,[129] which is isolated as either the BF_4^- or the $[PhC(SO_2CF_3)_2]^-$ salt. I.r. results show the presence of terminally coordinated cis-carbonyl and terminal hydride ligands. In addition, magnetic susceptibility and ESR results shows that the cation is diamagnetic, suggesting that the paramagnetic, $[VH(CO)_2)(dmpe)_2]^+$ species has dimerized, with the formation of a V-V bond. The structure shown in Fig.19 has been proposed.

1.3.4. Cr, Mo and W.

A very large number of phosphine substituted metal carbonyls has been synthesized from this subgroup. Table.[5] indicates the wide variety of interesting compounds obtained with mono and bis-phosphines and also includes some bimetallic complexes.

The highly substituted $M(CO)Y_5$ complexes have been prepared[130] from metal carbonyls by

Table [5]:

Complexes	Metal	Method of synthesis and comments		Ref
$ML(PR_3)_5$	Cr,Mo,W	A^a	R= Me(OMe)$_2$,OMe	130
$MLXY(PR_3)_2$	Mo	J	R=Me; X=S_2CNMe_2,Cl; Y=Acetone; $COCH_2SiMe_3$	131
$ML_2X_2(PR_3)$	Mo,W	D,H	R=Et,Bu^n,Ph; X=S_2COMe,$S_2P(OEt)_2$,$S_2P(Pr^i)_2$ S_2CNMe_2,S_2CNEt_2	132,133
$ML_2X_2(PR_3)_3$	W	$D^{a,b}$	X=I; R=Me (7-coordinated)	179
$ML_2X_2(PR_3)_2$	W	I^b	R=Ph; X=I	134
$ML_2XY(PR_3)_2$	Cr	D	R=Ph_2Me; X=I; Y=NO	135
$ML_3(PR_3)_3$	Cr,Mo	A^b, D^b	R=Ph,OBu,Cl,	136,138
$ML_3X(PR_3)_2$	Mo,W	D	R=Cy; X=N2,C_2H_4,H_2O,D_2O,MeCN	139
$ML_3(PR_3)_2$	Mo,W	D	R=Cy,Cy_2Pr^i,Pr^i (5-coordinated)	139
$ML_3X_3(PR_3)$	Mo	D	R=Ph; X=Cl,Br (7-coordinated)	140
$ML_3X_2(PR_3)_2$	W	D	R=Ph; X=I (7-coordinated)	134
$ML_4(PR_3)_2$	Cr,Mo, W	A^b D^b	R=Pr^i,Ph,$PhEt_2$,Me_2Ph, $MePh_2$	136,10, 139,141, 142
$ML_4Y(PR_3)$	Cr,W	G,E^b D^b	R=Ph; Y=PBu_3,$P(OMe)_3$,$P(OPh)_3$,PPh_2H	143,144, 146
$ML_4X(PR_3)$	Cr,	G,D^b	R=Bu,(OMe),(OPh),Ph; X=Cl,CS	143,145
$ML_5(PR_3)$	Cr,Mo, W	A^b	R=Bu,Bu^t,Ph,Ph_2Bu,Ph_2Me,Ph_2Et, Ph_2Pr^i,$PhBu_2$	136,144
$M_2L_8(PR_2)_2$	Cr,Mo, W	A^b	R=Me,Et	147
$MLX(P-P)_2$	Mo,W	$C^{b,d}$	P-P=dppe; X=N_2,CS	145,14

		I^b		
[MLX(P-P)][Z]	Mo	D^b	P-P=dppm,dppe; X=C_7H_7;Z=PF_6	163
[MLXY(P-P)][Z]	W	I^e	P-P=dppe; Z=I_3; X=I; Y=CS	149
$MLX_2(P-P)_2$	Mo,W	D^b	P-P=dppm; X=I	179,180
[MLX$(P-P)_2$[Z]	W	I^e	P-P=dppe; Z=SO_3F; X=CSMe,CSEt	149
[MLXY$(P-P)_2$][Z]	W	I^e	P-P=dppe; Z=CF_3SO_3; X=CS; Y=H	149
[ML_2X(P-P)][Z]	Mo	D^b	P-P=dppm; X=C_7H_7; Z=PF_6	163
$ML_2(P-P)_2$	Cr,Mo	$A^{a,b}$	P-P=dmpe,dppe	150,148
	W	$C^{b,d}$		10,169
		D^b		
[$ML_2X(P-P)_2$][Z]	MO,W	$D^{b,e}$	P-P=dppm.dmpe,dppe; X=Cl,I,Et,H;	150,151
		E	Z=Cl,I,PF_6,Br,BF_4.CF_3SO_3	149,170
				171
$ML_2XY(P-P)_n$	Mo,W	D^b,	P-P=dppm,dmpe,dppe,X=Cl; Y=NO; X=Y=Cl,	152,153,
		E^b	Br,I,PPh_3;N=1,2,$P(OEt)_3$,$ASPh_3$,CNS	177,154,
				170,178
$ML_2X_2Y(P-P)$	W	H	P-P=dppe; X=I; Y=Cs	149
$ML_2X(P-P)$	Cr	D^a	P-P=dppe; X=C_6H_6	168
$ML_3X_2(P-P)$	Mo,W	D,I^b	P-P=dppm,dppe,dmpe; X=Cl,Br,I	150,153,
				170
$ML_3X(P-P)$	Cr,Mo,	I^b	P-P=dppe; X=$SbPh_3$,$C_6H_{11}NH_2$,C_5H_5N,PPh_3,	145,154
	W	E^b	$ASPh_3$,CS	
[ML_2X(P-P)][Z]	Mo,W	E^b	P-P=dppe; X=NO; Z=PF_6	155
		D^b		
$ML_3(P-P)_2$	Cr,Mo,	D^b	P-P=dppm,dmpm	162,176
	W			
$ML_4(P-P)$	Cr,Mo,	A^b,J	P-P=dmpe,dppe,dmpm,Ph_2POPPh_2	156,10,
	W	D^b		162,166
$ML_4(P-P)_2$	Cr,Mo	G^b	P-P=dppe	10
	W			

$[ML_4X(P\text{-}P)][Z]$	Mo,W	E	P-P=dmpe; X=I; Z=I,I_3	150
$M_2L_4X_2(P\text{-}P)$	Cr	D^a	P-P=dppe; X=C_6H_6	168
$M_2L_4X_2(P\text{-}P)_3$	Mo,W	D,I	P-P=dppe; X=Cl,Br,Il	153
$[M_2L_4X_2(P\text{-}P)][Z]_2$	Mo	D^b	P-P=dppe; X=C_7H_7; Z=PF_6	163
$M_2L_4X_4(P\text{-}P)_3$	Mo,W	I	P-P=dppm,dmpe; X=I,Cl,Br	150,171 153
$ML_5(P\text{-}P)$	Cr,Mo, W	D,A	P-P=dppm,dppe,dmpe,Ph_2POPPh_2	156,164 166,167 182,183
$[ML_5X(P\text{-}P)][Z]$	Cr	E^e	P-P=dppe; X=Me; Z=BF_4	156
$M_2L_6X(P\text{-}P)_2$		J,D	P-P=dppe; X=CS,biPy	149,165
$M_2L_6X(P\text{-}P)_3$	Cr,Mo, W	D,I^c	P-P=dmpm,dppe	162,165
$ML_3(P\text{-}P)_3$	Mo,W	A^b	P-P=dmpm	162
$ML_2X(P\text{-}P)_2$	Mo	C^d	P-P=dppe; X=N_2	169
$ML_2(P\text{-}P)_3$	Mo,W	D^b	P-P=dmpm	162
$M_2L_{10}(P\text{-}P)$	Mo	A	P-P=dppe,dppp	164

Bimetallic Complexes:

Complexes	Comments		Ref
$MM'L_3X(P-P)_2$	M=Cr,Mo,W M'=Cu,Ag,Au	X=Cl,I,CN P-P=dppm	157,158
$MM'L_3XY(P-P)_2$	M=Cr,Mo,W M'=Pt	X=Cl,Br,CN,N_3,H,C≡CCPh Y=H; P-P=dppm	159
$MM'L_4(P-P)_2$	M=Cr,Mo,W M'=Rh,Ir,Pt	X=Cl,BrI,H,C≡CMe,C≡CPh P-P=dppm	159,173 174
$[MM'L_5(P-P)_2][Z]_n$	M=Cr,Mo,W M'=Ru,Rh,Ir	P-P=dppm; Z=PF_6; n=0,1	172,174,
$MM'L_5X(PR_3)$	M=Cr,W M'=Ag,Au	X=H; R=Me,Ph	160
$[MM'L_5X_2(P-P)_2$	M=Mo; M'=Ru,	X=H; P-P=dppm	172
$MM'L_6(P-P)_2$	M=Cr,Mo,W M'=Fe,Ru	P-P=dppm	161,172
$[MM'L_4X(P-P)_2][Z]$	M=Mo M'=Rh	P-P=dppm; Z=PF_6,Cl X=NCMe,NCEt,NCPh,$CNBu^t$	173
$MM'L_4(PPh_3)(PCy_2)_2$	M=Mo,W M'=Ni,Pd,Pt		

photochemical means. The ease of substitution decreases in the order of Mo>W>Cr. Thus, when $M(CO)_6$ (M=Cr, Mo, W) are treated with $P(OMe)_3$ under U.V. irradiation over a week, white to yellow monocarbonyl complexes are obtained.

Very recently, Wasserman *et.al.*[139] have reported that when $M(CO)_3(C_7H_8)$ (M=Mo, W) are treated with phosphines (PCy_3 or PCy_2Pr^i) the five coordinated complexes $M(CO)_3L_2$ ($L=PCy_2Pr^i$) are obtained. It has been suggested that the formation of such coordinatively unsaturated complexes and their stability is largely due to the steric demands imposed by the bulky phosphine ligands. An X-ray diffraction[139] study on $W(CO)_3(PCy_3)_2$ shows that the formally five coordinated species appears in fact to be nearly octahedral. The sixth coordination site of the distorted octahedron is occupied by a hydrogen atom of one cyclohexyl group, and is almost directly opposite to one of the CO groups.

The potential for high reactivity of such coordinatively unsaturated complexes is quite obvious. Thus, when treated with a variety of ligands, complexes of the type $M(CO)_3(PCy_3)_2X$[139] (M=Mo, W, $X=N_2$, C_2H_4, H_2O, D_2O, Et_2S, MeCN etc.) are readily formed.

Magee _et.al_.[136,137] have reported that when $M(CO)_6$ (M=Cr, Mo, W) are treated with PPh_3 in diglyme under refluxing conditions, the pale yellow complexes $M(CO)_5(PPh_3)$ are obtained. Under prolonged refluxing conditions, disubstituted complexes of the type $M(CO)_4(PPh_3)_2$ were obtained. Further substitution could not be achieved under these conditions. However, when arene complexes such as $M(CO)_3(C_6H_6)$ (M=Cr, Mo) are treated with phosphines, then tri-substituted complexes $M(CO)_3(phosphine)_3$ (phosphine= PPh_3, PPh_2Cl, $PPhCl_2$ and PCl_3) are formed. The large variation in the carbonyl stretching frequency in going from PPh_3 to PCl_3 (1949-2041 cm^{-1}) is attributed to the decrease in the σ-donor capability of the phosphorus ligand, which results in a decrease in electron density on the metal and a reduced π-donation to the carbonyl ligand, due to the greater electronegativity of the halogen. Octahedral structures with three CO groups in a _fac_-arrangement have been suggested for these complexes.

Seven-coordinated complexes with monophosphines have also been prepared. Thus when $[Mo(CO)_3X_3][NEt_4]$ are treated with PPh_3, the yellow complexes[140] $[Mo(CO)_3X_3(PPh_3)][NEt_4]$ (X=ClBr) are formed.

The related seven coordinated W complex is prepared by treating $W(CO)_6$ with iodine under U.V. irradiation[134]. This initially produces $W(CO)_4I_2$ which reacts further with PPh_3 to yield the yellow complex $W(CO)_3I_2(PPh_3)_2$.

An extraordinarily large variety of bisphosphine complexes have been prepared from this subgroup, and this presents probably the richest chemistry outside the group VIII metal carbonyls.

For example, Tatsumi *et.al.*[167] have reported that when $Mo(N_2)_2(dppe)_2$ is treated with benzyl propionate at elevated temperatures, an orange complex, formulated as *trans*-$Mo(CO)N_2(dppe)_2$, is obtained. One of several proposed mechanisms for the formation of this complex involves the oxidative-addition of the ester to the starting complex to give the acyl complex $Mo(COC_2H_5)(OCH_2Ph)(dppe)_2$ complex, which is converted into $Mo(CO)(C_2H_5)(OCH_2Ph)(dppe)_2$ via an acyl-alkyl rearrangement. This, by β-elimination, gives $Mo(CO)H(C_2H_5)(dppe_2)$ which reductively eliminates alkane to form the five coordinate $Mo(CO)(dppe)_2$. Addition of a dinitrogen molecule gives the final product $Mo(CO)N_2(dppe)_2$. This addition is reversible, as shown by the fact that when argon gas is passed through a solution of this compound, $Mo(CO)(dppe)_2$ is formed.[131] An X-ray analysis[131] shows that this sixteen electron complex has a square pyramidal geometry. In addition, an ortho hydrogen atom from one of the dppe phenyl groups interacts with the vacant sixth coordination site of this complex.

Semmelhack et.al.[163] earlier reported that when $Cr(CO)_3(C_6H_6)$ is treated with dppe under U.V. irradiation, an orange complex characterized as $Cr(CO)_2(C_6H_6)(dppe)$ is obtained. Spectroscopic data suggest that the dppe ligand is coordinated through only one phosphorus atom as shown in Fig.20. Under prolonged irradiation conditions, the dimeric complex $Cr_2(CO)_4(C_6H_6)_2(dppe)$ is obtained, with the proposed structure as shown in Fig.21.

In contrast, when $M(CO)_4X_2$ (M=Mo,W; X=Cl, Br,I) are treated with an excess of dppe at room temperature over several hours, orange complexes are formed.[153] Spectroscopic data suggest that these complexes are dimeric, with one bridging dppe ligand as shown in Fig.22. However, when these reactions were performed under refluxing conditions, monomeric $M(CO)_2X_2(dppe)$ (M=Mo, W; X=Cl, Br, I) complexes were

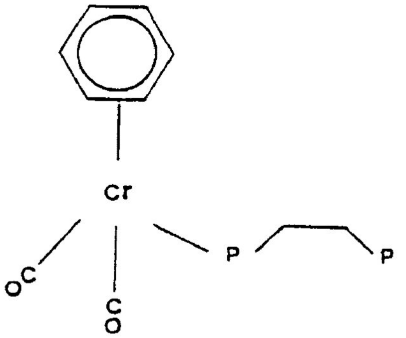


Fig. 20.

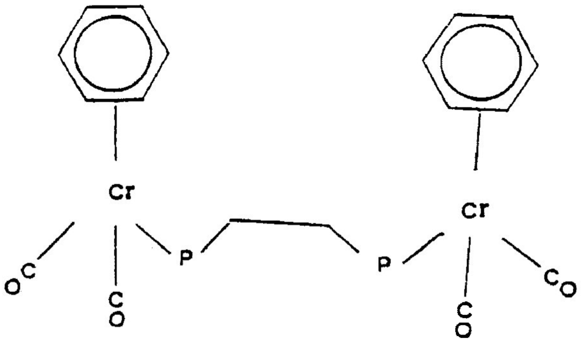


Fig. 21.

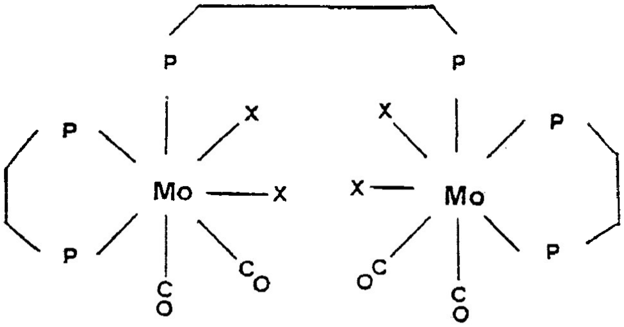


Fig. 22.

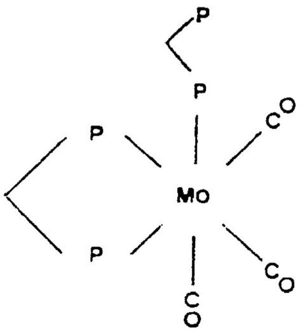


Fig. 23.

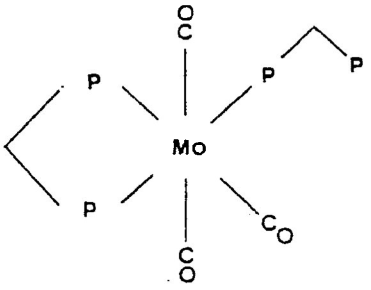


Fig. 24.

obtained.

Relatively recently, Wong et.al.[167] have reported that treatment of $[Mo(CO)_5(PPh_2O)][NEt_3H]$ with sodium hydride followed by the addition of PPh_2Cl yields a white complex containing Ph_2POPPh_2 (dppo). X-ray crystallography confirms that the molecule is $Mo(CO)_5$(dppo)[166] and that the dppo is coordinated through only one phosphorus atom. This complex can also be prepared by refluxing $Mo(CO)_6$ with dppo.[166] The Cr and W analogues have also been prepared by treating $M(CO)_5(MeCN)$ (M=Cr, W) with dppo.[166] However when $M(CO)_6$ (M=Cr, Mo, W) are treated with dppo at elevated temperatures, the tetracarbonyl complexes, $M(CO)_4$(dppo), are obtained,[166] where the dppo ligand is coordinated in a chelating fashion.

Some very interesting dppm complexes have been obtained from the carbonyls of this group. For example Isaacs and Graham[176] have reported that $Mo(CO)_3(C_7H_8)$ reacts with dppm to produce white and yellow isomeric complexes. The white isomer exhibits two νCO bands in the i.r. spectrum, while the ^{31}Pn.m.r. spectrum shows three resonances with relative intensities of 1:2:1 and each one shows phosphorus-phosphorus coupling. These data are consistent with the proposed fac-configuration as shown in Fig.23. (The W analogue has also been prepared similarly.[159]) The yellow isomer shows three νCO bands in its i.r. spectrum and the four resonances in its ^{31}P n.m.r. spectrum again show phosphorus-phosphorus coupling. This complex is assigned a mer-configuration as shown in Fig.24. These fac- and mer- Mo complexes have also been prepared by treating $[Mo(CO)_3(C_7H_7)]PF_6$ with dppm at elevated temperatures.[162] The Cr and W analogues have also been prepared by refluxing the corresponding fac-isomers.[159]

In contrast to the above, when $Mo(CO)_3(C_7H_7)$ is refluxed with dppe instead of dppm, an orange-red ionic complex is formed,[162] (isolated as the PF_6^- salt) with a single dppe ligand bridging two $Mo(CO)_2(C_7H_7)$ units.

Very recently, Andy-Hor[164] has reported that TMNO (TMNO=trimethylamine N-Oxide) initiated decarbonylation of $Mo(CO)_6$. Addition of dppm gives $Mo(CO)_5(dppm)$, which, from n.m.r. results, contains dppm coordinated through only one of its phosphorus atoms. The analogous Cr and W complexes containing monodentate dppm ligands have also been reported.[182],[183] It has been noted that when $Mo(CO)_5(dppm)$ is treated with a stoichiometric amount of TMNO, further decarbonylation occurs, giving $Mo(CO)_4(dppm)$[164] in which dppm now acts in a chelating fashion.

In contrast, when other bisphosphines are used under similar conditions, complexes of the type $Mo_2(CO)_{10}(P-P)$ (P-P=dppe, dppp), containing two $Mo(CO)_5$ units linked by a single P-P ligand,[164] are formed. It has been observed that increasing the phosphine concentration, does not cause further CO replacement and the formation of the dibridged species $Mo_2(CO)_8(P-P)_2$.[164] Such compounds can however be prepared (when P-P=dppe) with Cr and Mo by treating, for example, cis-$Mo(CO)_4(PPh_2H)$ with cis-$Mo(CO)_4\{PPh_2(CH=CH_2)\}$[134] at room temperature in the presence of KBu^tO as catalyst. Spectroscopic results indicate that these binuclear complexes form 10 membered rings, with cis-geometry around each metal as shown in Fig.25.

However, when fac-$Mo(CO)_3(MeCN)_3$ is treated with dmpm under refluxing conditions followed by chromatography, a very interesting yellow complex is obtained.[162] Analytical and spectroscopic results suggest that the molecule is monomeric with three dmpm ligands coordinated in a monodentate fashion as shown in Fig.26.

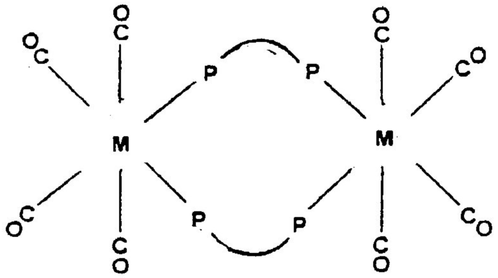


Fig. 25.

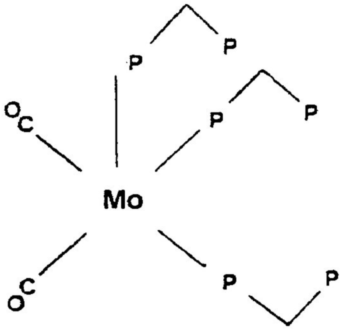


Fig. 26.

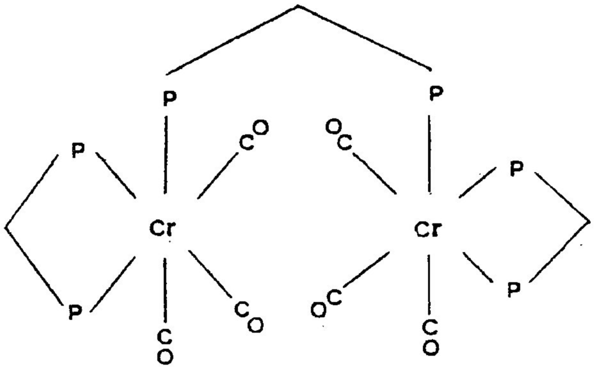


Fig. 27.

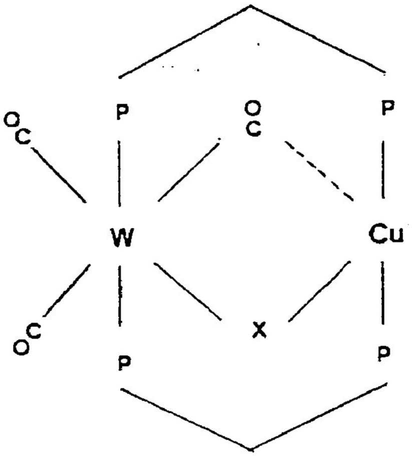


Fig. 28.

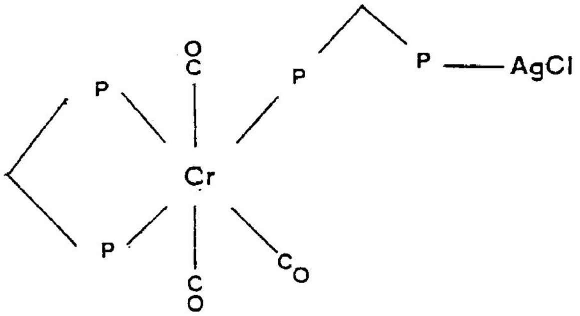


Fig. 29.

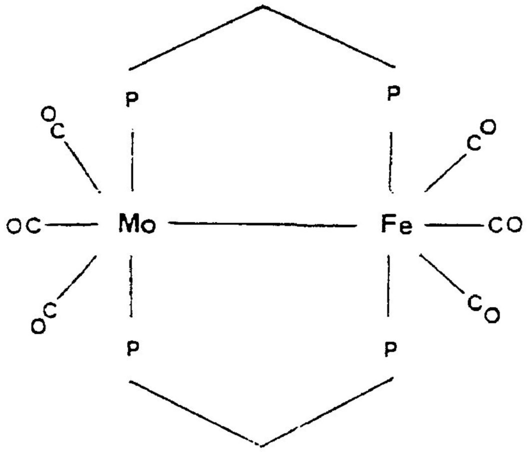


Fig. 30.

Very recently Blagg, Hutton and Shaw[178] have reported that when fac- or mer-$Mo(CO)_3(dppm)(\eta^1$-dppm) is treated with $Hg(SCN)_2$, a seven coordinate Mo(II) complex, characterized on the basis of analytical and spectroscopic results as $Mo(CO)_2(SCN)_2(dppm)_2$, is obtained. X-ray diffraction shows that the molecule is monomeric, with two cis-CO and two NCS groups. In addition, one of the dppm ligands is coordinated in a monodentate fashion. The geometry around the Mo is intermediate between a capped trigonal prism and a capped octahedron and the four membered dppm chelate ring is rather puckered. Another related molybdenum complex $Mo(CO)_2I_2(dppm)(\eta^1$-dppm), is prepared[177] by treating $[Mo(CO)_4I_3][NEt_4]$ with dppm. A similar geometry has been revealed from X-ray results.[177]

A seven-coordinated W complex has been prepared[179] by treating $W_2(CO)_8I_4$ with dppm. X-ray crystallography shows that the red complex, $W(CO)I_2(dppm)_2$, contains chelating dppm ligands with an overall pentagonal bipyramidal geometry. One iodine and the CO group are in the axial positions. The analogous Mo complex has also been prepared.[180]

The nbd group can be readily displaced by phosphines.[162] For example, King and Raghuveer have reported that when $M(CO)_4(nbd)$ (M=Cr,Mo,W, nbd=norbornadiene) are refluxed with dmpm, $M(CO)_4(dmpm)$ complexes result. However, when $Cr(CO)_3(nbd)$ is treated with dmpm, a binuclear complex is obtained.[162] Elemental analyses, a molecular weight determination together with spectroscopic results show that two $Cr(CO)_3(dmpm)$ units are bridged by a single dmpm ligand as shown in Fig.27.

From the number of complexes containing bisphosphines behaving as monodentate ligands referred to already in this section, it is apparent that there is great potential for the use of such species as precursors to bimetallic systems via interactions with the uncoordinated phosphorus atom(s). For example, Blagg et.al.[158] have reported that when *mer*-$M(CO)_3(dppm)(\eta^1$-dppm) (M=Cr,Mo,W) are treated with CuX (X=Cl,I),complexes of the type $MCu(CO)_3X(dppm)_2$ are formed. An X-ray diffraction study[158] on a W complex reveals that the metal-metal bond is supported by two bridging dppm ligands and a bridging Cl ligand. In addition, a CO ligand acts in a semi-bridging mode. Furthermore, it has been found that the $W(\mu$-dppm$)_2Cu$ ring is in a pseudo boat conformation as shown in Fig.28.

In contrast, when *mer*-$M(CO)_3(dppm)(\eta^1$-dppm) (M=Cr, Mo, W) is treated with $Ag_4Cl_4(PPh_3)_4$, complexes with the formula $MAg(CO)_3Cl(dppm)_2$ are formed.[158] Analytical and spectroscopic results suggest that the molecules have a *mer*-configuration with one dppm ligand coordinated in a chelating fashion to the M atom while the other bridges the two hetro-atoms in the manner shown in Fig.29.

Jacobsen *et.al*[161] very recently reported that treatment of *mer*-$M(CO)_3(dppm)(\eta^1$-dppm) (M=Cr, Mo, W) with $Fe_2(CO)_9$, yields the bimetallic complexes $MFe(CO)_6(dppm)_2$. An X-ray analysis of the complex with M=Mo shows that the Mo and Fe atoms are linked by two bridging dppm ligands forming an eight membered MoP_4C_2Fe ring as shown in Fig.30. A weak Fe--→Mo donor-acceptor interaction has been suggested to satisfy the 18-electron rule.

Bimetallic complexes have also been synthesized by other routes. For example, when *cis*-$Cr(CO)_4(PPh_2H)_2$ is treated with *cis*-$Mo(CO)_4(PPh_2CH{=}CH_2)_2$ in the presence of KBu^tO as catalyst, a yellow complex is formed.[134] Analytical and spectroscopic results suggest that the molecule is the dimeric species $CrMo(CO)_8(dppe)_2$, having a 10 membered ring formed by the two bridging dppe ligands, with a structure quite analogous to that shown in Fig.25.

In addition, Chaudret <u>et</u>.<u>al</u>.[172] have reported that an interesting heterobimetallic complex is formed when $Mo(CO)_6$ is treated with $RuH_2(dppm)_2$ at elevated temperatures. This orange complex has been characterized by X-ray diffraction as $MoRu(CO)_6(dppm)_2$. The Mo and Ru atoms are bridged by two <u>trans</u>-dppm ligands. Three terminal carbonyl groups are bonded to the Mo atom and two CO groups are terminally coordinated with the Ru atom. The remaining carbonyl ligand bridges the two metal centers in an "atypical semi bridging" fashion as shown in Fig.31. However, when this complex is recrystallized from THF, a yellow complex with the same chemical formula is obtained. EDAX (Energy dispersive analysis by X-rays) studies confirm that it also contains Mo and Ru atoms. In solution, both complexes shows similar i.r. spectra in the νCO region, although in the solid state the band at 1685 cm^{-1} in the orange complex is shifted to $1715 cm^{-1}$ in the yellow complex. In solution, ^{31}P n.m.r. spectra of both show an AA'BB' pattern consistent with the dppm ligands bridging the two metals. Similarly, ^{13}C n.m.r. spectra show a single peak suggesting fluxional behavior of these complexes consistent with the solution i.r. results. In the solid state, the yellow complex is therefore believed to have essentially the same structure as shown in Fig.31 except that the "semi bridging" CO group now bridges in the normal fashion.

When these complexes are heated in solution under vacuum, a very air-sensitive red complex is formed. Spectroscopic data show that it has two bridging CO groups and the proposed structure is shown in Fig.32. [A double bond has been proposed to satisfy the E.A.N rule]. It has also been noted that all three complexes (i.e. orange, yellow and red) in solution react rapidly with molecular hydrogen forming a yellow complex Characterized on the basis of analytical and spectroscopic data as $MoRu(CO)_5H_2(dppm)_2$, having bridging hydride ligands as shown in Fig.33.

1.3.5. Mn, Tc and Re:

A large number of complexes, mainly of Mn and Re, have been reported for this triad and some of

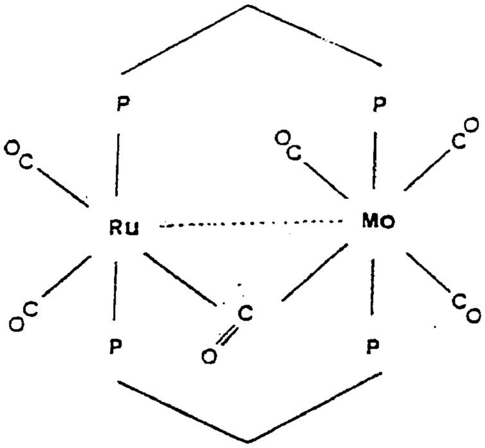


Fig. 31.

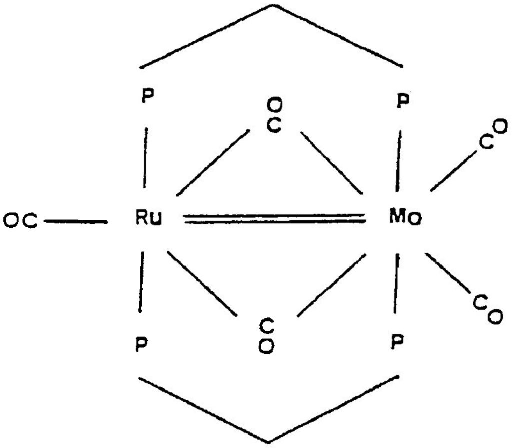


Fig. 32.

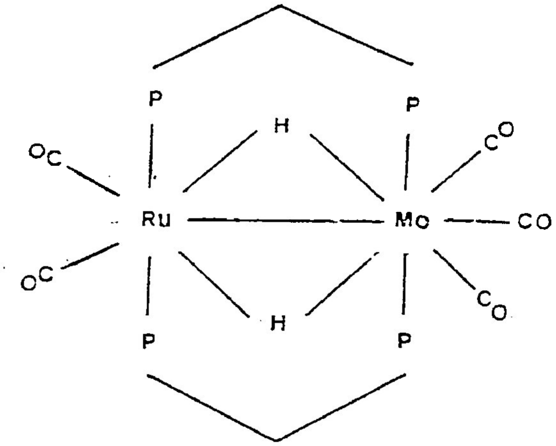


Fig. 33.

these are listed in Table [6]. This is the second most extensively studied group after group VIII, and a wide variety of phosphine and phosphite ligands have been used.

Thus, Chatt <u>et.al</u>.[135] reported that when $ReCl_2(PhCON_2)(PPh_3)_2$ is refluxed under CO followed by the addition of PMe_2Ph, the white complex <u>trans</u>-$Re(CO)Cl(PMe_2Ph)_4$ is obtained. this can be prepared by heating $ReCl_2(PhCON_2)(PPh_3)_2$ and PMe_2Ph in a stream of CO over a longer period.

In another example, when $Mn(CO)_3(MeCO)\{P(OMe)_3\}_2$ is irradiated with U.V. light under reflux, it gives the mono- and di-carbonyl complexes[136] $Mn(CO)Me\{P(OMe)_3\}_4$, and $Mn(CO)_2Me\{P(OMe)_3\}_3$. These complexes react with CO gas at 300 Psi to give the tricarbonyl complex $Mn(CO)_3(MeCO)\{P(OMe)_3\}_2$.

The mono- and di-carbonyl complexes referred to above also react with bromine[136], giving $Mn(CO)Br\{P(OMe)_3\}_4$ and $Mn(CO)_2Br\{P(OMe)_3\}_3$ respectively. A similar reaction with the tricarbonyl complex gives $Mn(CO)_3Br\{P(OMe)_3\}_2$. The dicarbonyl complex $Mn(CO)_2Br\{P(OMe)_3\}_3$ can also be prepared by treating

Table [6].

Complex	Metal	Method ofsyntheses and comments.		Ref
$MLX(PR_3)_4$	Mn,Re	C^b,	R=Me_2Ph,OMe	185,186
		$D^{a,b}$	X=Cl,Br,Me	
		H		
$[MLX(PR_3)_4][Z]_n$	Mn,Re	I^e	R=OMe,PMe_2Ph; X=NO; Z=PF_6,$FeCl_4$	185,187
			n=1,2	
$MLX_3(PR_3)_3$	Re,Tc	C^b,E	R=PMe_2Ph; X=Cl,Br	188
$ML_2X(PR_3)_3$	Mn,Re	$D^{a,b}$	R=Me,Ph,$MePh_2$,OMe	186,189
		C	X=H,Me,Cl,Br,NHPh	-192
$[ML_2(PR_3)_4][Z]$	Mn	I^e	R=OMe,OEt; Z=BPh_4	187
$ML_2X(PR_3)_2$	Re	C^b,I^b	R=Ph; X=CL,Br,I,S_2CH.	189,193,
		E		185
$[ML_2X(PR_3)_3[Z]$	Mn	D^b,I^e	R=Me,Me_2Ph,OMe,(OMe_2)Ph,OEt; X=PF_6	187,195
$ML_2(PR_3)_3$	Mn	$D^{a,b}$	R=OMe	186
$ML_2X(PR_3)_3$	Mn	D^b,I	R=Me,Me_2Ph,OMe,$(OMe)_2$Ph; X=Br	187,194
$ML_2X_2(PR_3)_2$	Re	C^b	R=Et; X=Cl	196
$ML_2X_3(PR_3)_2$	Re	H	R=Me_2Ph; X=Cl	188
$ML_3X(PR_3)_2$	Mn,Re	A^b,C	R=Et,Pr^n,Bu,Ph,Me_2Ph,$MePh_2$	185,186,198

		E^b,	$Ph_2Et,PhCl_2,OMe,OEt,OBu$	189,196,199
		$I^{b,c}$	$Ph(OMe)_2,OPh$	200,192,
		D^b	X=H,Cl,Br,I,NHPh	201,194
$ML_3(PR_3)_2$	Re	A^a	$R=MePh_2$	191
$[Ml_3X(PR_3)_2][Z]$	Mn,Re	D^b,I^e	$R=Me,Ph,Me_2Ph,OMe;\ Z=BF_4,PF_6$	187,202
			X=Cl,Br,MeCN	195
$[ML_3X_2(PR_3)][Z]$	Mn	D^b	$R=OMe;\ X=MeCN;\ Z=PF_6$	195
$[ML_3X(PR_3)_3][Z]$	Mn,Re	$D^{b,e}$	$R=OMe;\ X=MeCN;\ Z=PF_6$	195
$ML_4X(PR_3)$	Mn,Re	D^b,H	$R=Et,Ph,P_{R2}Me,Ph_2Et,OPh;$	203,198,199
			$Ph(OMe)_2,Ph_2(OMe);\ X=H,Cl,Br,I$	200,190,205
$[ML_4X(PR_3)][Z]$	Mn	H^e	$R=Me_2Ph;\ Z=BPh_4;\ X=MeCN$	187
$ML_5(PR_3)$	Re	A	$R=Me_2Ph$	190
$[ML_5(PR_3)][Z]$	Mn	E^e	$R=OMe,Ph(OMe)_2,Ph_2(OMe);\ Z=PF_6$	198
$M_2L_6(PR)_4$		G^b	R=Ph	189
$M_2L_7(PR_3)_3$	Mn,Re	A^a	$R=MePh_2,OEt$	206,190
$M_2L_8(PR_3)_2$	Mn,Re	$A^{a,b}$	$R=Et,Ph,Me_2Ph,OEt,OPh$	190,201,203,
			$Ph(OMe)_2,Ph_2(OMe)$	206,207
$M_2L_9(PR_3)$	Mn,Re	A^a,G^b	$R=H,Ph,Me_2Ph,MePh_2$	190,208,
				209,210
$MLX(P-P)_2$	Mn,Re	C^b,D^a	P-P=dppm,dppe,dppee;	211,185,
			X=Cl,Br,CN,SCN	212,230
$[MLX(P-P)_2][Z]$	Mn,Re	D^a,I^e	P-P=dppm,dppe; X=Cl,Br,CNMe	185,211
			$Z=FeCl_4,Br_3,I_3,PF_6$	212,230
$[MLXY(P-P)][Z]$	Mn	I^a	$P-P=dppe;\ Y=P(OMe)_3,P(OEt)_3;$	
			$Y=P(OPh)_3;X=phen,bipy;Z=ClO_4$	229
$ML(P-P)_2$	Mn	A^a	P-P=dppe	211,212
$[MLX(P-P)][Z]$	Mn	I^e	$P-P=dppe;X=\eta^5-C_6H_6Ph;Z=PF_6$	226
$MLX(P-P)$	Mn	D^a	$P-P=dmpm,dppe;X=Cp,\eta^5-C_6H_6Ph$	2,226,
				162
$M_2LX_4(\mu-P)_2$	Re		P-P=dppm,X=Cl	213

$ML_2X(P\text{-}P)_2$	Mn,Re	D^b	P-P=dppm,dppe;X=Cl,Br	196,224, 225,231
$[ML_2X(P\text{-}P)][Z]$	Mn	E^b	P-P=dppe;X=phen,bipy;Z=ClO_4	229
$[ML_2(P\text{-}P)][Z]_n$	Mn	D^e,H^e	P-P=dppm,dppe;Z=ClO_4;n=1,2	214,231
$ML_3X(P\text{-}P)$	Mn,Re	A^b, $D^{a,b}$ H	P-P=dppm,dppe,dppp,dppb;X=Cl,Br,HCS_2, H,CN,SCN,ClO_3	215,216 217,211 212,218, 219,230, 232
$ML_3(P\text{-}P)$	Mn	A^a	P-P=dppe	211,212, 216
$[ML_3(P\text{-}P)_2][Z]$	Mn	$D^b,^d$, D^c	P-P=dppm;Z=PF_6	231
$ML_4X(P\text{-}P)$	Mn	D	P-P=dppm,dppe,dppb;Z=ClO_4	232
$M_2L_5X(P\text{-}P)_2$	Mn	E^b	P-P=dppm;X=SO_2,CS_2,CH_2N_2,$C_5Cl_4N_2$ BF_3,H,$N_2C(CO_2Et)_2$	220
$[M_2L_5X(P\text{-}P)][Z]$	Mn	$E^{b,e}$	P-P=dppm;Z=BF_4;X=N_2Ph,N_2Me	220
$M_2L_5(P\text{-}P)$	Mn	A^b	P-P=dppm	218,197
$M_2L_6(P\text{-}P)_2$	Mn,Re	A^b	P-P=dppm,dmpm,dppe	2,211, 212,216 162
$[M_2L_6X(P\text{-}P)_2][Z]$	Mn	H^d	P-P=dppm;X=H;Z=BF_4	233
$M_2L_6XY(P\text{-}P)$	Re	D^b,E^a H^a	P-P=dppm,tedip;X=Y=H,OH,OMe,Cl X=H;Y=OMe,OH,Cl	221,219
$M_2L_7(P\text{-}P)$	Mn,Re	$A^{a,b}$ D	P-P=dppm,dmpm,dmpe,dppe	211,212, 216,2 219,221 162
$M_2L_8X_2(P\text{-}P)$	Mn	E	P-P=dppm;X=Br	211,212 216,2

Bimetallic Complexes:

Complexes	Comments	REf
$MM'L_2X_2Y(P-P)_2$	M=Re,Mn M'=Rh,Pt P-P=dppm; $Y=H,\eta^2-C_2H_4,\eta^2-C_3H_4$	224,225
$ReM'L_2X_2Y_2(P-P)_2$	M'=Rh P-P=dppm;X=Cl;Y=H	224
$MnM'L_3X(P-P)_2$	M'=Pt,Pd P-P=dppm;X=Cl,Br,I,NCO,N_3,SCN,SnCl	225,227 228
$ReM'L_3X_2(P-P)_2$	M'=Rh P-P=dppm;X=Cl	224
$MnM'L_3XY(P-P)_2$	M'=Rh,Ir P-P=dppm;X=H,Cl;Y=Cl,Br	223
$[MnM'L_3XY(P-P)_2][Z]$	M'=Pt;X=Br,Cl P-P=dppm;Y=H;Z=BF_4,PF_6	225
$[ReM'L_4X(P-P0][Z]$	M'=Rh,Ir P-P=dppm;X=Cl;Z=PF_6BPh_4	224
$[MnM'L_4X(P-P)_2[Z]$	M'=Rh,Ir P-P=dppm;X=Cl,Br;Z=PF_6,Br,Cl	223
$MnM'L_8(PR_3)_2$	M'=Re Re=Ph,Bu^n,OPh	208,222
$MnM'L_9(PR_3)$	M'=Re R=Ph,Bu^n,OPh	208,222

$Mn(CO)_5Br$ with $P(OMe)_3$ under reflux. I.r. results suggest that X (X=Me, Br) is trans- to the CO ligand in the mono- and di-carbonyl complexes and that the phosphine ligands occupy equatorial sites.

When PMe_2Ph is refluxed with $Mn(CO)_5Br$, the tricarbonyl complex trans-$Mn(CO)_3Br(PMe_2Ph)$ is obtained[174] and reactions of $ReOX_3(PPh_3)_2$ or $ReO(OEt)X_2(PPh_3)_2$ with CO in the presence of PPh_3 under refluxing conditions also give the tri-carbonyl complexes[135] trans-$Re(CO)_3X(PPh_3)_2$ (X=Cl, Br, I). In addition, when trans-$Re(CO)_3Cl(PPh_3)_2$ is refluxed in benzonitrile, it gives the dicarbonyl complex $Re(CO)_2Cl(PPh_3)_2$[135].

In contrast, when CO gas is passed through a refluxing 2-methoxy ethanol solution of mer-$ReCl_3(PMe_2Ph)_3$, two isomers are obtained.[136] One of the isomers exhibits three strong carbonyl absorptions in the terminal carbonyl region of the i.r. spectrum and two overlapping doublets in the ^1H n.m.r. spectrum. The other isomer shows only two strong and a weak terminal νCO band in the i.r. spectrum and a triplet, with relative intensities 1:2:1 in the ^1H n.m.r. spectrum. These isomers have been formulated as fac- and mer-

$Re(CO)_3Cl(PMe_2Ph)_2$ respectively. The analogue of the *mer*-isomer has also been isolated in a similar reaction using *mer*-$ReBr_3(PMe_2Ph)_3$.

The complex *mer*-$Re(CO)_3Cl(PMe_2Ph)_2$ can also be prepared by treating *trans*-$ReCl_4(PMe_2Ph)_2$ with CO or by the action of formic acid on *mer*-$ReX_3(PMe_2Ph)_3$ (X=Cl, Br).

Reduction of $Re(CO)Cl_3(PMe_2Ph)_3$ with $NaBH_4$, under refluxing conditions followed by the addition of H_2O gives the yellow complex[138] $Re(CO)_2Cl(PMe_2Ph)_3$, which can also be prepared by reducing *mer*-$ReCl_3(PMe_2Ph)_3$ with Na-Hg followed by passing CO gas through the solution.

Earlier, Freni *et.al*.[139] reported that on treatment of a benzene solution of $ReH_3(PPh_3)_4$ with CO, the white crystalline complex $Re(CO)_2H(PPh_3)_3$ is formed. Moreover, when $ReH_3(PPh_3)_4$ is treated with CO over an extended period of time, another white complex, $Re(CO)_3H(PPh_3)_2$, is obtained.

When $Mn_2(CO)_{10}$ is irradiated with U.V. light in the presence of PPh_3, it gives an orange complex[207], which can also be prepared by heating $Mn_2(CO)_{10}$ with PPh_3 in an evacuated tube. Analytical and i.r. data suggest that the product is dimeric with symmetrically substituted PPh_3 groups occupying axial positions as shown in Fig.34. The Re analogue has also been prepared[208] under similar conditions using $Re_2(CO)_{10}$ and PPh_3.

A large variety of bis-phosphine complexes have been prepared for this subgroup. For example, when a mixture of $Mn(CO)_5Br$ and P-P (P-P=dppm, dppe) is irradiated, the orange monocarbonyl complexes[211] $Mn(CO)Br(P-P)_2$ are obtained. It has been suggested that the least restricted structure for these complexes is one with a trans-configuration of the P-P ligands as shown in Fig.35. This is also supported by the extreme resistance to substitution shown by the carbonyl group trans- to the bromide ligand in $Mn(CO)_5Br$.

Analogous Re complexes (when (P-P)=dppe, dppp) have also been prepared[185] by treating $ReCl_2(PhCON_2)(PPh_3)$ with CO under refluxing conditions followed by the addition of P-P.

Very recently Carr, Shaw and Pett[224] have

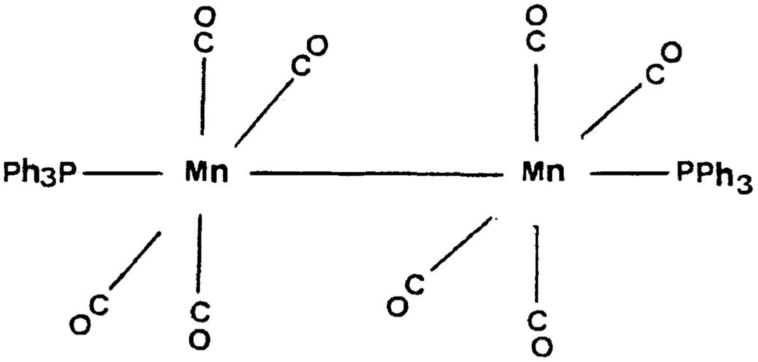


Fig. 34.

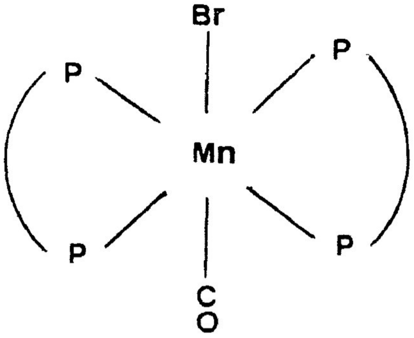


Fig. 35.

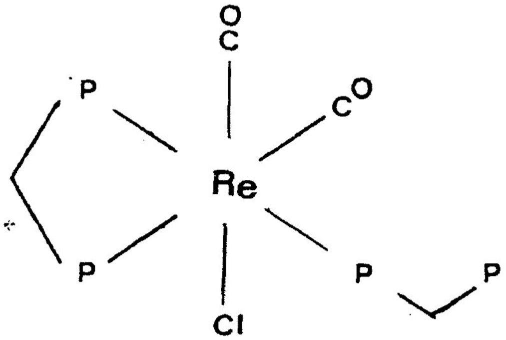


Fig. 36.

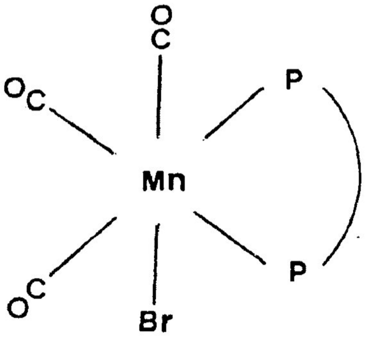


Fig. 37.

reported that treatment of $Re(CO)Cl_5$ solution with dppm under refluxing conditions yields a white complex which exhibits two strong bands in the terminal carbonyl region, at 1936 and 1837 cm^{-1} respectively while the ^{31}P n.m.r. spectrum shows four non-equivalent phosphorus nuclei with chemical shifts δ=-43.7, -27.0,-20.2 and 10.3 each showing phosphorus-phosphorus coupling. In addition, the ^{1}H n.m.r. spectrum in the PCH_2P region shows two AB type patterns. The one at higher frequency is assigned to the chelating dppm ligand, and the other the monodentate ligand. On the basis of these results, the authors have suggested that the complex is monomeric having the chemical formula $Re(CO)_2Cl(dppm)_2$ where one of the dppm ligand acts as a monodentate ligand as shown in Fig.36. The Mn analogue has also been prepared and characterized similarly.[225,231] Mention of this will be made again in the discussion section of this thesis.

When dppm or dppe is added to a warm benzene solution containing $Mn(CO)_5Br$ followed by U.V. irradiation, yellow complexes are obtained.[211] These complexes can also be prepared by the bromination of $Mn_2(CO)_6(P-P)_2$ (P-P=dppm, dppe). Analytical and i.r. data suggest that these complexes are monomeric with the formulation _fac_-[$Mn(CO)_3$ Br(P-P)] as shown in Fig.37.

Colton and Commons[218] had reported earlier that a very interesting red complex is formed on prolonged refluxing of $Mn_2(CO)_{10}$ with dppm. This complex shows four strong νCO bands in the terminal carbonyl region, together with a strong band at 1645 cm^{-1}. The ^{31}P n.m.r. spectrum shows a single resonance at δ=69.45 consistent with bridging dppm. An X-ray diffraction study[197] revealed that the molecule is dimeric, with the two metals linked by two dppm ligands, and two CO groups are terminally bonded to each metal. In addition, one CO group is coordinated in an unusual bridging fashion, being bonded through both the C and the O atoms. This is apparently the first example of a CO group acting as a novel four electron donor, with two electrons going to each manganese atom. The geometry around each metal (ignoring the metal-metal bond) is distorted trigonal bipyramidal as shown in Fig.38.

The treatment of a CH_2Cl_2 solution of this complex with SO_2, produces an orange complex[220] which has been characterized as $Mn_2(CO)_5(SO_2)(dppm)_2$ with the structure shown in Fig.39. I.r. data suggest that the bridging CO group behaves as a normal two electron donor in this complex. It was also noted that the addition of

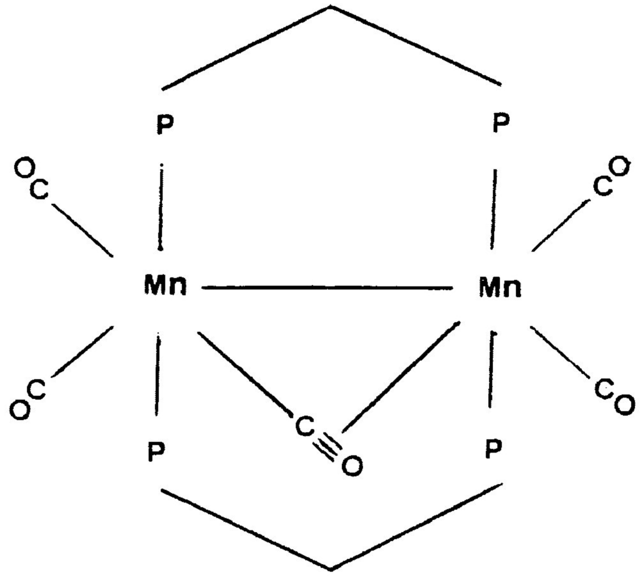


Fig. 38.

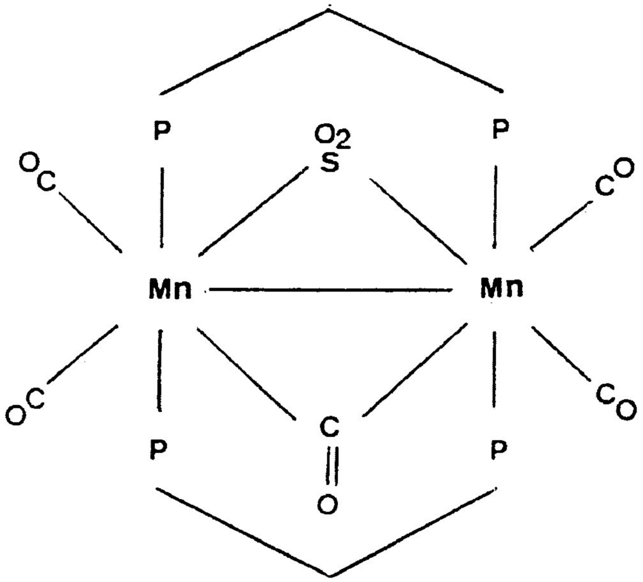


Fig. 39.

SO_2 is reversible and, on heating a solution of the SO_2 complex, regeneration of the parent $Mn_2(CO)_5(dppm)_2$ complex occurs.

Recently, Prest <u>et.al</u>.[219] have reported that when $Re_3(CO)_{12}H_3$ is refluxed with an excess of dppm, followed by chromatography,it gives, in addition to other products, a dihydride complex, $Re_2H_2(CO)_6(dppm)$, which has been characterized by X-ray diffraction studies as a dimeric system in which six carbonyl groups are terminally coordinated with three on each metal atom. In addition, the two hydrides and the dppm ligand bridges the two metal atoms. The Re-Re bond distance, at 2.893Å, is significantly shorter than expected for a single Re-Re bond. A metal-metal double bond has been proposed in order to satisfy the EAN rule. The structure is shown in Fig.40.

Similar reactions of $Re_3(CO)_{12}H_3$ with tedip $[(EtO)_2POP(OEt)_2]$ gives the analogous $Re_2(CO)_6(\mu\text{-}H_2)(\mu\text{-tedip})$ complex.[219]

However, reactions of $Re_3(CO)_{12}H_3$ with dppe gives, in addition to other products, a colourless complex which has been tentatively[219] assigned the

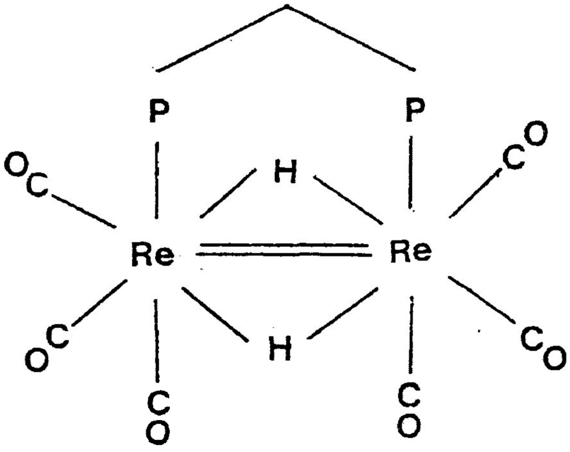


Fig. 40.

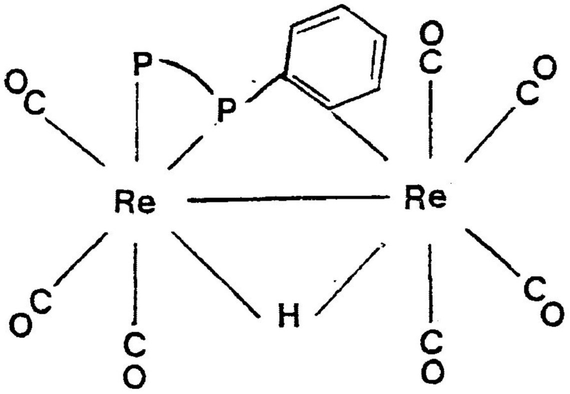


Fig. 41.

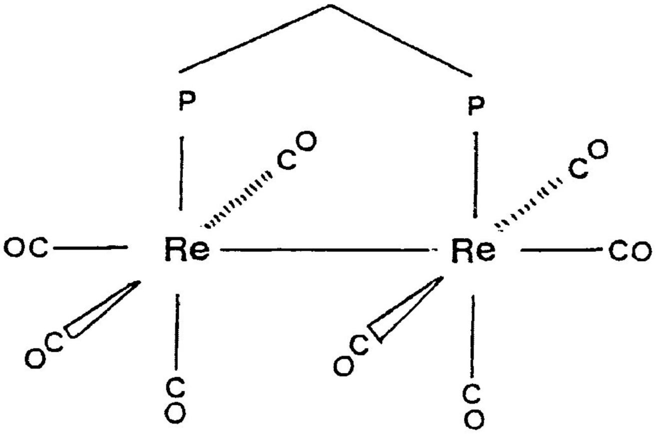


Fig. 42.

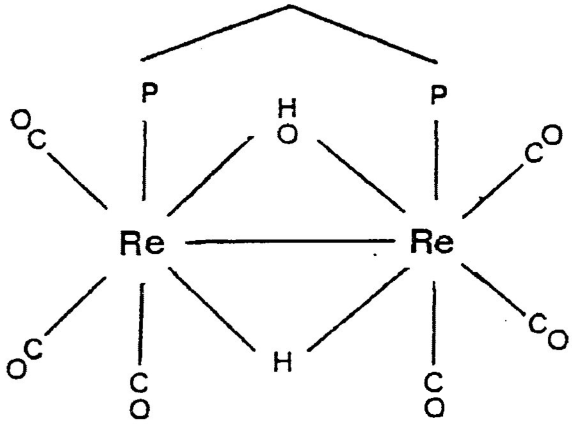


Fig. 43.

compared to the remaining four CO groups which have no *trans*-ligands with π-acceptor properties. It has been suggested that this is partly due to the competition for dπ electron density between the carbonyls and phosphorus.

The reaction of $Re_2(CO)_8(P-P)$ (P-P=dppm,dmpm) with MeOH proceeds similarly to that of $Re_2(CO)_8$(dppm) with H_2O and gives $Re_2(CO)_6(\mu-H)(\mu-OMe)(P-P)$ and $Re_2(CO)_6(OMe)_2(P-P)$ respectively.

The authors[221] have suggested that metal-metal bond homolysis is involved in the formation of these complexes. However, the bridging ligand in $Re_2(CO)_8(P-P)$ (P-P=dppm,dmpm) retains the two metal centers in close proximity and the radicals produced by photolysis rapidly reform the metal-metal bond. This reformation competes with ligand substitution for CO. Furthermore, the steric and electronic properties of the phosphine ligands have also been suggested to reduce the labilities of carbonyl radicals toward substitution. At the same time, prolonged irradiation makes other pathways, particularly CO dissociation, more likely. Photolysis of $Re_2(CO)_8(P-P)$ with ROH (R=H, Me) has been suggested to occur via either dissociation or homolytic metal-metal bond cleavage. Dissociation of CO would result in the formation of the coordinatively unsaturated species $Re_2(CO)_7(P-P)$ which could pick up one ROH group followed by dissociation of a CO group from the other metal center, thus forming $Re_2(CO)_6(\mu-H)(\mu-OR)(P-P)$ via an O-H oxidative addition process. The same product is obtained via homolytic bond cleavage which is followed by the substitution of a CO group on each metal center by ROH, reformation of the metal-metal bond , and then loss of the one of the ROH groups followed by O-H oxidative addition process, forming finally $Re_2(CO)_6(\mu-H)(\mu-OR)(P-P)$.

Only a few heterobinuclear complexes from this subgroup have been reported and these are listed in Table[6]. Thus, recently, Hoskins, Steen and Turney[227] have reported that when a mixture of $Mn(CO)_5X$ (X=Cl, Br, I) and $Pd(dba)_2$ (dba=dibenzylidene acetone) and dppm is stirred in hot toluene followed by refluxing for 30 minutes, deep-red crystalline complexes are produced. These can also be prepared by treating $Na[Mn(CO)_5]$ with $Pd_2Cl_2(dppm)_2$ in THF at 0°C. One of these complexes was characterized by a single crystal X-ray diffraction study which showed that the molecule consists of an essentially planar $(CO)_3MnPdBr$ unit which is approximately perpendicular to the plane containing four phosphorus atoms of the two bridging dppm ligands. The Mn atom is six-coordinate having an edge-capping trigonal bipyramidal geometry where the metal-metal bond occupies the capping position. The three CO groups form the trigonal plane. The remaining two sites of the t.b.p. are occupied by the two phosphorus atoms from the bridging dppm as shown in Fig.44. The Mn-C distance is comparatively long while the Mn-C-O bond is close to linear, suggesting the presence of bridging CO and the absence of Pd-O interactions. On the basis of these observations, together with a νCO band in the i.r. spectrum at 1860 cm^{-1}, the authors have suggested the presence of a semi-bridging carbonyl group. It has been further suggested that the gross distortion of the carbonyl geometry is probably the result of substantial steric pressure arising from the CO ligands themselves and the phenyl groups of the dppm ligands which force two of the CO groups into the cavity surrounding the Pd atom, resulting in a relatively close approach made by Pd to two CO groups.

The analogous complexes, $MnPt(CO)_3X(dppm)_2$ where Pt takes the place of Pd, have been reported[225] as being formed when <u>mer</u>-$[Mn(CO)_2X(dppm)(\eta^1\text{-}dppm)]$ (X=Cl, Br) is treated with $Pt(PPh_3)_4$ under a CO atmosphere, at

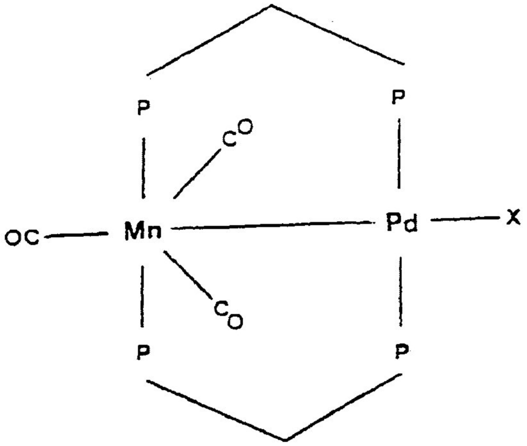


Fig. 44.

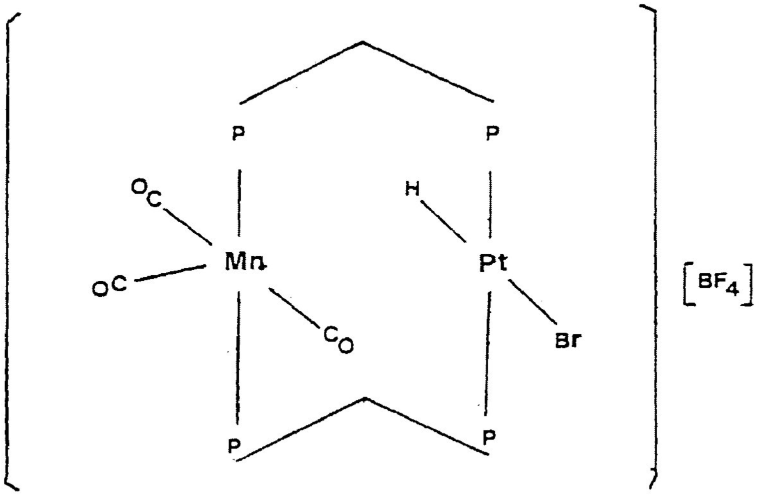


Fig. 45.

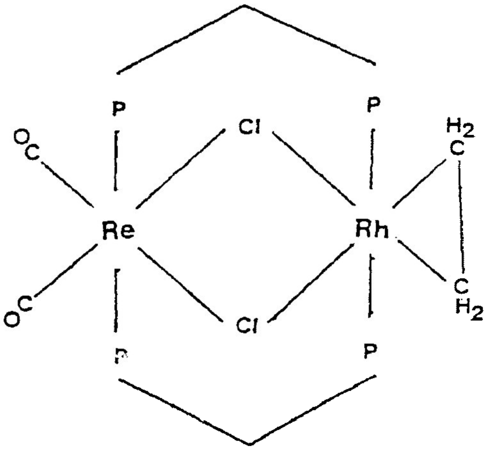


Fig. 46.

elevated temperatures.

On treatment of these bimetallic complexes with an excess of $HBF_4.Et_2O$, the deep red crystalline complexes $[MnPt(CO)_3H(X)(dppm)_2]BF_4$ are obtained[222] (X=Cl, Br). However, the i.r. spectra show that the CO groups are now entirely terminal. In addition X-ray analysis on the Cl complex reveals that the Mn and Pt atoms are linked by two dppm bridges forming an eight membered MnP_4C_2Pt ring in the boat conformation as shown in Fig.45. The ^1H n.m.r. spectrum shows a sharp singlet for the CH_2 group, with satellites due to ^{195}Pt coupling, and it did not resolve from room temperature to $-90^{\circ}C$, indicating that the hydride in this complex moves rapidly from one side of the P_4 plane to the other causing equivalence of the CH_2 hydrogens.

Complexes of the type $[MnM(CO)_4Cl(dppm)_2]PF_6$ (M=Rh, Ir) have also been reported to form[223] when $Mn(CO)_2Cl(dppm)(\eta^1\text{-dppm})$ is treated under a CO atmosphere with $Rh_2(CO)_4Cl_2$ and $Ir(CO)_2Cl(H_2NC_6H_4Me\text{-}P)$ respectively.

Very recently, Carr, Shaw and Pett[224] have reported that when $Re(CO)_2Cl(dppm)(\eta^1\text{-dppm})$ is treated with $Rh_2Cl_2(C_2H_4)$, a yellow complex is obtained. The ^{31}P

n.m.r. spectrum shows a singlet and a doublet at δ=6.9 and 28.0 respectively of equal total relative intensity. This is in contrast to the general AA'XX' or AA'BB' pattern frequently observed in the spectra of heterobimetallics where dppm bridges the two metals. The i.r. spectrum shows two νCO bands at 1952 and 1849 cm^{-1}. A single-crystal X-ray diffraction study shows that the $(CO)_2Re(\mu\text{-}Cl)_2Rh(C_2H_4)$ unit is approximately perpendicular to the plane of the four phosphorus atoms, the two CO ligands are terminally coordinated to the Re atom and the two Cl atoms symmetrically bridge the Re and Rh atoms. In addition, C_2H_4 is η^2-terminally bonded to the Rh atom, with a long C-C distance, while the Re-C distance in the ReC_2H_4 unit is short suggesting that C_2H_4 is unusually strongly bonded to the Rh. It has been suggested that this may be due to the strongly donating phosphine ligands promoting back bonding of the type $d\pi(Rh) \dashrightarrow \pi^*(C_2H_4)$. Moreover, the ^1H n.m.r. spectrum shows the C_2H_4 resonance at 0.98 ppm, again suggesting unusual bonding of the C_2H_4 in which this unit is coordinated into a Rh-cyclopropane type of structure as shown in Fig.46.

1.3.6. Fe, Ru and Os:

Table [7].

Complex	Metal		Method of syntheses and comments	Ref
$[MLX(PR_3)_3[Z]$	Fe,Ru,Os	I^b	R_3=PMe_2Ph,$PMePh_2$,PCy_3,PPh_3,P(OMe)3	234-235
			Z=PF_6,BPh_4;X=NO	
$[MLX(PPh_3)_a(Y)][Z]_b$	Fe,Os	D	R=PhN_2,$P(OMe)_3$	235,236
			Z=BPh_4;a=1,2;b=0,1	
$ML(NO)X(PPh_3)$	Fe,Os		X=$MeCO_2$;	234,235
$ML(Cp)(PPh_3)X$	Ru,Os	$C^{b,e}$	X=Cl,Br	237
$[M2LX_3(PR_3)_5][Z]_3$	Os	$F^{b,d}$	R=Ph;X=Z=Cl	238
$MLXR(PPh_3)_2$	Ru,Os	I^c	R=N_2Ph;H_2Ph;X=H,D	239
MLXX'(PR)	Ru,Os	$F^{b,d}$	X=Cl,Br,I;X´=H,NO,Cl;R=Cy,Ph	235,238
′ 3 2				
				240
$MLHX(PPh_3)_3$	Ru,Os	$F^{b,d}$	X=H,Cl,Br	241-248
		C		259
$MLXX'(PR_3)_2$	Ru,Os	J	X=NO,,NO_3,OAc;X´=H,Cl;R=Cy,Ph	246-247
$MLXR'(PR_3)_2$	Ru,Os	H	X=Cl,MecN;R´=PH_2Ph,HCS_2;R=Cy,Ph	240,248
$ML_2XR'(PR_3)_2][Z]_a$	Fe,Ru,Os	H	Y=H,D,N_3,NO,NCO,HCO,NO_2,$MeCO_2$,Cl,	236,239
			Br,I,;Z=BF_4;a=0,1	
$ML_2R'(PR_3)_2][Z]a$	Fe,Ru,Os	$H^{b,c}$	R´=N_2Ph,NO;R=Cy,Ph,Me_2Ph,$MePh_2$,	244,235
			OMe,OPh,Et_3;Z=BF_4,BPh_4	239
$MLH_2(PR_3)_3$	Ru	C	R_3=Ph_3,$MePh_2$;	244,245
				259
$ML_2XR'(PR_3)_2$	Fe,Ru,Os	D^b,	X=H,OAC,Cl,I;R´=H,Me,SMe,CF_2H,	240,242
		H^b,	CHNMe,CHSMe,PPhMe,CHO,MeCO,OAC,	247,
		$I^{d,b}$	NO_3,CH_2Cl,Cl,Br	249-256
		E		260,261

$ML_2R'(PR_3)_2$	Os	E	$R'=\eta^2-CH_2O,\eta^2-CH_2S,R=Ph$	254,255
$ML_2R_2(PR_3)_2$	Os	E^b	$R=H,HCO_2$	257,251
$ML_2R(PPh_3)_2$	Ru,Os	H	$R=PPH(OMe);CNMe,=CF_2$	248,260
$ML_2XR(PPh_3)_2][Z]$	Os	$I^{b,c}$	$X=Cl,H_2O;R=CH_2OMe;Z=CF_3SO_3,$	254,
			$AlCl_4,S_2N_2$	258
$M_2L_2(PR_2)_2$	Fe	H^a	$R=Ph$	262
$[ML_2(Cp)(PR_3)][PF_6]$	Fe	I^e	$R_3=PMe_2Ph;PPh_2H,Ph_2Me$	262
$M_2L_2(Cp)_2(PPh_2)_2$	Fe	I^b		262
$ML_3(Pr_3)_2$	Fe,Ru,Os	$A^{b,c}$	$R=Ph$	263,249
		D^b		251,264,
		F^d		265,287
$ML_3(PR_3)_2$	Fe	A^b,	$R_3=Me_3,Ph_2H,(OMe)_3$	250,266
		I^b		267
$M_2L_3R'_3X(PR_3)_2$	Ru	I^b	$R'=CH_3CO_2;X=OH,R=Bu^n$	268
$ML_3XX'(PPh_3)$	Ru,Os	D^a,	$X'=X=H,Me,Cl,Br,I$	251,238
		$E^{a,b}$	$X=H,X'=Me,SiPh_3,Cl$	256,265
		$F^{b,d}$		269,270
$[ML_3X(PPh_3)_2][Z]$	Os	E,H	$X=H,Br,I;Z=Br,I,HCl_2,ClO_4,$	257,
			$BF_4;PF_6$	265
$ML_4(PPh_3)$	Fe,Ru,Os	$A^{a,b}$		251,271,
				287
$ML_4(PR_3)$	Fe,Os	A^a,	$R=Et,OMe,OPh$	256,
		b,c,		263,
		D^b		267
$ML_4(PR_3)$	Fe	A^b	$R_3=MeH_2,Me_2H,Et_2H,PhH_2,Ph_2H$	266,
			$PhMeH,(p\text{-toluene})_2H$	272
$ML_4X_aR'_b(PR_2)_c$	Fe	$I_{a,b}$	$X=Cp;a=1,2;R'=PEt_3,PPh_3,P(OMe)_3$	262,
			$P(OEt)_3,P(OPr^i)_3;b=0,1,2;R_2=Ph_2;$	273
			PhH	
$M_2L_5(Cp)(PR_2)X_a$	Fe	I^a	$R=Ph;X=PR'_3,P(OR')_3$	273

			R'=Me,Et,Pr^i,Ph;a=o,1	
$M_2L_6X(Y)_2$	Fe	A^b	X=H_2;Y=$P(CF_3)_2$	274
$M_2L_6Y(Y')$	Fe	A^b,H	Y=Y´=PMe$_2$,PEt$_2$,PMeH,PPhMe,PPh$_2$C$_2$Ph	272,273,
			Y=C$_2$Ph,Cp;Y=PMe$_2$;PPh$_2$	275-
				279
$M_2L_8(PM_{e2})_2$	Fe	A^b		276,278
$M_2L_8(PPh)_4$	Fe	A		280
$MLX_3(P-P)_2$	Os	$F^{b,d}$	P-P=dppm,dppe	238
$[ML(X)(Y)_a(P-P)][Z]$	Fe,Ru,Os	D^b	P-P=dppm,dppe;X=CH,PPh$_3$,I;Y=NO,Cp	235,281
			Z=BPh$_4$,PF$_6$,BF$_4$;a=1,2;b=0,1	317
$[M_2L(Cp)_2X(P-P)][Z]_a$	Ru		X=CH,CH$_2$,CH$_3$;P-P=dppm;	282
			Z=BF$_4$;a=0.1	
$[ML(X)(P-P)][Z]_n$	Fe,Ru	C^c	P-P=dppe;dppee;Z=BPh$_4$;PF$_6$;SbF$_6$,Cl	281
		$I^{a,e}$	X=Cp,COD;n=0,1	318
$ML(P-P)_2$	Ru	C	P-P=dmpe	283,294
$[ML(X)(P-P)_2][Z]_a$	Ru	H,C	P-P=dppm,dppe,depe,dppp	285
			X=H,CHO,^{13}CHO,CDO;L=CO,^{13}CO	286
			Z=SbF$_6$;BEt$_4$,PF$_6$;a=0,1	
$[M_2L_2(X)_a(Y)_2(P-P)][Z]$	Fe	H^e,	P-P=dppm;dppe,dppp,;Y=Cp;X=I,	281
		I^e	a=0,1;Z=BF$_4$,BPh$_4$,SbF$_6$,Cl$_2$	
$ML_2(P-P)(\eta^1-P-P)$	Fe	B,	P-P=dmpm,dppe	283,294
$ML_2X_2(P-P)$	Ru	F^b	X=I;P-P=dppm	290
$[ML_2X_2(P-P)][Z]_n$	Fe,Ru	D^b,	X=NO,Cp,COD;P-P=dppm,dppe	234,163
		F^e	Z=PF$_6$;n=0,1	318
$[M_2L_2(Cp)_2(P-P)][Z]n$	Fe	$D^{b,e}$	P-P=dppm,dmpm,dppe,dppea	281,292
			Z=BPh$_4$,SbF$_6$,Cl$_2$;n=0,1	293,162
$M_2L_2(Me-Cp)_2(P-P)$	Fe	D^b	P-P=dppm,dppe,dppee,dppea;	281,292
			dppea=Ph$_2$PNEtPPh2;	
			dppee=Ph$_2$PC$_2$H$_2$PPh$_2$	
$M_2L_2(Cp)_2X_2(P-P)$	Fe	H^b	P-P=dppe;X=I	281
$ML_3(P-P)$	Fe,Ru	A^a,	P-P=dppe	295,281

		D^a		316
$ML_4(P-P)$	Fe	A^a	P-P=dppm	316
$M_2L_4XR(P-P)$	Ru	A^a,	P-P=dppm,$Ph_2PCHPPh_2$;X=R=I,	290
		H^b	X=H,Cl;R=PPh_2,$PhPC_6H_4$,$PhPC_6H_4C(O)$	297
$M_2L_4R(P-P)$	Ru		R=dppm;P-P=dppee	315
$M_2L_5(P-P)_2$	Fe	A^a,	P-P=R_2PXPR_2;R=Me,F,	298,309
		B^a	X=CH_2,MeN	162
$M_2L_6(P-P)_2$	Fe,Ru	A^b	P-P=R_2PXPR_2;R=F;X=MeN	298,315
$M_2L_6H(Ph_2PCHPPh_2)$	Fe	H^b		314
$M_2L_7(P-P)$	Fe	$A^{a,b}$	P-P=R_2PXPR_2;R=Me,Ph,F	298,28
		B^a	X=CH_2,MeN	162,316
$M_2L_8(P-P)$	Fe	A^a	P-P=R_2PXPR_2;R=F,Ph	298
			X=MeN,$(CH_2)_n$;n=	

Bimetallic Complexes:

Complexes	Comments	Ref
$[MM'L_2X(P-P)]$	M=Os;M'=Rh;X=Cl,Br	307
	P-P=dppm	
$[MM'L_3X(P-P)]$	M=Ru;M'=Rh;X=Cl	
	P-P=dppm	306
$[MM'L_3R(P-P)]$	M=Fe;M'Co,Rh;R=C_7H_7,$(NO)_3$	305,313
	P-P=dppe	
$[MM'L_4X_2(P-P)]$	M=Fe;M'=Pt;X=Br	299
	P-P=dppm	
$[MM'L_5X(P-P)]$	M=Fe;M'=Rh;X=Cl	299
	P-P=dppm	
$[MM'L_5R(Y)]$	Y=PPh_2;R=$(PPh_2H)_2$;$(PPh_2Me)_2$;$(PMe_2Ph)_2$;	310
	$(Ph_2PC{\equiv}CPh)_2$	
	M=Ru,M'=Co	

$[MM'L_6(P-P)_2]$	M=Fe;M'=Cr P-P=dmpm	283, 309
$[MM'L_6R(Y)]$	M=Ru;M'=Co;R=PMe_3,PPh_3,PPh_2Me,PMe_2Ph, $(Ph_2PC{\equiv}CBu^t)_n$;$Ph_2PC{\equiv}CPh$ Y=PPh_2;n=1,2	310
$[MM'L_7(PR_2)]$	M=Fe;M'=Co R=Ph	300
$[MM'L_7X(P-P)]$	M=Fe;M'Mn;X=Br P-P=dppm	307
$[MM'L_8X_a(Y)]$	M=Fe,Os;M'=Mn,Re X=Br,H;a=0,1;Y=PMe_3,PPh_2,dppm	302,301,
$[MM'L_8(P-P)]$	M=Fe;M'=Mo,Ru P-P=dppm,dppe	302,307
$[MM'L_9(Y)]$	M=Fe,Os;M'=Mo,W Y=PMe_3,dppm	303,307

Again, from this group, a very large number of complexes showing a wide varity of structural types has been prepared using mono and bisphosphines. Representative examples are listed in Table[7], and these can be conveniently generalized by the formula $[M(CO)_{n-x}Y_x]_z$ where n=5, z=1 or 2 and x=1-4; M=Fe,Ru,Os; L=CO; Y=phosphine.

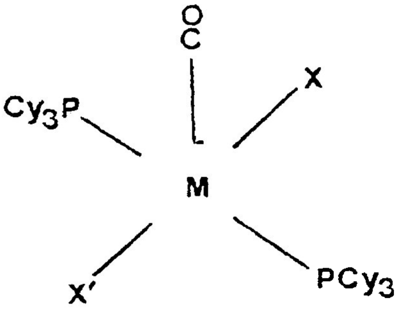
Highly substituted complexes of the type $[M(CO)X_aY_{b-a}][Z]$ (a=1,2, b=4) with monophosphines have been reported for all three metals. Thus, Johnson and Segal[234] have reported that when PMe_2Ph is added to a solution of $[Fe_2(CO)_2(NO)(PMe_2Ph)]_2[PF_6]$ a complex formulated, on the basis of analytical and i.r. data, as $Fe(CO)(NO)(PMe_2Ph)_3$ was obtained. In a similar reaction, they also prepared $[Fe(CO)(NO)\{P(OMe)_3\}_3][PF_6]$. However, when PPh_3 or PCy_3 were used in analogous reactions, the fact that monocarbonyl complexes were not formed was attributed to the steric bulk in these ligands. The analogous Ru and Os complexes were prepared[235] where $[M(CO)_2(NO)(PR_3)_3][BPh_4]$ (R=Ph,Cy,$MePh_2$) was reacted with PR_3 under refluxing conditions. X-ray diffraction results on the complex $[Ru(NO)(dppe)_2][BPh_4]$[237] and $[Os(CO)_2(NO)(PPh_3)_2][ClO_4]$[238] showed the metals to be coordinated in a trigonal bipyramidal geometry with linearly bonded NO located in the equatorial plane of the trigonal bipyramid. However, treatment of complexes of the type $M(CO)_2(NO)X(PR_3)_2$ (M=Ru,Os) with halide ions resulted in attack at the metal center leading to neutral complexes of the type $M(CO)(NO)(PR_3)_2$ (X=halide). In contrast, reactions with methoxide ion (when M=Fe,Os) occurred at coordinated carbonyl sites, forming neutral carboxy-derivatives,[234,235] which were isolated and characterized except for the Ru compound which could not be isolated due to its instability.[235]

A red dimeric complex of Os was obtained[238] when Os(IV) chloride was treated with PPh_3 and concentrated in 2-methoxyethanol. The complex, formulated as $[Os_2(CO)Cl_3(PPh_3)_5]Cl_3$, shows i.r. signals consistent with a terminally coordinated CO and bridging Cl groups although no further details were given.

Moers et.al reported[240] that on passing CO gas through an ethanolic solution containing M(III) or M(IV) halide salts (M=Ru,Os) in the presence of PCy_3 or simply by mixing these metal salts with PCy_3 in 2-methoxyethanol and heating over an extended period of time, orange to brown complexes were obtained. On the basis of analytical and i.r. data the authors proposed that the complexes have five-coordinated square pyramidal structures, with phosphine ligands occupying, for steric reasons, trans-positions as shown in Fig.47.

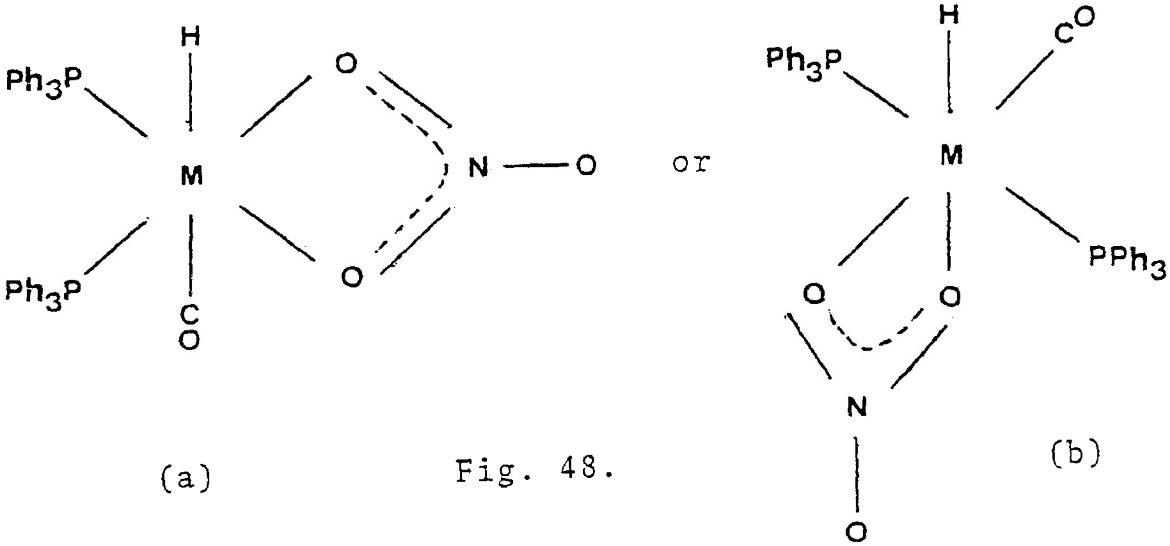
Similarly, carbonyl hydride complexes of Ru and Os were also obtained on treatment of either hydrated metal chlorides with ethanolic potassium hydroxide in the presence of phosphine ligands or by treating metal(IV) chlorides with potassium hydroxide and phosphines at elevated temperatures, giving systems which were characterized[241,243,259] by analytical and spectroscopic data as $M(CO)HX(PPh_3)_3$ (X=H,Cl,Br).

In addition, alcoholysis of $M(CO)(NO_3)_2(PPh_3)_2$ (M=Ru,Os) type complexes results in the formation of white, crystalline hydrido carbonyl complexes.[247] ^1H n.m.r studies reveal the hydride signal as a high field triplet while the ^{31}P spectrum shows a singlet due to magnetically equivalent ^{31}P nuclei. These results, together with i.r. and other evidence, suggested the structures shown in Fig. 48(a) and (b) for these carbonyl hydrido complexes. However, the relatively high values of the hydride resonances in the ^1H n.m.r. spectrum and the νM-H frequencies in the i.r. spectrum favour the structure 48(b).



X=Cl,Br
X'=H,Cl
M=Ru,Os

Fig. 47.



(a) Fig. 48. (b)

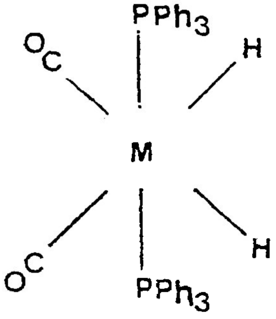


Fig. 49.

Di- and tri-substituted complexes of the type $M(CO)_3(PPh_3)_2$ and $M(CO)_2(PPh_3)_3$ have been prepared for all three metals. Thus, the reactions of $Fe(CO)_2(C_7H_8)$ with PPh_3 in ethylcyclohexane produced a yellow solution which, on chromatography, yielded a yellow complex formulated (analytical and i.r. results) as $Fe(CO)_3(PPh_3)_2$.[247] This complex can also be prepared by treating $Fe(CO)_5$ with PPh_3 at elevated temperatures in an evacuated sealed tube.[287] The presence of a single νCO band in the i.r. spectrum has been interpreted as being due to a molecule with D_{3h} symmetry in which the CO is assigned to the trans-geometry.

On the other hand, when PPh_3 was treated with $Fe(CO)_3(C_4H_4)$ in a manner similar to that described above for the C_7H_8 derivative, another yellow complex was obtained which was formulated as $Fe(CO)_2(PPh_3)_3$.[247] Two strong bands in the νCO region in the i.r. spectrum were interpreted as being due to the presence of two isomers having trigonal bipyramidal structures with the CO groups occuping either the axial positions or adjacent positions to one another.[247]

The similar Ru and Os compounds,

$M(CO)_3(PPh_3)_2$, M=Ru,Os, have been prepared from reactions of $M(CO)_5$ with PPh_3.[251] These complexes react with hydrogen at elevated temperatures and pressures in THF to form the colourless complexes $M(CO)_2H_2(PPh_3)_2$. N.m.r. and i.r. data show[251] that these complexes have the structure shown in Fig.49.

Monosubstituted derivatives of the type $M(CO)_4(PPh_3)$ have been reported for all three metals. Thus, $Fe(CO)_4(PPh_3)$ has been prepared from the reaction of $Fe(CO)_5$ with PPh_3 and spectroscopic data are consistent with the molecule having C_{3V} symmetry[237]. The analogous Ru and Os complexes have been prepared by treating $M(CO)_5$ compounds (M=Ru,Os) with one equivalent of PPh_3 in THF under UV irradiation.[251]

A wide variety of bisphosphine complexes is known. For example, Haines and Dupreez[231] reported that treatment of $Fe(CO)_2(Cp)Cl$ with dppe or <u>cis</u>-dppee in THF under UV irradiation in the presence of certain anions, produced yellow complexes formulated as [Fe(CO)(Cp)(P-P)][Z], (P-P=dppe,<u>cis</u>-dppee;Z=BPh_4 or SbF_6) Similarly, when $Fe(CO)_2(Cp)I$ was treated with dppm under refluxing conditions in benzene, a green complex formulated, on a similar basis, as [Fe(CO)(Cp)(dppm)]I was obtained.

Another example of CO displacement by a phosphine is illustrated by the fact that treatment of $Ru_2(CO)_3(Cp)_2CH_2$ with dppm under U.V. light produces[222] the complex $Ru_2(CO)(Cp)_2(CH_2)(dppm)$ which can be protonated with $HBF_4.OEt_2$ to form $[Ru_2(CO)(Cp)_2(Me)(dppm)]^+$, isolated as the BF_4^- salt. Slow crystallization of the latter from THF-Hexane, resulted in the formation of $[Ru_2(CO)(Cp)_2(CH)(dppm)]BF_4$ A single crystal X-ray diffraction study on this orange complex revealed that the Cp ligands are cis to each other, due to the coordination of the dppm ligand having bulky phenyl groups. The central $Ru_2(\mu\text{-}C)_2$ unit is somewhat puckered and the μ-CH ligand bridges the Ru_2 units symmetrically with the $Ru_2(CH)$ being near planar as shown in Fig.50.

These authors further noted that the Ru(μ-CH) distance at 1.937(7)Å was significantly shorter than the Ru(μ-CO) distance at 2.028(6)Å, which is attributed to the superior π-acceptor qualities of CH^+ as compared to CO. It was further suggested that the formation of these complexes probably involves a mechanism where the μ-CH_2 complex is readily oxidized to

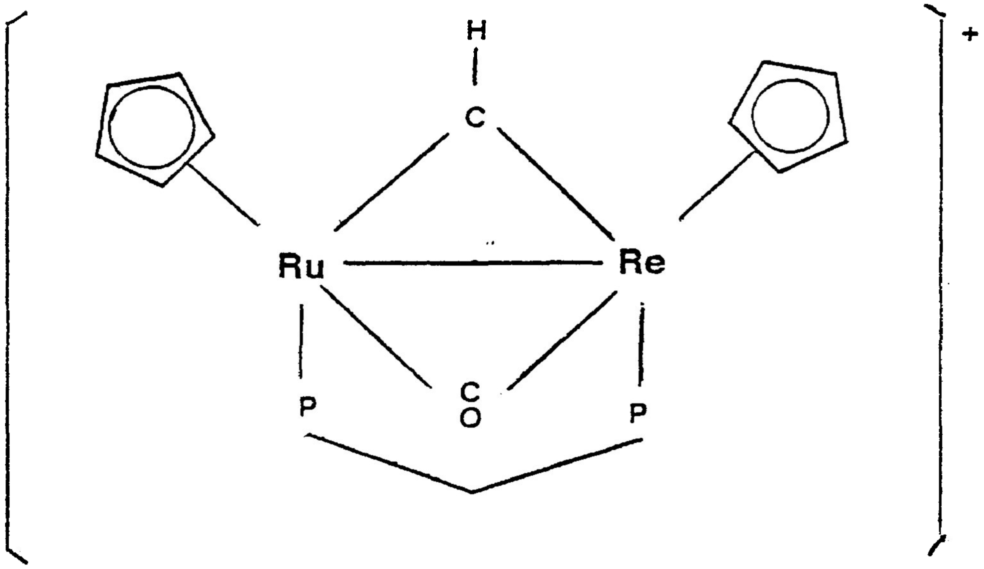


Fig. 50.

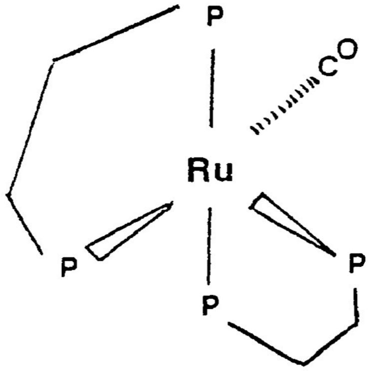


Fig. 51.

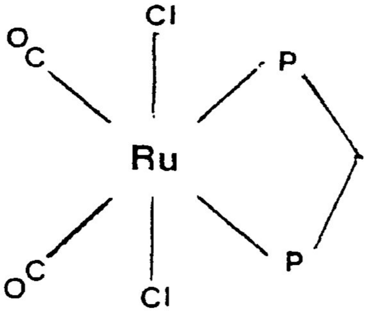


Fig. 52.

its radical cation which loses a hydrogen radical upon treatment with $Ph_3C^{\cdot}$ to give the μ-CH complex. However, the μ-CH_2 complex could not be converted into the μ-CH complex upon treatment with $[Ph_3C][BF_4]$. Furthermore, the μ-CH complex, even under 1 atm. of hydrogen, does not revert to the μ-CH_3 complex.

Johnson and Segal reported[235] that when $M(CO)(NO)(PPh_3)_2Cl$ (M=Ru,Os) are treated with $AgPF_6$ in CH_2Cl_2/acetone followed by the addition of dppe, the cationic species $[M(CO)(NO)(PPh_3)(dppe)]PF_6$ is formed. A trigonal bipyramidal structure was suggested on the basis of i.r. data.

Very recently, Jones and Libertini[310] reported that when CO gas is passed through a benzene solution containing $Ru(dmpe)_2(PMe_3)$ at 25°C, the pale yellow complex $Ru(CO)(dmpe)_2$ is formed. A single crystal X-ray diffraction study showed that the molecule has a trigonal bipyamidal structure with the CO ligand being on an equatorial position as shown in Fig.51. These authors suggested that this complex is formed either via an SN_2 type mechanism which involves an octahedral transition state formed by the attack of CO at the vacant site of the base of the square pyramid in $Ru(dmpe)_2(PMe_3)$

or via reversible dissociation of one end of a dmpe ligand followed by the coordination of the CO and rapid dissociation of PMe_3.

In contrast, Mague and Mitchener[312] reported that when CO gas is passed through an ethanol solution containing Ru(III) chloride under refluxing conditions followed by the addition of dppm, the yellow complex $Ru(CO)_2Cl_2$(dppm) results. Spectroscopic data show that the chlorine atoms occupy mutually *trans* positions while the CO groups are *cis* to each other as shown in Fig.52. However, when CO gas is passed through a refluxing solution containing *trans*-$RuCl_2(dppm)_2$, the white cationic complexes $[Ru(CO)Cl(dppm)_2][Z]$ (Z=Cl, BF_4 or PF_6). are formed. Spectroscopic data suggests that these complexes are octahedral with *trans* chlorine and CO groups.

In a very brief report, Khan *et.al*[238] have described that when Os(III) chloride and Os(IV) chloride are treated with dppm and dppe in DMF under refluxing conditions following by the addition of a few drops of concentrated HCl, the pale-yellow complex $Os(CO)Cl_3(dppm)_2$ and the green complex $Os(CO)Cl(dppe)_2$ are formed respectively. It has been suggested that in the dppe complex the chloride ligands occupy *trans*-positions to each other and *trans*- to a phosphorus atom in a *mer* arrangment, while n.m.r. spectra of the dppm complex show resonances due to the methylene protons of dppm ligands consistent with the phosphine acting in both a monodentate and bidentate manner. No further details were given.

Hydridocarbonyl complexes containing bisphosphine ligands have been reported to form for all three metals. Thus, on passing CO gas through an acetone solution containing *trans*-$MHCl(depe)_2$ (M=Fe,Ru,Os) and a stoichiometric amount of $NaBPh_4$, the yellow to colourless complexes $[M(CO)H(depe)_2][BPh_4]$[284] were formed. Again, no further details were given.

Relatively recently, Smith *et.al*[285] reported that treatment of either *trans*-$[Ru(CO)_2(dppe)_2][Z]_2$ or *cis*-$[RuCO)_2(dppm)_2][Z]_2$ ($Z=SbF_6$) with $Na[HB(OEt)_3]$ or $K[HB(OPr^i)_3]$ resulted in the formation of the complexes $[Ru(CO)(CHO)(P-P)_2][Z]$ (P-P=dppm,dppe). Moreover, treatment with $Li(HBEt_3)$ yielded the complex $[Ru(CO)(CHO)(P-P)_2][BEt_4]$ while $Li(DBEt_3)$ gives the complex $[Ru(CO)(CDO)(P-P)_2][Z]$ in which the X-ray crystallography shows that the CO and CDO groups are trans to each other. The ^{13}C labelled analogue was also prepared from trans-[Ru(^{13}CO)$_2$(dppe)$_2$][Z]$_2$ in a similar manner. It was noted that the reaction of trans-[Ru(CO)$_2$(dppe)$_2$][Z]$_2$ with Li(DBEt$_3$) was much slower than the reaction with Li(HBEt$_3$).

Recently, Wong et.al.[283] have reported that when a suspension of FeCl$_2$(dmpm)$_3$ in THF is treated with sodium amalgam and pressurized to 60 Psi of CO at elevated temperatures over three days, formation of two complexes, one yellow and one orange occurred. These complexes can also be obtained on pressurizing a hexane solution containing Fe(dmpm)$_3$ to 60 Psi of CO over two days. The ^{31}P n.m.r. spectrum of the yellow complex exhibits three resonances, a multiplet, a doublet and a singlet of relative intensities 1:2:1 centered at 46.4,-6.3 and -58.7 ppm. These resonances has been assigned to the P atoms of a coordinated monodentate ligand, a bidentate ligand (i.e.chelating ligand) and the uncoordinated P atom of a monodentate dmpm ligand respectively. In addition, the i.r. spectrum shows two CO bands in the terminal carbonyl region indicating a cis-dicarbonyl configuration, and on the basis of these results, a trigonal bipyramidal geometry shown in Fig.53 has been proposed. The orange compound exhibits a single νCO band in its i.r. spectrum and the ^{31}P n.m.r. spectrum

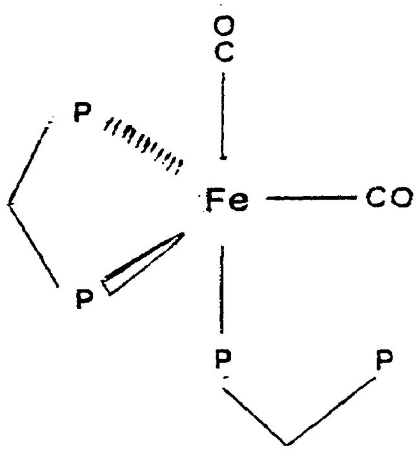


Fig. 53.

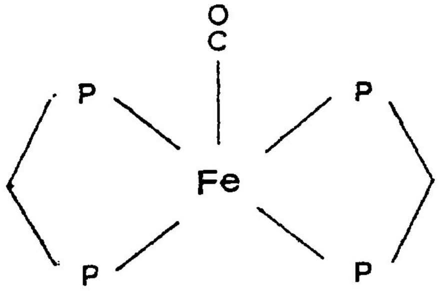


Fig. 54.

shows a singlet at 47.3 ppm.consistent with a square pyramidal structure as shown in Fig.54.

Earlier, Wegner _et.al._[316] reported that treatment of $Fe(CO)_5$ with dppm under U.V. irradiation yielded the yellow complex $Fe(CO)_4(dppm)$ in which the dppm ligand is coordinated via only one P atom thus forming a complex which is clearly closely related to that shown in Fig.53. Similarly, Isaacs and Graham[163] reported that reaction of $[Fe(CO)_2(Cp)(MeCN)][PF_6]$ with dppm and dppe in ethanol under refluxing conditions yield the yellow complexes $[Fe(CO)_2(Cp)(P-P)][PF_6]$ (P-P=dppm, dppe). Spectroscopic data reveal that the dppm and dppe are also coordinated through only one phosphorus atom in these complexes.

There are several examples in which dppm acts as a monodentate ligand to Ru. For example, recent work of Coville and Darling[317] revealed that the reaction of $Ru(CO)_2(Cp)I$ with dppm in toluene in the presence of $Fe(CO)_2(\eta^5-C_5Me_5)$ as a catalyst results in the formation of the yellow complex, Ru(CO)(Cp)I(dppm). Spectroscopic evidence suggests that the dppm is bonded to the Ru atom, utilizing only one phosphorus atom. In related work, Chaudret _et.al._[318] described that $Ru(COD)(dppm)_2$ reacts with CO gas in toluene to form the yellow complex Ru(CO)(COD)(η^2-dppm). This 5-coordinated Ru complex is monomeric with chelating dppm. However, CO reacts further with a solution of this complex in toluene to form $Ru(CO)_2$(COD)(η^1-dppm). Spectroscopic data indicate that dppm now bonds through only one phosphorus atom. It is interesting to note that it is one of the dppm ligands that was substituted rather than the COD, which is normally easily displaced from transition metal complexes.

In another recent report, Colombie et.al.[290] described that when $Ru_3(CO)_8$(dppm) is treated with iodine in toluene at elevated temperatures, a yellow solution forms which, on chromatography, yields the two complexes $Ru_2(CO)_4I_2$(dppm) and $Ru(CO)_2Cl_2$(dppm). The latter is analogous to $Ru(CO)_2Cl_2$(dppm)[312] shown in Fig.52, and an X-ray diffraction study on the former has revealed that the two Ru centers are bridged by a dppm ligand and two iodine atoms. The octahedral environment of each metal atom is achieved by two CO ligands as shown in Fig 55. In addition, a metal-metal bond has been proposed on the basis of a Ru-Ru distance of 2.7074(6)Å, as well as from electron counting (34 electron species).

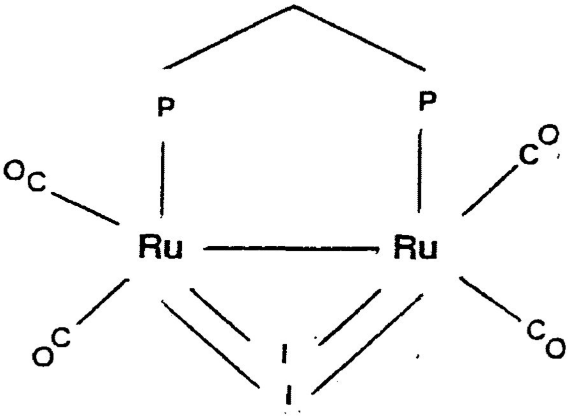


Fig. 55.

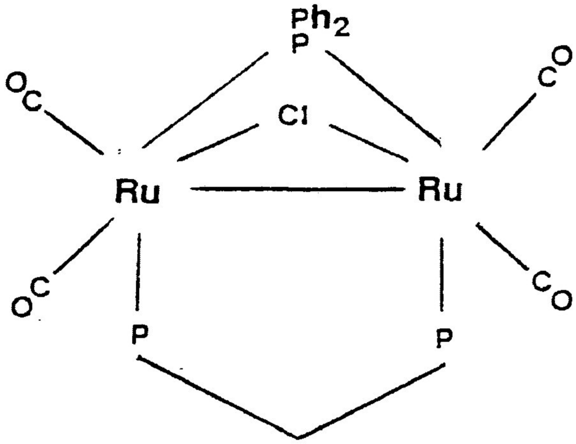


Fig. 56.

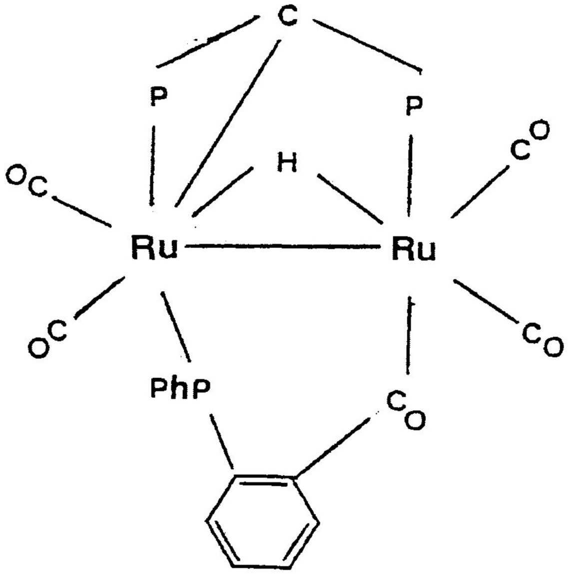


Fig. 57.

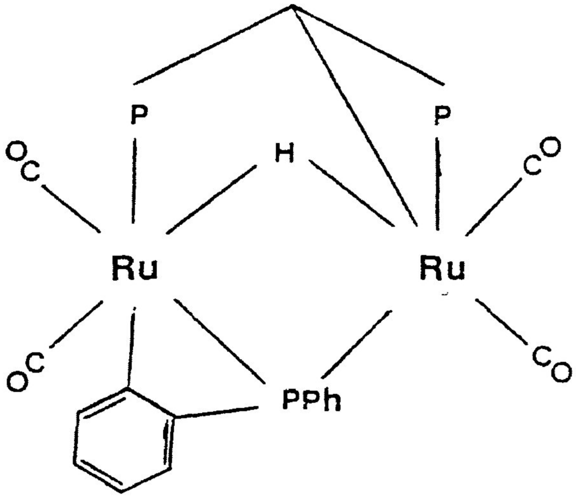


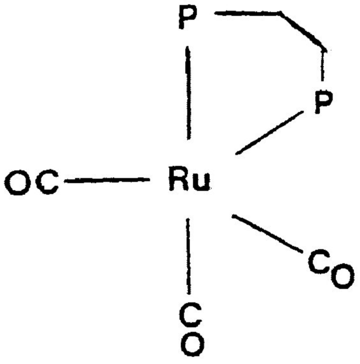
Fig. 58.

Reactions between $Ru_3(CO)_{12}$ and $HC(PPh_2)_3$ in THF at elevated temperatures have yielded several products,[297] formulated as $M_2(CO)_4(X)R(P\text{-}P)$ (where X=Cl, H; R=PPh_2, $PhPC_6H_4$, $PhPC_6H_4C(O)$; P-P=dppm, $Ph_2PCHPPh_2$). A single-crystal X-ray diffraction study on $Ru_2(CO)_4Cl(PPh_2)(dppm)$ shows that the molecule contains two Ru atoms bridged by a PPh_2 group, a dppm group and a Cl atom. In addition, there are two terminally coordinated CO ligands on each metal as shown in Fig.56. It was suggested that PPh_2 and dppm are presumably derived from $HC(PPh_2)_3$ by cleavage of a P-C bond to give PPh_2 and $HC(PPh_2)$ followed by the protonation of the central carbon atom on the $HC(PPh_2)_2$ unit to give dppm. The Cl probably comes from CH_2Cl_2 present as solvent of crystallization in the solid $HC(PPh_2)_3$. The hydrido complex $Ru_2(CO)_4H\{PhPC_6H_4C(O)\}$- $(Ph_2PCHPPh_2)$ has also been characterized by an X-ray diffraction study and has been shown to have the structure shown in Fig.57. This complex has been suggested to form by the cleavage of a P-C bond in $HC(PPh_2)_3$ as described above, except that instead of being protonated, the central carbon atom coordinates to a Ru atom forming Ru-C-P and Ru-P-C-Ru rings in a similar way to the formation of $(OC)_3Fe(\mu\text{-}Ph_2PCHPPh_2)FeH(CO)_3$[314] from the reaction of $Fe_2(CO)_7(dppm)$ and LiMe. The yellow-brown complex

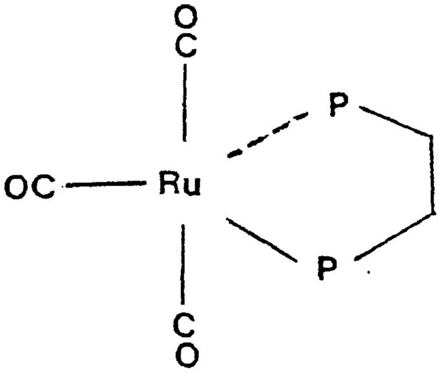
$Ru_2(CO)_4(H)(PhPC_6H_4)(Ph_2PCHPPh_2)$ was characterized by analytical and spectroscopic data, which together with a comparison of the spectroscopic data of the complex shown in Fig.57 led to the proposed structure shown in Fig.58.

In contrast, when $Ru_3(CO)_{12}$ is treated with dppe in benzene at elevated temperatures, under 100 atm. of CO pressure, the pale yellow complex $Ru(CO)_3(dppe)$ is formed[276]. The available spectroscopic evidence favours the structure shown in Fig.59(a), but (b) cannot be ruled out at the present time.

Cotton and Troup[23] have reported that when $Fe_2(CO)_9$ is treated with dppm in THF, a brown crystalline complex results.The molecule contains two iron atoms, each having three terminally coordinated CO ligands connected by a relatively long Fe-Fe bond at 2.709Å, and symmetrically bridged by a CO and a dppm ligand. The geometry around each iron atom is roughly trigonal bipyramidal with a P atom at an apical position as shown in Fig.60. ^{13}C n.m.r. spectroscopy in the CO region shows only a triplet with 1:2:1 intensity, consistent with the rapid scrambling of CO ligands over all sites, with the bridging and terminal CO ligands interchanging at a rate faster than can be detected on



(a)



(b)

Fig. 59.

the n.m.r. time scale.

In contrast, Newton <u>et.al</u>.[298] reported that treatment of $Fe_3(CO)_{12}$ with dFPma, $CH_3N(PF_2)_2$, in boiling THF solution, followed by rapid removal of solvent and recrystallization of the product from CH_2Cl_2, results in the formation of $[Fe(CO)_3(dFPma)]_2$. A single-crystal X-ray diffraction study revealed that there are two bridging dFPma units and each metal has three terminally coordinated CO ligands. An interesting feature of this complex is the geometry around each iron atom which is square pyramidal rather than the usual trigonal bipyramidal, as shown in Fig.61. One of the CO ligands occupies the apical position while two CO groups together with two P atoms of dFPma are at the basal positions. However, this complex is unstable at room temperature and evolves CO to form $Fe_2(CO)_5(dFPma)_2$. This can also be prepared (a) from the reaction of $Fe_3(CO)_{12}$ with dFPma in boiling ether or THF over several hours or in hexane at room temperature over an extended period of time and (b) from the reaction of $Fe(CO)_5$ with dFPma in ether under U.V. irradiation. X-ray diffraction reveals[298] that each iron atom is coordinated to two terminal CO ligands, and the two metals are bridged by two dFPma groups and a CO ligand as shown in Fig.62. The geometry around each metal

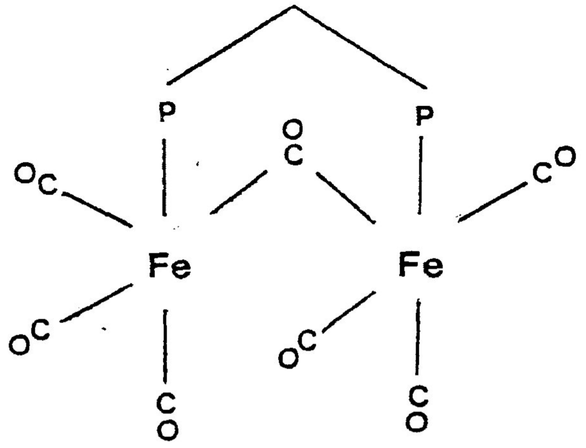


Fig. 60.

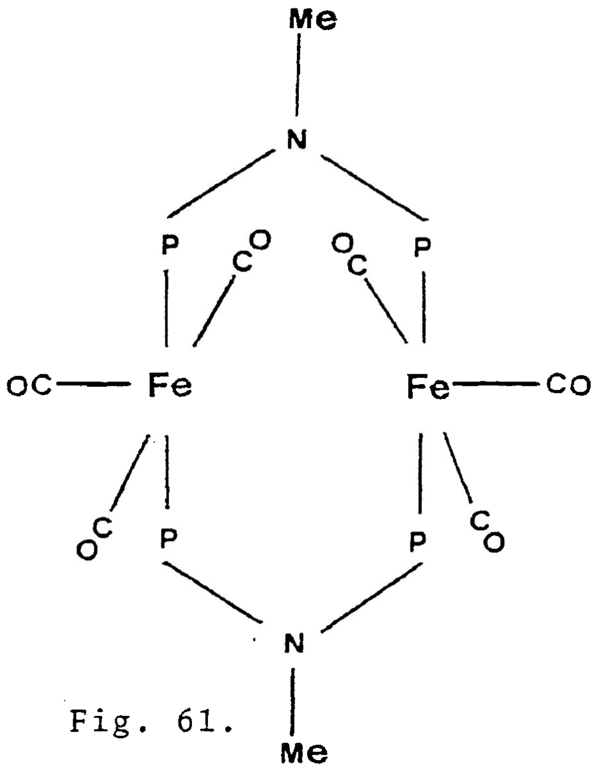


Fig. 61.

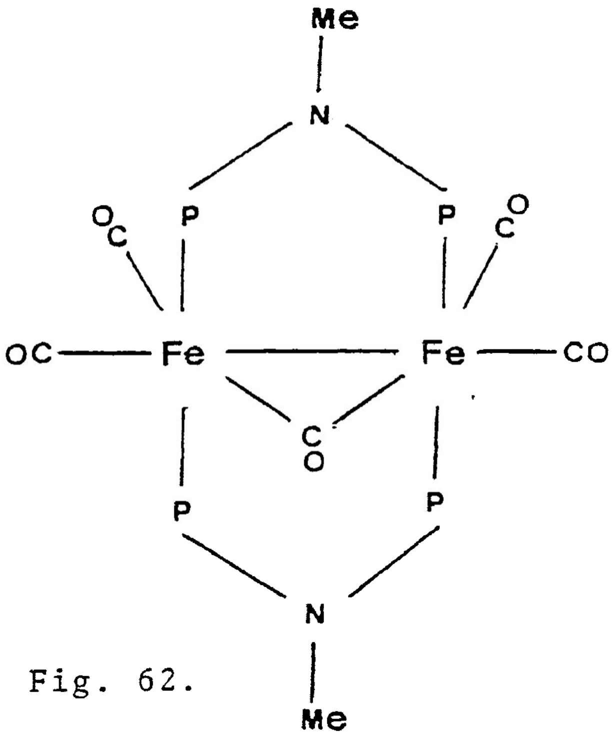


Fig. 62.

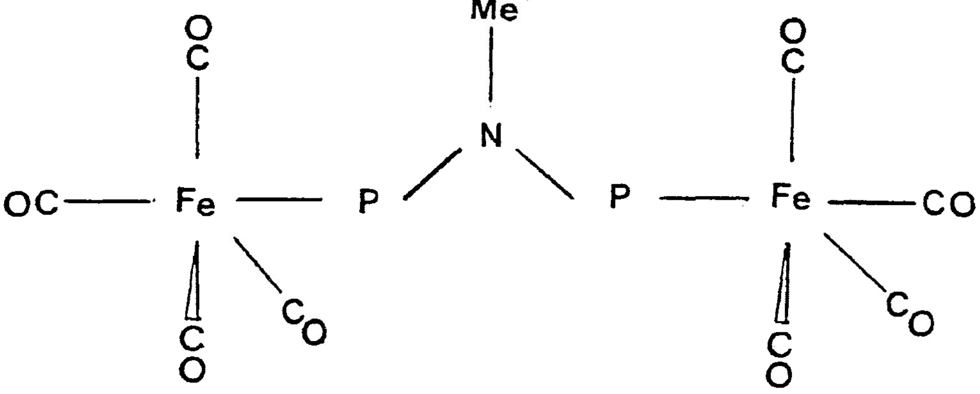


Fig. 63.

atom can be best regarded as either a distorted octahedron or a trigonal bipyramid depending upon whether a coordination position is allocated to the metal-metal bond. An interesting difference between the structures shown in Fig.61 and 62, containing the same bidentate ligands, is the existence of a metal-metal bond in the former. Newton et.al.[278] have reported that $Fe_2(CO)_9$ reacts with dFPma in ether at room temperature to give a mixture of yellow $Fe_2(CO)_8$(dFPma) and red-orange $Fe_2(CO)_7$(dFPma) complexes. They have suggested that the latter is analogous to $Fe_2(CO)_7$(dppm)[28] shown in Fig.60 while the former has been assigned the structure shown in Fig.63. Analogous complexes having similar structures were also reported for the ligands dppm, dppe, dppp and dppb earlier by Wegner et.al.[316] who reacted $Fe(CO)_5$ with the appropriate ligand in benzene under U.V. irradiation conditions.

Similarly, King and Raghuveer[162] reported that $Fe_2(CO)_9$ reacts with dmpm in THF under U.V. irradiation to produce the red complex $Fe_2(CO)_5(dmpm)_2$, having an analogous structure to that of $Fe_2(CO)_5(dFPma)_2$ shown in Fig.62. In contrast, when $Fe_2(CO)_9$ is treated with dmpm in Et_2O over an extended period of time, the orange complex $Fe_2(CO)_7$(dmpm) is obtained. These authors have suggested that this complex has a structure analogous to that of the dppm complex[23] shown in Fig.60. However, when a toluene solution containing $[Fe(CO)_2(Cp)]_2$ is reacted with dppm under refluxing conditions over an extended period of time, a green complex, shown to be $Fe_2(CO)_2(Cp)_2$(dmpm), is formed. The proposed structure is shown in Fig.64. Analogous complexes containing dppm, dppe, *cis*-dppee, dppp and dppea ligands have also been prepared.[281,272]

In another interesting study, Brouce *et.al*.[315] reported that $Ru_3(CO)_{12}$ reacts with *cis*-dppee, in THF in the presence of a catalyst, to form a pale yellow complex , which can also be prepared either by refluxing $Ru_3(CO)_{12}$ with cis-dppee in refluxing THF or via pyrolysis of $Ru_3(CO)_{10}$(*cis*-dppee) in THF. X-ray diffraction shows that the complex is binuclear with a *cis*-dppee ligand bridging the two metal atoms in such a way that both phosphorus atoms are bonded to one Ru atom while the olefinic double bond is coordinated to the other Ru atom. Three carbonyl groups on each metal complete the coordination as shown in Fig.65. On the basis of these findings, a $Ru_1 \dashrightarrow Ru_2$ donor interaction has been suggested. It has also been reported that when this complex is reacted with dppm in hexane under

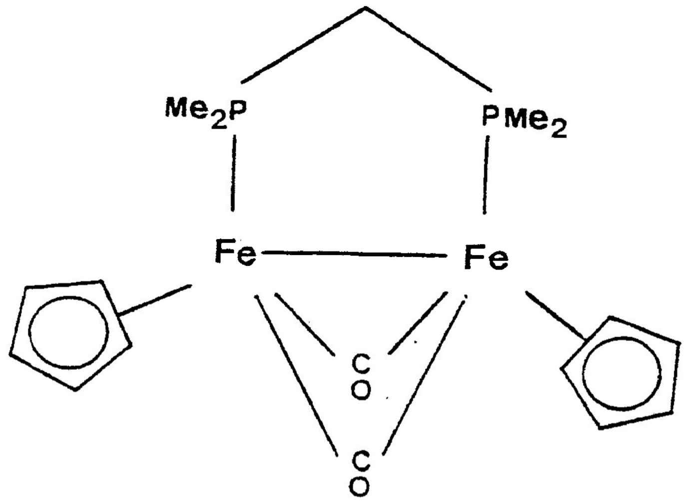


Fig. 64.

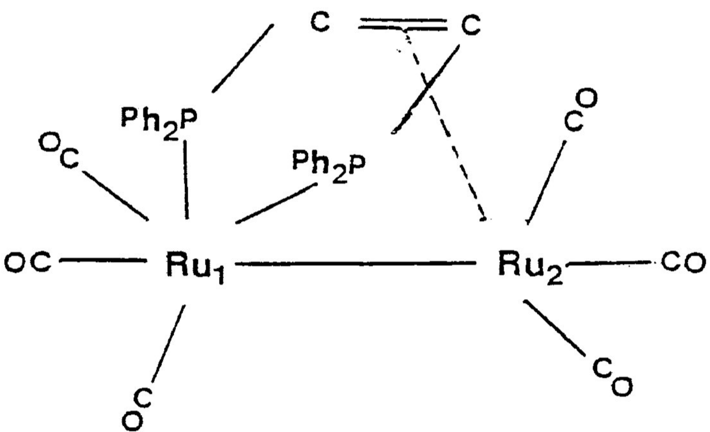


Fig. 65.

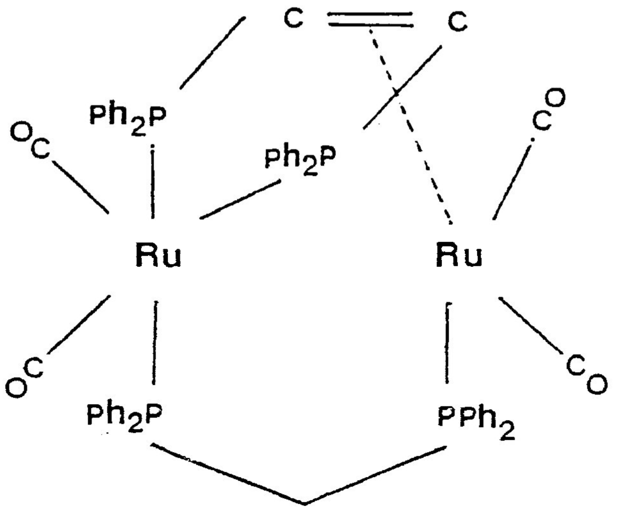


Fig. 66.

refluxing conditions, a yellow complex was isolated and characterized, on the basis of elemental analysis and spectroscopic data, as $Ru_2(CO)_4$(dppm)(*cis*-dppee) where the dppm ligand also occupies a bridging position as shown in Fig.66.

Several bimetallic complexes, listed in Table.[7], have been reported from this subgroup. For example, Laggo *et.al*.[308] reported that a rapid and specific ring opening reaction occurs when *trans*-$OsCl_2(dppm)_2$ is treated with $Rh_2(CO)_4Cl_2$ in methylene chloride in a 1:1 molar ratio forming the orange complex $OsRh(CO)_2Cl_3(dppm)_2$. Treatment of this with a variety of reagents, such as LiBr, NaI, NaN_3, KSCN, produce complexes of the type $OsRh(CO)_2Y_2X(dppm)_2$ where X=Br,I,N_3,SCN and Y=Cl. An X-ray structural determination on the complex where Y=Cl and X=Br reveals that the dppm and CO ligands bridge the two metal atoms, the Br atom is coordinated to Ru and the two Cl atoms are coordinated to Os as shown in Fig.67. However, addition of a large excess of LiBr or NaI (30 fold) in boiling methylethyl ketone resulted in the formation of complexes where X=Y=Br and X=Y=I, respectively. All of these complexes are presumed to have similar structures, as shown in Fig.67.

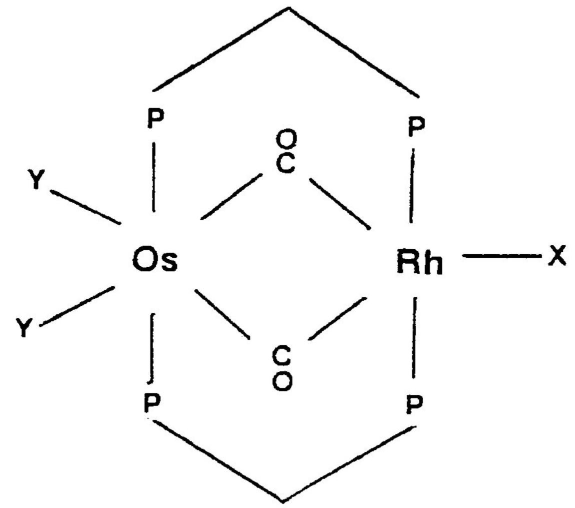


Fig. 67.

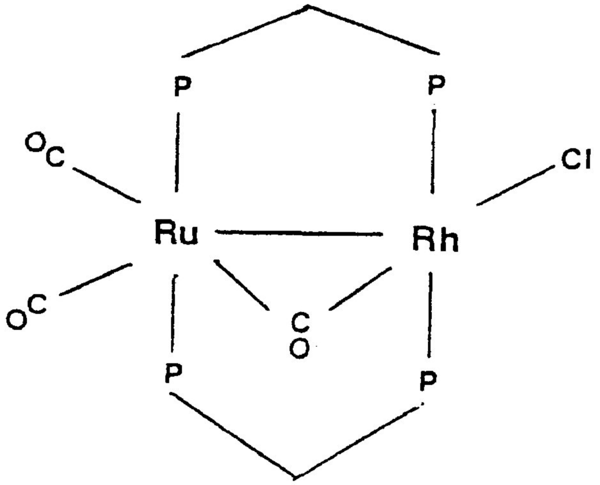


Fig. 68.

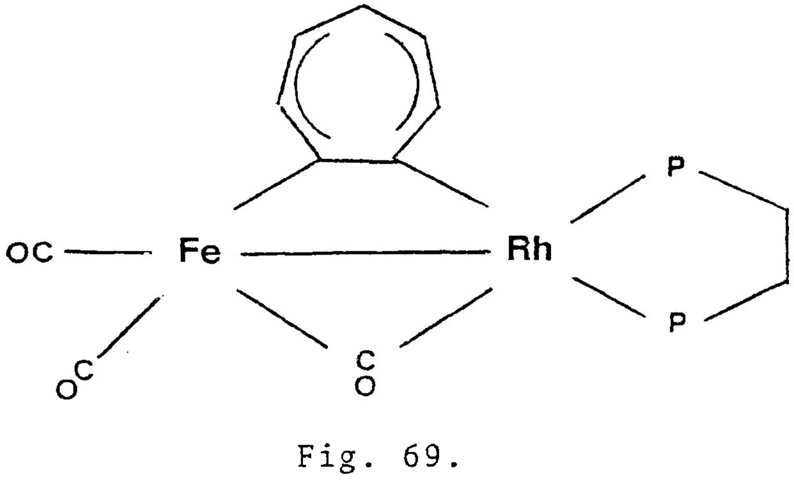


Fig. 69.

In contrast, the reaction between $RuH_2(dppm)_2$ and $[RhCl(COD)]_2$ in toluene at room temperature yields the heterobimetallic complex $RuRhH_2Cl(COD)(dppm)_2$[306]. Treatment of this complex with CO results in the formation of $RuRh(CO)_3Cl(dppm)_2$ for which spectroscopic studies suggest that the dppm and at least one CO are bridging. The proposed structure is shown in Fig.68, and has two CO groups terminally coordinated to the Ru atom while the Cl is terminally bonded to the Rh atom.

Recently, Lin and Takats[305] have reported that varying amounts of CO can be replaced by phosphines in the bimetallic complex, $FeRh(CO)_5(C_7H_7)$. For example, reaction with one mole of PMe_3 or PPh_3 produces $FeRh(CO)_4(C_7H_7)(PR_3)$ (R=Me,Ph) but the use of two moles of PMe_3 or one mole of a bisphosphine produces $FeRh(CO)_3(C_7H_7)(P-P)$ (P-P = $2PMe_3$, dppm, dppe, dmpe). A single crystal X-ray diffraction study on the dppe complex revealed that the C_7H_7 group and one CO ligand bridge the two metals while two CO ligands are terminally coordinated to the Fe atom. In addition, dppe is bonded in a chelating fashion to the Rh atom as shown in Fig.69. Similar structures were also suggested for the dppm, dmpe and PMe_3 analogues.

Very recently, Jacobsen et.al.[299] reported that the reaction of $Fe(CO)_4(\eta^1$-dppm) with $Rh_2(CO)_4Cl_2$ in a 1:0.5 molar ratio in benzene rapidly forms $FeRh(CO)_5Cl$(dppm). The i.r. spectrum shows only terminal carbonyl groups as confirmed by single crystal X-ray diffraction which revealed that the two metal atoms are bridged by a single dppm ligand, as shown in Fig.70. A metal-metal distance of 2.699Å suggests the presence of a metal-metal bond which is thought to be largely of the donor-acceptor type viz.Fe--→Rh.

In contrast, the reaction of $Fe(CO)_4(\eta^1$-dppm) with PtX_2(COD) (X=Cl,Br) produces[299] $FePt(CO)_4X_2$(dppm), the i.r. spectra of which indicate the presence of both terminal and bridging CO ligands. An X-ray diffraction study[299] on the Br complex shows that the molecule has the structure shown in Fig.71. The metal-metal distance of 2.647 Å. is consistent with the presence of a metal-metal bond. There appears to be a very weak interaction between the Pt and the CO, (i.e., the CO is best described as a bridging ligand) and this is consistent with the position of νCO at 1860cm^{-1}. The bonding between Fe and Pt is unusual and is largely of the donor acceptor type, viz Fe → Pt. This appears to be the only reported example so far of a crystal structure of a bimetallic complex containing a Fe-Pt bond. The same authors have also reported that treatment of $Fe(CO)_4(\eta^1$-dppm) with $PdCl_2(PhCN)_2$ results in the formation of a complex characterized, only in solution, as $FePd(CO)_4Cl_2$(dppm). Similarly, treatment of $Fe(CO)_4(\eta^1$-vdpp) with $Rh_2(CO)_4Cl_2$ yields $FeRh(CO)_5Cl$(vdpp), believed to have an analogous structure to that of $FeRh(CO)_5Cl$(dppm), shown in Fig.70.

Recently, Wong et.al.[309] reported that when a solution of $Fe(dmpm)_2(\eta^1$-dmpm) in THF is treated with $Cr(CO)_6$ under U.V. irradiation over an extended period of time, a red crystalline complex thought to be $FeCr(CO)_5(dmpm)_2$ is obtained. However, X-ray diffraction reveals[309] the presence of six CO groups, i.e. there are two $M(CO)_3$ units bridged by two dmpm ligands. The geometry around the iron is distorted trigonal bipyramidal while Cr is in a distorted square pyramidal arrangement as shown in Fig.72. Electron counting indicates 18 electrons at iron but only 16 electrons at Cr, and the authors have suggested a donor-acceptor type of interaction between the metals, viz. Fe--→Cr, might be involved even though the Fe-Cr bond distance is quite

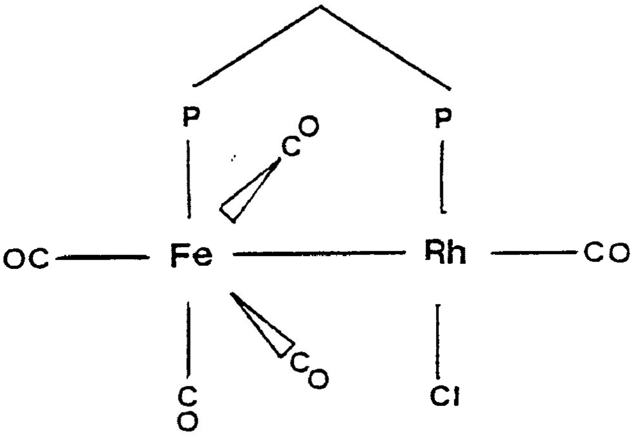


Fig. 70.

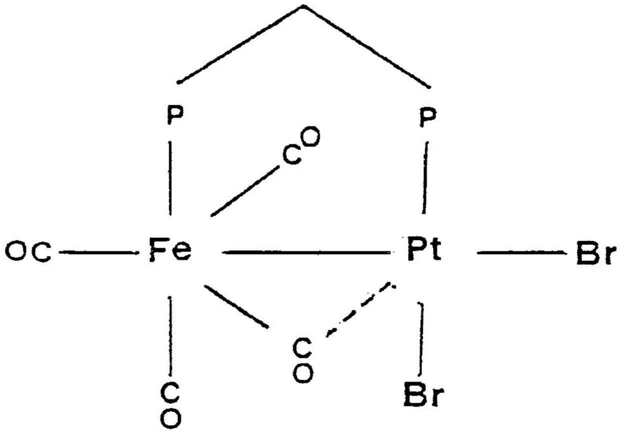


Fig. 71.

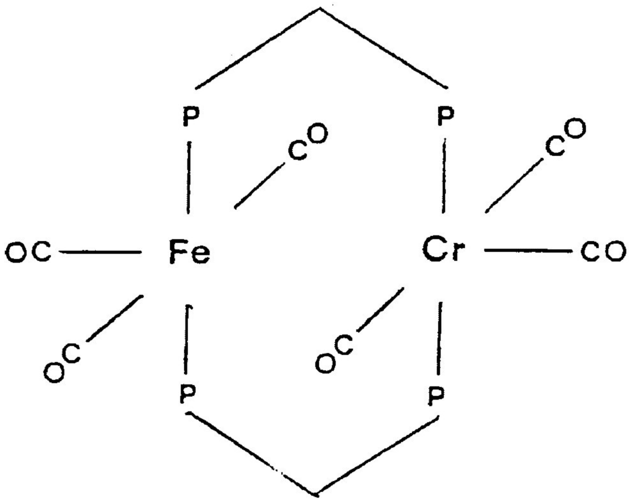


Fig. 72.

long at 3.111Å.

Benson et.al,[300] in an earlier study, reported that on treatment of $Fe(CO)_4(PPh_2H)$ with $Co(CO)_3(\pi-C_3H_5)$, the brown complex $FeCo(CO)_7(PPh_2)$ is obtained. Spectroscopic data suggest that the PPh_2 group symmetrically bridges the two metal atoms, and the carbonyls are terminally coordinated as shown in Fig.32. Similarly, reactions with $Mn(CO)_4(\pi-C_3H_5)$ give the related complex $FeMn(CO)_3(PPh_2)$, believed to have a structure analogous to that shown in Fig.73.

Relatively recently, Coleman et.al.[302] reported that when $\{RuCl_2(p\text{-Cymene})\}_2(dppe)$ is treated with $Fe_2(CO)_9$ in benzene under refluxing conditions, the yellow complex $FeRu(CO)_8(dppe)$ is obtained. Spectroscopic studies suggest the presence of only terminal CO groups and a bridging dppe unit, as shown in Fig.74.

Even more recently, Jacobsen et.al.[307] reported that $Fe(CO)_4(\eta^1\text{-P-P})$ (P-P = dppm or vdpp) reacts with $Mn(CO)_5Br$ in toluene at elevated temperatures to produce $FeMn(CO)_7Br(P\text{-}P)$ (P-P=dppm or vdpp). Similarly, when $[Fe(CO)_4(\eta^1\text{-dppm})]$ is treated with $Mo(CO)_4(nbd)$ in benzene it forms an analogous orange complex. An X-ray

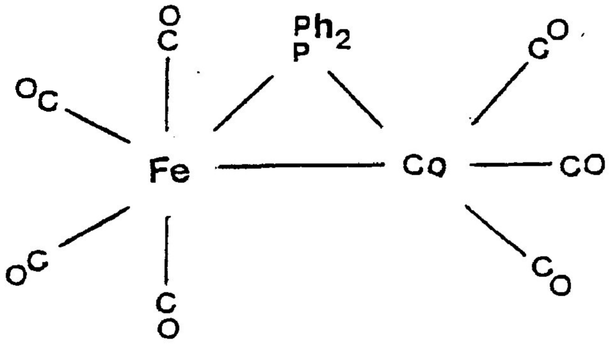


Fig. 73.

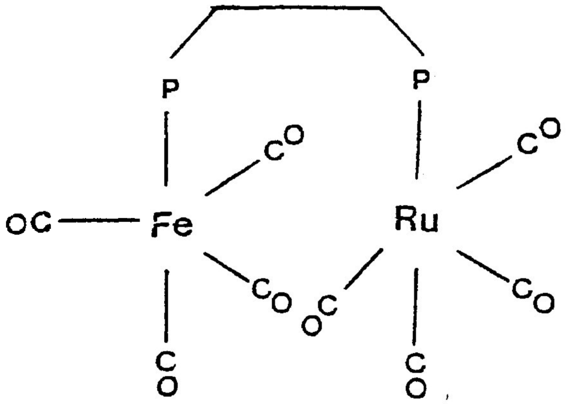


Fig. 74.

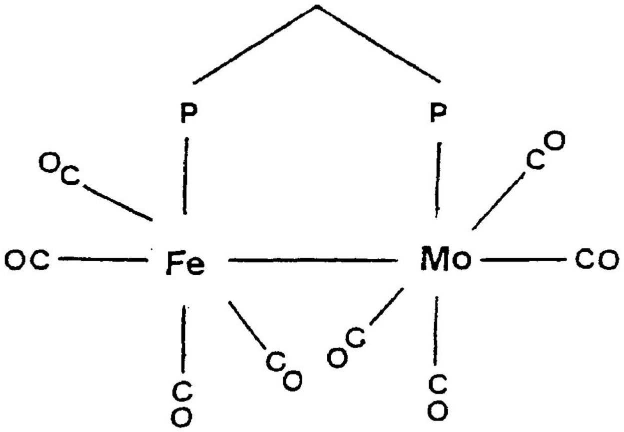


Fig. 75.

diffraction study shows[307] that $Fe(CO)_4$ and $Mo(CO)_4$ units are linked together by a single dppm bridge giving a five membered FePCPMo ring. The Fe-Mo distance of 3.024Å indicates the presence of a metal-metal bond as shown in Fig.75. In order to satisfy an 18 electron configuration on each metal, it has been suggested that this is another example where the metal-metal bond is of the donor-acceptor type, viz Fe--→Mo. These authors also reported that when CO gas is passed through a benzene solution of $FeMn(CO)_7$(dppm), the yellow complex $FeMn(CO)_8Br$(dppm) results. When a solution of this complex in benzene is treated with N_2, it loses one CO molecule and reverts to $FeMn(CO)_7Br$(dppm). Similarly, when $FeMo(CO)_8$(dppm) is treated with CO gas in methylene chloride solution over an extended period of time the complex $FeMo(CO)_9$(dppm) is formed which was characterized only in solution.

1.3.7. Co, Rh and Ir:

Again, a large number of phosphine-substituted carbonyl complexes have been prepared from this subgroup and representative examples of these are listed in Table [8]. These complexes can be conveniently generalized by the formula $[M(CO)_{5-n}Y_n]^+$ where Y= phosphine and n=1-4.

Table [8].

Complexes	Metal	Method of syntheses and comments		ref
$MLX(PR_3)_3$	Co,Rh,	C,D^b	$X=H,D,Cl,Br,I;R_3=Me_3,Ph_3,MePh_2$	319,320,330,
	Ir	$G^{b,c}$		334,321
				322,330,
				339
$[ML(PR_3)_4][Z]$	Co	D^b,G^e	$Z=Cl,Br,I,BPh_4;R=Me,OMe$	323,324,335
$[ML(PPh_3)_3][Z]$	Rh,Ir	G	$Z=ClO_4,PF_6,BPh_4$	325,327,328
$MLX(PR_3)_2$	Co,Rh,	A^b,C	$X=Cl,Br,I,ClO_4,NCO,NO_2,CN,N_3$	328,329,330,
	Ir	H,D	$NCSe,C_8H_{13};R_3=Me_3,Et_3Ph_3,$	331,332,320
			$Bu^tMe_2,Bu^tEt_2,Bu^tPr_2{}^n,Bu^tBu^n{}_2,$	333,340,
			$Bu^t{}_2Et,Bu^t{}_2Pr^n$	341
$ML(Cp)(PR_3)$	Co,Rh	H^b	R=Ph	335,336
	Ir			338,337
$[ML(Cp)X(PR_3)][Z]$	Rh,Ir	H^e	$X=Me,Et,CH_2CN$	342,343,
			$Z=Cl,Br,I,BPh_4$	338,336
$M_2L_2(PR_3)_6$	Co,Rh	A^b,C	$R=Bu^n,Ph$	344
$M_2L_2(PR_3)_2$	Co,Ir	C,D,	$R_3=Ph_3,MePh_2,(OMe)_3,(OEt)_3,$	335,345,
		H,F^e	$(OPh)_3,X=H,D,\pi-C_3H_5,Br,I$	347
$M_2L_2X_2(PR_3)_4$	Rh	H	$X=EtOH,CHCl_2,Cl,Br,I$	342,334,

			R=Ph	346
$ML_2X_3(PR_3)$	Ir	H	X=Br,I;R=Ph	347
$[ML_2(PR_3)_3][Z]$	Co,Rh	G^b	R=Me,Et,Ph;Z=BPh_4	324,325
$MLHX_2(PR_3)_2(PR_3)_2$	Ir	I^b,	X=H,Cl,Br	341
			$R_3=Me_3,Et_3,Me_2Ph$	
$[ML_2X_2(PR_3)_2][Z]$	Ir	I^e	R=Ph;X=H;Z=PF_6	347
$ML_2X(PR_3)_2$	Co	C,H^b,	X=H,MeCO,C_6F_5,$SnMe_3$,ClO_4,Cl,	323,319,347
		C,F^e	Br,I,$R_3=Me_3,Ph_3,(OMe)_3$,	335,324,
		A^b	$Ph(OE)_2$	350,328
$ML_2X_2(PR_3)$	Co,	F^c	X=Cl,Br;R=Ph	335
$[ML_2(PR_3)_3][Z]$	Co,Rh	G,A^e	$R_3=(OMe)_3,MePh_2$	335,325
		D^e	Z=ClO_4	324
$[ML_3(PR_3)_2][Z]$	Co,Rh	C,G^b,	R=Me,Et,Ph,NMe_2	324,325,
		I^e	Z=BPh_4,PF_6,ClO_4	335
$ML_3(PR_3)$	Co,Ir	A,E	X=$SnMe_3$,$SnPh_3$,MeCO,$CONMe_2$	327,349,
			R=Ph	351
$M_2L_3X(PRh_3)$	Rh	D	X=CO_2Me,CO_2Et	352
$M_2L_4(PR_3)_4$	Rh	G^b	R=Ph	353,329,
				354,334
$M_2L_5(PR_3)_3$	Co	J	R=Me,Et	349
$M_2L_6(PR_3)_2$	Co,Rh	A^b,C	R=Me,Et,Bu^n,Rh,(OMe),Ph	355,349
		G^b,J		344,353,
				356
$M_2L_7(PR_3)$	Co	A	R=Bu^n,Cy,Ph,OMe,OEt;OPr^i	357
$[ML(P-P)_2][Z]$	Co,Rh,	B,C^e	P-P=dppm,dppe,dmpe,dppp,dppb	358-363,
	Ir	D,F,G	Z=Cl,Br,I,BF_4,BPh_4,ClO_4,Pz	368,336,
			$\{S_2P(OPh)_2\}$,$\{S_2PCy_2\}$	335,385
$[M_2LXY(P-P)][Z]_a$	Rh	E	P-P=dppm,X=Y,Br,I;X=Br,	364-367
			Y=SO_2;Z=Br;a=0,1	
MLX(P-P)	Rh	G^b,F	P-P=dppm,dppe	361,14,

		$I^{b,d}$	X=Cl,Br,Cp	405
$MLX_2R(P-P)_2$	Rh	H	P-P=dppe,dppp;X=Cl;R=H	361
$M_2LX_2Y(P-P)_2$	Rh	H	P-P=dppe;X=Cl,I	380,
			$Y=C_2S_4$,Cl	382
MLXX´Y(P-P)	Rh	H	P-P=dppe;X=Cl;X´=I;Y=COMe	361
$ML_2X(P-P)$	Co,Rh	C^c,E	P-P=dppm,dppe;X=I,C_2H_4,PhC_2H_4	369,370,
		H,J	C_6F_5,$SyPh_3$	345,368
$[M_2L_2X(P-P)_2][Z]$	Rh,Ir	E,H^e	P-P=dppm,X=H,S,SH,SEt,SCH_2Ph,	366,371-
			Se,OH,Cl,PH(Cy);Z=BPh_4,PF_6,	375,388
			$Rh(CO)_2Cl_2$	
$M_2L_2X(P-P)_2$	Ir	I^c	P-P=dppm;X=OHCl	388
$[M_2L_2X_2R_2(P-P)][Za]_2$	Rh	H	P-P=dppb;X=Cl,Br,I,Me,CH_2CN,	404
			$HgCl_2$,Z=Cl,Br,I,PF_6,BPh_4,$HgCl_2$;a=2,3;	
$M_2L_2X_2(P-P)_2$	Rh	F	P-P=dppm,dppe,dppp,dppb	361,14,
			X=Cl	376
$M_2L_2R_2(P-P)$	Rh	D^b	P-P=dppb;R=Cp,Cl	404,405,
$[M_2L_2XR(P-P)_2][Z]$	Rh,Ir	H	P-P=dppm;X=S,Cl;R=SO_2	366,371,
			Z=BPh_4,IrL_2Cl_2	376
$M_2L_2(P-P)_2$	Rh	I^c	P-P=dppm	368
$M_2L_2X_2R(P-P)_2$	Rh	F	P-P=dppe;X=Cl;R=COD	361
$[M_2L_2X_3(P-P)_2][Z]$	Ir	I^e	P-P=dppm;X=H;Z=Cl,BF_4	386
$M_2L_2X_6(P-P)_2$	Rh	E^d	P-P=dppe;X=Cl	361
$M_2L_2X_4R(P-P)_2$	Rh	H	P-P=dppe;X=Cl;R=H	361
$[M_2L_3X(P-P)][Z]$	Co,Rh	D^e	P-P=dppm;X=H,S,Cl,I	377,371,
	Ir	E^b	Z=I,BPh_4,BF_4,PF_6,$Ir(CO)_2Cl_2$	368,374,
		$F^{b,c}$	$Ir(CO)_2Cl_2$	387,388
		H		
$M_2L_3(P-P)_2$	Co,Ir	I^c	P-P=dppm	377,388
$[M_2L_3X_2(P-P)_2][Z]_2$	Ir	J	P-P=dppm;X=MeCN;Z=BF_4	388
$[M_2L_3X(dmpm)(dppm)][Z]$	Co	H^b	X=Z=I	377

$[M_2L_4(P\text{-}P)_2][Z]_n$	Co,Ir	B^e, G^b, $I^{c,d}$	P-P=dppm,dmpm Z=Hg,Cl n=0,1	369,378, 390,391
$[M_2L_4(P\text{-}P)_3][Z]$	Co	A	P-P=dppe;Z=$[Co(CO)_4]_2$	378
$[M_2L_4(P\text{-}P)_2$	Ir	I^d	P-P=dppm	388
$[M_2L_4X_2(P\text{-}P)_2][Z]_a$	Rh,Ir	H^d,I	P-P=dppm; X=I,H;Z=BF_4;a=0,2	373 388
$[M_2L_4X(P\text{-}P)_2][Z]_n$	Ir	F^e,H	P-P=dppm,dmpm;X=Cl Z=BFh_4,SO_3CF_3;n=1,2	371,390, 391
$[M_2L_5(P\text{-}P)_2][Z]_2$	Ir	I^e	P-P=dppm;Z=BF_4	388
$M_2L_6(P\text{-}P)$	Co	A,J^b	P-P=dppm,dppe,dppb	379,378, 389
$[M_2L_3X(P\text{-}P)_2][Z]$	Rh	I^d	P-P=dppm;X=Cl	383
$M_2L_6X_2(P\text{-}P)$	Co	D	P-P=dppe;X=C_6F_5	384

Bimetalic Complexes:

Complexes	Comments		Ref
$MM'LRX(dppm)_2$	M=Ir M'=Cu,Ag	R=PhC≡C X=Cl	406
$[MM'LR(dppm)_2][Z]$	M=Ir M'=Ag,Au	R=PhC≡C Z=Cl,BPh_4	406
$MM'L_2RX(dppm)_2$	M=Ir M'Rh	R=PhC≡C X=Cl	406
$[MM'L_3X(dppm)_2][Z]$	M=Ir M'=Rh	X=Cl Z=Cl	406
$MM'LX_2(dppm)_2$	M=Rh M'=Ag	X=Cl	406
$MM'LX_3(PPh_2py)_2$	M=Rh M'=Pd	X=Cl	407
$MM'LX_5(PPh_2py)_2$	M=Rh M'=Pt	X=Cl	408

Otsuka and Rossi[320] have reported that $Co(CO)(C_8H_{13})(C_8H_{12})$ reacts with several phosphines (PR_3) in toluene at low temperature, producing the dark brown complexes $Co(CO)(C_8H_{13})(PR_3)$, (R=Ph,OPh,$MePh_2$). These complexes react further with free ligands at elevated temperatures to produce the hydrido complexes $Co(CO)H(PR_3)_3$. The Rh and Ir analogues of these hydrides were prepared by reducing $M(CO)Cl(PPh_3)_2$ with hydrazine[321]. The Rh analogue has also been reported to form[334] when trans-$Rh(CO)Cl(PPh_3)_3$ is treated with $NaBH_4$ in the presence of PPh_3, in refluxing ethanol solution. In addition, treatment of $RhCl_3.3H_2O$ with PPh_3 in refluxing ethanol followed by the addition of aqueous formaldehyde yields trans-$Rh(CO)Cl(PPh_3)_3$, which on further treatment with $NaBH_4$, gives the hydrido complex $Rh(CO)H(PPh_3)_3$. Hydrogen-deuterium exchange occurs when deuterium is passed through the benzene solution of the latter, producing $Rh(CO)D(PPh_3)_3$. An X-ray diffraction study[322] on $Rh(CO)H(PPh_3)_3$ revealed that the molecule has a trigonal bipyramidal geometry with all three phosphine groups occupying equatorial sites and trans hydride and carbonyl groups. Similar structures have been suggested for the Co and Ir complexes.[320,321] When CO gas is passed through a suspension of $Rh(CO)_2(PPh_3)_3$ in cyclohexane, the yellow, dimeric complex $[Rh(CO)_2(PPh_3)_2]_2$ is formed. However, when solutions of $Rh(CO)H(PPh_3)_3$ are treated with CO followed by concentration with molecular nitrogen, the red complexes $[Rh(CO)_2(PPh_3)_2(S)]_2$ ($S=EtOH, CH_2Cl_2$) are obtained. Similarly, treatment of a benzene solution of the ethanol solvate with molecular hydrogen, or alternatively by stirring $Rh(CO)H(PPh_3)_3$ in benzene solution under N_2 gas over 24 hrs. followed by vacuum concentration, produces the orange complex $[Rh(CO)(PPh_3)_2]_2$. A four-center transition state has been suggested as being involved in the formation of this complex as shown in Scheme.I. Furthermore, it was noted that on treatment of this orange complex with CO in the presence of PPh_3, the closely related, yellow, dimeric complex $[Rh(CO)_2(PPh_3)_2]_2$ is obtained. This is also reported to form[327] when benzene solutions of $Rh_6(CO)_{16}$ are treated with PPh_3 under a slow stream of CO gas. I.r. spectroscopic data show the presence of both bridging and terminal CO groups and on this basis, the structure shown in Fig.76 has been proposed. The variety of interesting reactions which this species undergoes is illustrated in Scheme II.

Klein and Karsch[328] reported that reactions of $CoX(PMe_3)_3$ ($X=Cl, Br, I$) with CO gas under

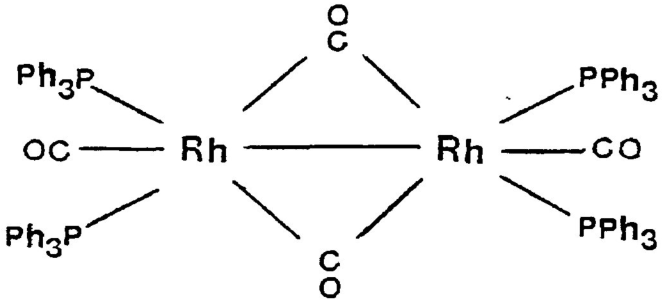


Fig. 76.

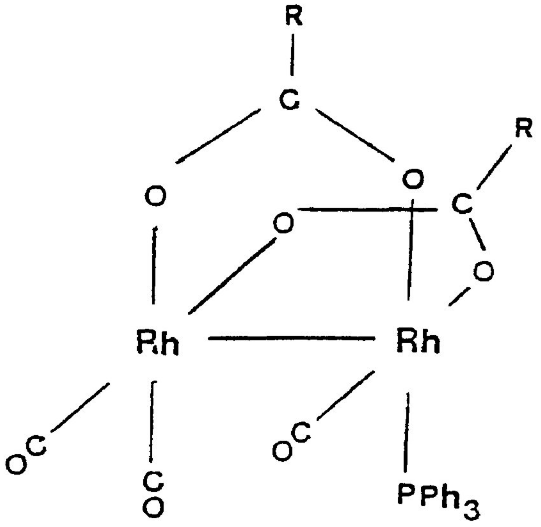


Fig. 77.

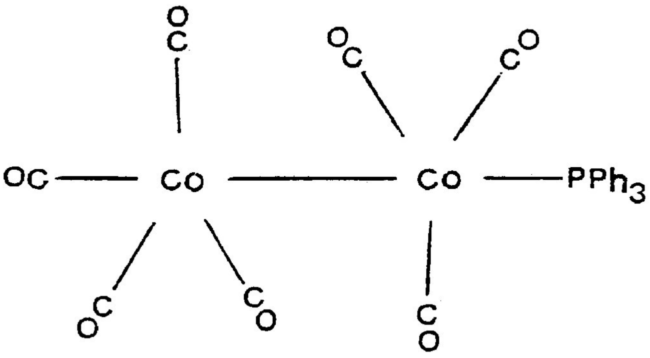
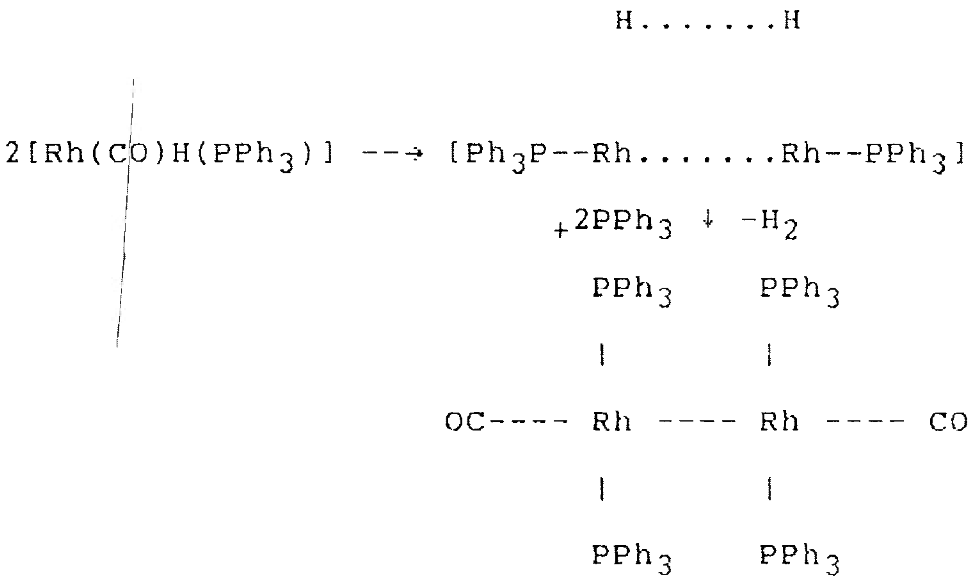


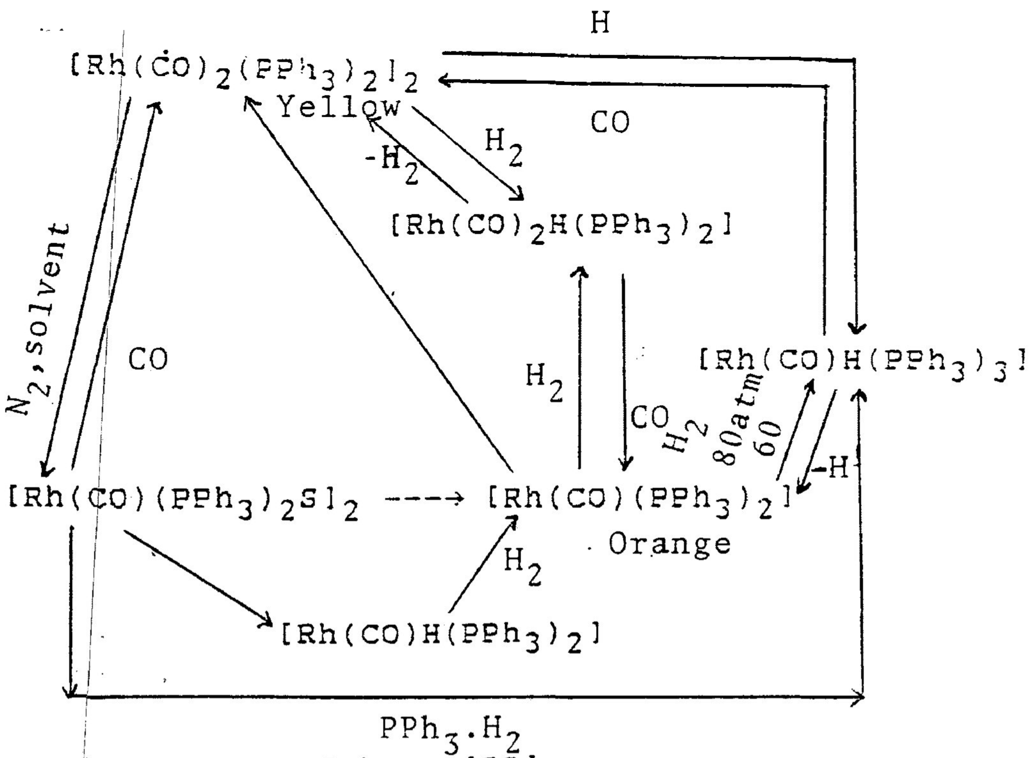
Fig. 78.

different conditions yield either the red complexes characterized as $Co(CO)X(PMe_3)_3$ having structures analogous to that of $Rh(CO)H(PPh_3)_3$,[222] or the neutral dicarbonyl complexes $Co(CO)_2X(PMe_3)_2$ probably having a trigonal bipyramidal geometry with axial PMe_3 ligands. Treatment of $Co(CO)X(PMe_3)_3$ with more PMe_3 at ambient temperatures over extended periods of time yield the cationic complexes formulated as $[Co(CO)(PMe_3)_4][Z]$ ($Z=Cl$, Br, I) with a proposed square-pyramidal geometry with CO being in the apical position.



$$\begin{array}{c} H\cdots\cdots H \\ 2[Rh(CO)H(PPh_3)] \longrightarrow [Ph_3P{-}{-}Rh\cdots\cdots Rh{-}{-}PPh_3] \\ {+}2PPh_3 \downarrow {-}H_2 \\ \begin{array}{ccccccc} & & PPh_3 & & PPh_3 & & \\ & & | & & | & & \\ OC & {-}{-}{-}{-} & Rh & {-}{-}{-}{-} & Rh & {-}{-}{-}{-} & CO \\ & & | & & | & & \\ & & PPh_3 & & PPh_3 & & \end{array} \end{array}$$

Scheme [I].



Scheme [II].

Perchlorato complexes of all three metals have been prepared. For example, treatment of $M(CO)Cl(PPh_3)_2$ (M=Rh, Ir) with $AgClO_4$ in the absence of light results in the formation of the complexes characterized as $M(CO)(ClO_4)(PPh_3)_2$[328], where ClO_4 is coordinated with the metal via a covalent metal-$OClO_3$ linkage. These react further with PPh_3 to form the tetragonal cationic complexes $[M(CO)(PPh_3)_3][ClO_4]$. On the other hand, treatment of $Co(CO)_2Cl(PPh_3)_2$ with $AgClO_4$ under similar conditions gives five coordinated $Co(CO)_2(ClO_4)(PPh_3)_2$ complex. These complexes present apparently the first examples of M^I (d^8) perchlorato complexes of the transition metals.

Carbonyl phosphine complexes incorporating the cyclopentadienyl group of the type $M(CO)(Cp)(PPh_3)$,(M=Co,Rh,Ir) are known. For example Oliver and Graham[333] have reported the synthesis of the Ir compound by reaction between $Ir(CO)Cl(PPh_3)_2$ and Na(Cp) in benzene under refluxing conditions. Solutions of $RhCl(PPh_3)_3$ react with CO to form, firstly, the yellow $RhCl(PPh_3)_2$ complex which reacts with Na(Cp) to form the orange $Rh(CO)(Cp)(PPh_3)$. The analogous cobalt complex can be prepared[337] by treating $Co(CO)_2(Cp)$ with PPh_3 in hexane under refluxing conditions, over an extended period of time.

Csontos, Heil and Marko[352] reported that CO can be replaced by PPh_3 in carboxylate complexes of Rh. Thus, when a hexane solution containing $Rh(CO)_2(RCO_2)$ (R=Me, Et) is treated with PPh_3, a dark brown complex, formulated on the basis of spectroscopic evidence as the unsymmetrical dimer shown in Fig.77, is formed However, with an excess of PPh_3, the yellow disubstituted mononuclear complex $Rh(CO)(MeCO_2)(PPh_3)_2$ is formed.

Yamamoto <u>et.al</u>.[344] reported that when CO gas is passed through a m-xylene solution containing $Co(C_2H_4)(PPh_3)_3$ at low temperatures, a reddish-brown complex is obtained. Analytical and spectroscopic data suggest that the complex is dimeric with the formula $[Co(CO)_3(PPh_3)]_2$. In addition, when a $CoH(N_2)(PPh_3)_3$ solution in toluene is treated with CO_2, a brown dimeric complex $[Co(CO)(PPh_3)_3]_2$ is obtained. This complex exhibits a νCO band in the i.r. spectrum at 1877 cm^{-1} consistent with bridging CO ligands.

As expected, COD is readily displaced by CO from complexes and, indeed, Schrock and Osborn[325] reported that treatment of $[Rh(COD)(PPh_3)_2][BPh_4]$ with CO gas in acetone, yields $[Rh(CO)_3(PPh_3)_2][BPh_4]$. This complex can also be prepared more conveniently by treating $[Rh(nbd)(PPh_3)_2][BPh_4]$ (nbd=norbornadiene) with molecular hydrogen in acetone followed by the passage of CO gas. Cobalt and iridium analogues have also been reported.[326] It has also been reported that these complexes lose CO slowly in the solid state but very readily in solution. For example, solutions in DMF, DMA, MeCN or acetone evolve CO and the complex $[Rh(CO)S(PPh_3)_2](BPh_4)$ can be isolated (S=coordinated solvent). The lability of two CO groups results in the reaction of $[Rh(CO)_3(PPh_3)_2][BPh_4]$ with nbd, 1,3-butadiene or PPh_3 to form $[Rh(CO)(diene)(PPh_3)_2][BPh_4]$ or $[Rh(CO)(PPh_3)_3$. If the PPh_3 reaction is carried out under a CO atmosphere, $Rh(CO)_2(PPh_3)_3$, having a <u>trans</u>-trigonal bipyramidal geometry, is produced. The most interesting feature of these complexes is the extreme lability in their solution chemistry. Thus, in solvents, olefin, phosphine and CO compete for, and exchange at, sites on the three-coordinate $[Rh(CO)(PPh_3)_2][BPh_4]$ moiety, forming a variety of 4- and 5- coordinated species.

It was further noted that the complex $[Rh(CO)Y(PPh_3)_2]^+$ (Y=1,3-butadiene) exhibits two bands in its i.r. spectrum in the solid state as well as in solution. The occurrence of three resonances in the ^1H n.m.r. spectrum suggests the presence of two energetically similar isomers in equilibrium in solution. However, the presence of two peaks in the ^{31}P n.m.r. spectrum indicates that the dynamic process observed in the proton spectrum does not result from a phosphine dissociation process.

In another report, Szabo <u>et.al</u>.[357] have described that treatment of $Co_2(CO)_8$ with PPh_3 in Nujol solution results in the formation of the monosubstituted derivative $Co_2(CO)_7(PPh_3)$, which can also be prepared by reacting $Co_2(CO)_6(PPh_3)_2$ with CO gas in hexane. The i.r.

spectrum shows only bands in the terminal νCO region and the structure shown in Fig.78 is therefore proposed. However, in concentrated solution, the i.r. spectrum shows two additional weak bands in the bridging νCO region suggesting that, under these conditions, the complex is in equilibrium with a low concentration of CO bridged isomers.

Recently, Carriedo <u>et.al</u>.[335] have reported a very interesting reaction in which an ethanol solution of Co(II) chloride was treated with $NaBH_4$ in the presence of PPh_3 and $[PBzPh_3]Cl$ under an atmosphere of CO gas resulting in the formation of a yellow-green complex, formulated as $[Co(CO)_2Cl_2(PPh_3)][PBzPh_3]$. The corresponding bromide was prepared from $CoBr_2$ and $[PEtPh_3]Br$. In contrast, a similar reaction with Co(II) iodide and $[PEtPh_3]I$ yielded $Co(CO)I(PPh_3)_2$. No structural details were given. These authors also reported that on passing CO gas through the ethanolic solutions of dimeric or polymeric complexes $[CoX(PPh_3)_2]_n$ (X=Cl,Br,I), the dicarbonyl complexes $Co(CO)_2X(PPh_3)_2$ are obtained. Moreover, when $Co(CO)_2Cl(PPh_3)_2$ is treated with $Mg(C_6F_5)Br$ in THF solution an orange crystalline complex is obtained; this can also be prepared by treating[345] $Co(CO)_4(C_6F_5)$ with

PPh_3 in hexane solution, and it has been characterized, largely on the basis of analytical and spectroscopic data, as $Co(CO)_2(C_6F_5)(PPh_3)_2$ with a trigonal bipyramidal geometry.

A large variety of structural types has been prepared, using bisphosphines, from this subgroup. Thus, Carriedo <u>et.al</u>.[335] reported that treatment of a $Co(CO)_2Cl(PPh_3)_2$ solution with $TlClO_4$ in the presence of dppm or dppe gives orange crystalline complexes, formulated as $[Co(CO)(P-P)_2](ClO_4)$ (P-P=dppm, dppe). N.m.r. data on the dppm complex indicate that the molecule is non-rigid in solution, and an X-ray diffraction study shows that both dppm ligands are coordinated in a chelating fashion. The geometry around the metal is distorted trigonal bipyramidal, with the CO ligand being in an equatorial site. It has been suggested earlier[358] that distortion occurs due to the expected requirements of the dppm bite angle being smaller than the 90° in the idealized trigonal bipyramidal geometry. This was confirmed by the cyrstallography results which found a value of 73.1°. The rhodium analogue has also been prepared[358] by passing CO gas through a CH_2Cl_2 solution containing $[Rh(dppm)_2]BF_4$ The analogous iridium-dppp complex has been reported to form[400] when

$Ir(CO)Cl(PPh_3)_2$ is treated with dppp at low temperature, giving $[Ir(CO)(dppp)_2][Cl]$.

In contrast, the reaction between $[NBu^n{}_4][Ir(CO)_2I_2]$ and dppp under CO gives two complexes[398]; the colourless $Ir(CO)I(dppp)_2$, with a single νCO band at $1930 cm^{-1}$ and analogous to $Ir(CO)Cl(dppe)_2$,[15] and a bright yellow, monomeric complex which shows two νCO bands in the terminal carbonyl region and a single resonance in the ^{31}P n.m.r. spectrum. The structure shown in Fig.79 has been proposed for the yellow complex. A benzene solution of this complex reacts with H_2 to give a colourless complex formulated as $Ir(CO)H_2(I)(dppp)$. The bromide analogue has also been prepared.

On the other hand, treatment of $[NBu^n{}_4][Ir(CO)_2X_2]$ (X=Br,I) with dppe gives the orange complexes Ir(CO)X(dppe) which, in solution react rapidly with hydrogen forming the colourless, mononuclear hydride species $Ir(CO)XH_2(dppe)$ with the proposed structure as shown in Fig.80. It was also noted that Ir(CO)X(dppe) (X=Br,I) react with CO, giving the dicarbonyl complexes, analogous to the dppp product as shown in Fig.79.

Espana <u>et.al</u>.[345] earlier reported that

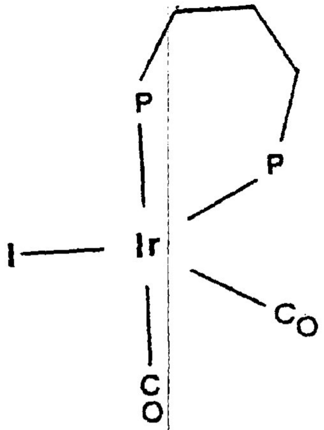


Fig. 79.

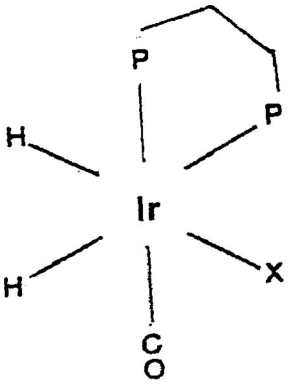


Fig. 80.

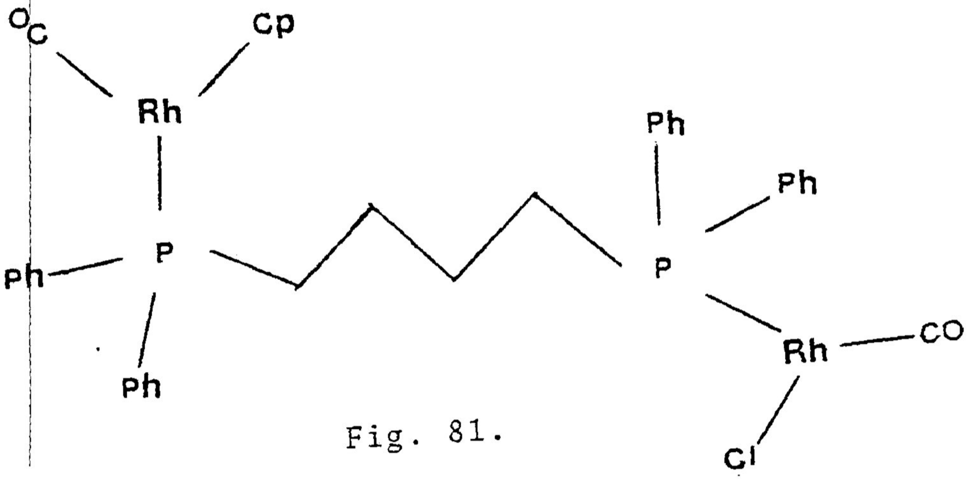


Fig. 81.

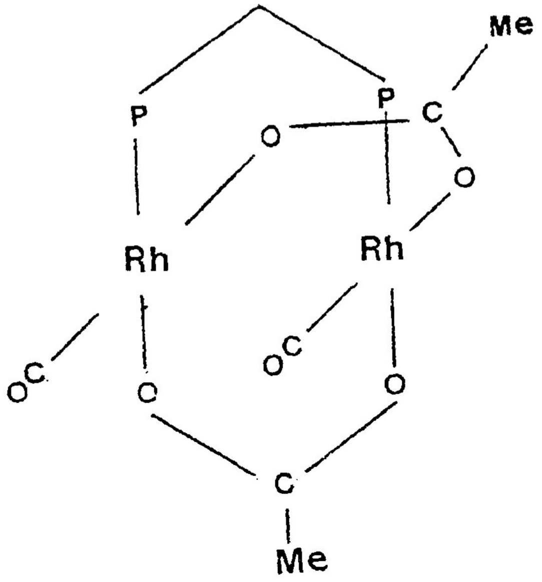


Fig. 82.

when $Co(C_6F_5)_2(dppe)$ is treated with $NaBH_4$ under a CO atmosphere, the orange complex $Co(CO)_2(C_6F_5)(dppe)$ formed. These authors also reported that the reaction of $Co(CO)_4(C_6F_5)$ with dppe gives a dinuclear complex, showing νCO bands in the terminal carbonyl region of the i.r. spectrum and a singlet at δ=71 in the ^{31}P n.m.r. spectrum. The complex was formulated as $Co_2(CO)_6(C_6F_5)_2$ (dppe), where the dppe ligand bridges two $Co(CO)_3(C_6F_5)$ units.

Relatively recently, Faraone et.al.[404] reported that treatment of benzene solutions containing $Rh(CO)_2(Cp)$ with dppb under refluxing conditions followed by column chromatography, yields an orange complex which was thoroughly studied by spectroscopic and X-ray methods and which consists of two Rh(CO)(Cp) units bridged by a single dppb ligand. The coordination around each Rh atom is trigonal with the coordination position being occupied by the centre of the Cp ring, the phosphorus and the CO group, as shown in Fig.81.

In contrast, when $Rh(CO)_2(Cp)$ is treated with dppm in refluxing heptane, the yellow orange monomeric complex[405] Rh(CO)(Cp)(dppm) is obtained. An X-ray analysis shows that the dppm ligand is bonded through only one P atom, thus presenting the first example of a complex from this subgroup in which the dppm ligand is coordinated in a monodentate fashion. The coordination around the Rh atom can again be described as either trigonal or pentagonal based upon the arguments presented for $Rh_2(CO)_2(Cp)_2(dppb)$. These authors noted that the reactions aimed at utilizing the uncoordinated P atom of dppm in attempts to make binuclear, dppm bridged species, may not be successful due to steric reasons. In fact, no changes occur when this complex is refluxed in heptane or when it is refluxed with $Rh(CO)_2(Cp)$.

Another interesting Rh complex has been reported by Balch *et.al.*[374] The reaction between $Rh_2(CO)_4(MeCO_2)$ and dppm in benzene, results in the formation of the red complex $Rh_2(CO)_2(MeCO_2)(dppm)$ which, on the basis of spectroscopic data, has been assigned the structure shown in Fig.82.

Sanger[15] reported that when solutions of $Ir_2Cl_2(COD)$ are treated with dppp under a CO atmosphere, a yellow complex is obtained. This same complex can also be prepared by the reaction of $IrCl_3$ with LiCl under 40 Psi CO pressure in the presence of dppp at elevated temperatures. The complex has a single band in the terminal νCO region in the i.r. spectrum and a single resonance in the ^{31}P n.m.r. spectrum. On the basis of these results together with analytical data, Sanger proposed the formulation $Ir_2(CO)_2Cl_2(dppp)_2$ in which the dppp ligands bridge the two metal atoms and in which the CO groups are *trans* to each other. However, a very recent X-ray diffraction study[372] revealed that the molecule actually consists of two planar $Ir(CO)P_2Cl$ units bridged by dppp ligands forming a 12 membered ring. The Co and Cl groups are in a non-parallel, *cis*-geometry as shown in Fig.83, thus minimizing coupling between the two CO groups, consistent with the single νCO band in the i.r. spectrum.

The corresponding complexes with bromide and iodide have also been reported.[373] The latter is made by simply exchanging iodide for chloride in the above complex and the former by the reaction between $[Ir(CO)_2Br_2][NBu^n{}_4]$ and dppp in acetone from which CO gas is evolved. Both complexes are believed to have structures similar to that of the chloride, although there are slight differences in the i.r. spectra. For example, the bromide complex shows two i.r. bands in the terminal carbonyl region while the iodide complex shows only one. Both have a single resonance in their ^{31}P

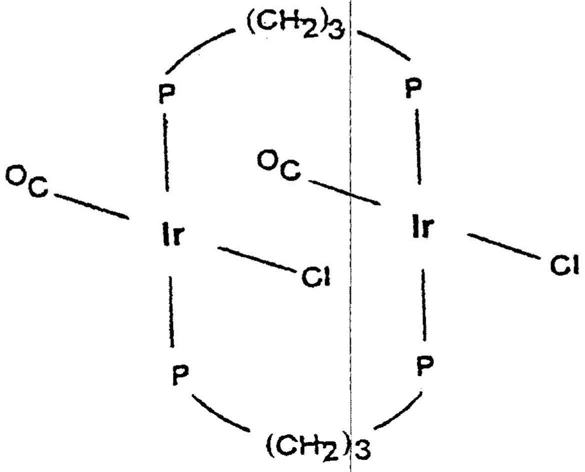


Fig. 83.

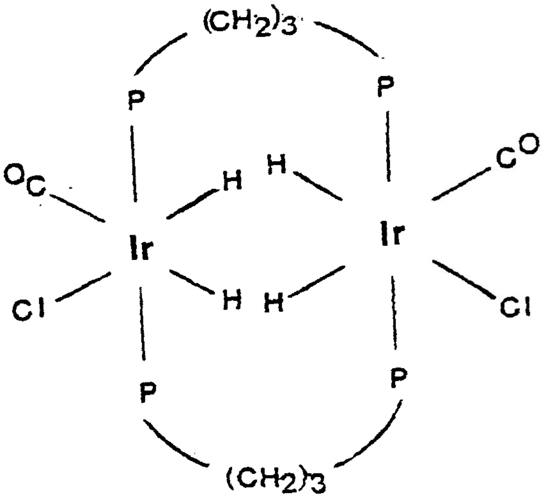


Fig. 84.

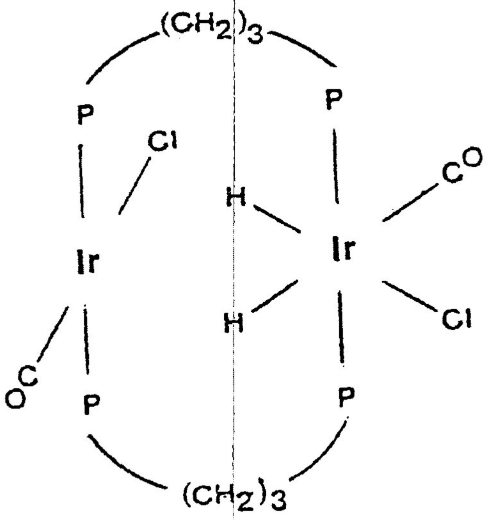


Fig. 85.

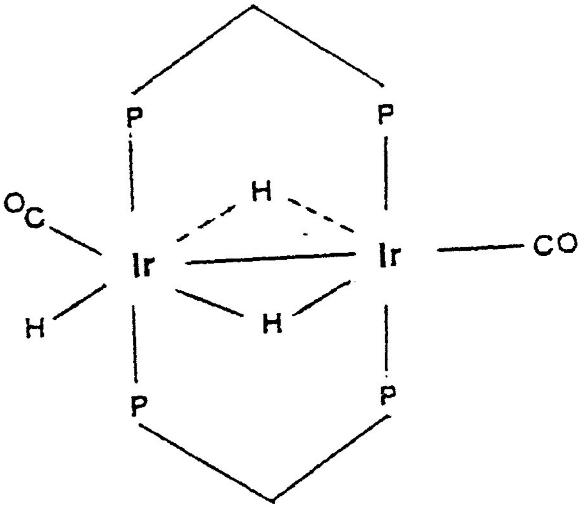


Fig. 86.

n.m.r. spectra consistent with bridging dppp ligands.

These complexes undergo ready oxidative addition of H_2 at 1 atm. in CH_2Cl_2 solution producing two complexes, the tetrahydrides $Ir_2(CO)_2X_2H_4(dppp)_2$ and the dihydrides $Ir_2(CO)_2X_2H_2(dppp)_2$.[372,378] An X-ray crystallographic study on the former reveals the presence of *cis*-hydrides on each Ir(III) as shown in Fig.84. On the other hand, the structure of a dihydride complex as shown in Fig.85 clearly shows the presence of four and six coordinated Ir(I) and Ir(III).

Another tetrahydrido complex of iridium $Ir_2(CO)_2H_4(dppm)_2$, has recently been prepared by McDonald *et.al*.[386] by the reaction between $Ir(CO)Cl(dppm)_2$ and $NaBH_4$ under a H_2 atmosphere. An interesting reaction occurs when $CHCl_3$ solutions of this complex are stirred under an atmosphere of N_2 gas. The resulting golden yellow complex, $[Ir(CO)_2H_3(dppm)_2]Cl$, has the unsymmetrical structure shown in Fig.86, consisting of two significantly different coordination geometries around each metal atom.

Earlier, Sanger[14] reported that reactions between $Rh_2(CO)_4Cl_2$ or $Rh_2Cl_2(COD)_2$ and dppm yield the dimeric complex $Rh_2(CO)_2Cl_2(dppm)_2$, which on the basis of spectroscopic data is believed to contain two dppm ligands bridging two Rh(CO)Cl units. The corresponding dppp and dppb complexes have also been prepared similarly, although the analogous reaction with dppe gives the monomeric complex characterized as Rh(CO)Cl(dppe).

Interesting asymmetric rhodium dimers have been prepared by reactions of either SO_2 or C_6N_4 with $Rh_2(CO)_2Cl_2(dppp)_2$. The yellow complexes so obtained have been characterized spectroscopically[394] as $Rh_2(CO)_2Cl_2L_2(dppp)_2$, ($L=SO_2,C_6N_4$), in which both L groups are coordinated to only one Rh atom, and the P atoms of the dppp ligands are <u>cis</u>- to one atom and <u>trans</u>- to the other as shown in Fig.87.

King and coworkers[395] have prepared some novel metal-CO-phosphine complexes using $MeN(PF_2)_2$, which is clearly related structurally to dppm. For example, the reaction between $Co_2(CO)_8$ and $MeN(PF_2)_2$ at low temperatures followed by chromatography gives a dark purple coloured complex. X-ray diffraction data shows it to be metal-metal bonded with three bridging $MeN(PF_2)_2$ ligands and terminally coordinated CO groups as shown in Fig.88. When this complex is exposed to U.V. irradiation

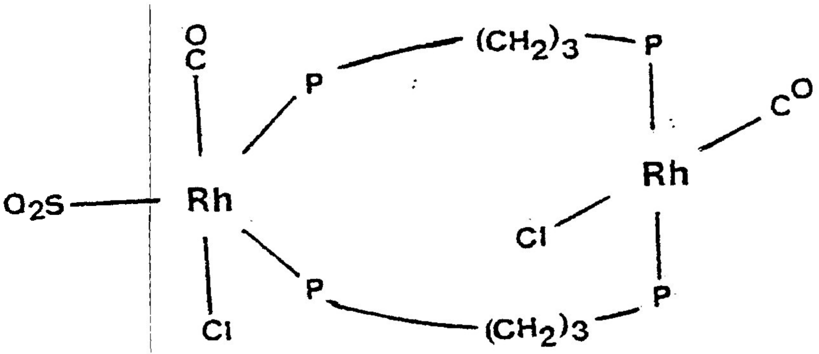


Fig. 87.

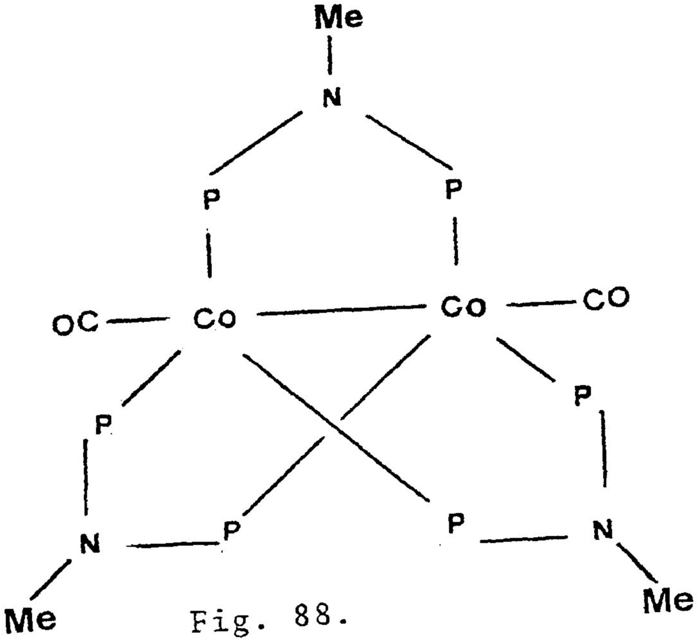


Fig. 88.

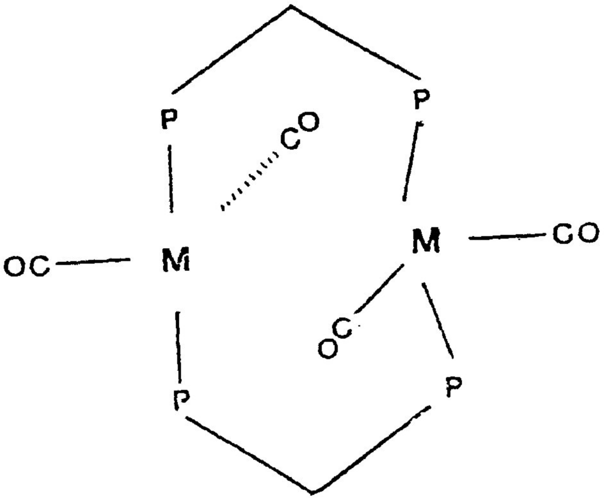


Fig. 89.

in the presence of dppe,[402] a purple-brown complex can be separated by column chromatography from the resulting mixture. This complex has been spectroscopically identified as the product shown in Fig.88 in which one CO group has been replaced by a dppe ligand coordinated through only one P atom.

The related ligand, $MeN\{P(OMe)_2\}_2$ also reacts with $Co_2(CO)_8$ at low temperatures, producing the violet-brown coloured complex $Co_2(CO)_4(MeN\{P(OMe)_2\}_2)_2$. X-ray diffraction reveals[376] that the molecule is dimeric and the metal-metal bond is supported by two bridging bis-phosphine ligands. In addition, each cobalt has two terminally bonded CO ligands, as shown in Fig.89. In this complex it is interesting to note that, in the same molecule, two identical atoms with identical ligands have different coordination geometries. One of the cobalt atoms has a localized trigonal bipyramidal geometry while the geometry of the other Co atom approaches square pyramidal. However, ^{31}P n.m.r. spectroscopy shows a single resonance in solution, indicating equivalent phosphorus atoms. It has been suggested that the molecule is a stereochemically non-rigid system in which the two cobalt atom and the phosphorus atoms became equivalent in solution on the n.m.r. time scale through a fluxional process. Very recently, a mechanism has been proposed[390,39] for this fluxional process in the analogous iridium complex $Ir_2(CO)_4(dmpm)_2$ which involves bending back of the two cis-phosphorus atoms at M(I) with a simultaneous rotation of the two terminal CO ligands toward the side which has the P atoms, to give a trigonal bipyramidal geometry at M(I). This is accompanied by a squeezing of the two phosphorus atoms together at M(II) along with rotation of the two terminal CO ligands away from the phosphorus nuclei, imposing a tetrahedral geometry at M(II). This has been described as a "windshield wiper" type of motion.

Relatively recently, Kubiak et.al.[397] have reported that on treatment of $Rh_2(CO)_2Cl_2(dppm)_2$ with $NaBH_4$ in ethanol, the purple, metal-metal bonded dimeric Rh(0) complex $Rh_2(CO)_2(dppm)_2$ is formed. This reacts with CO gas to form a red-orange compound which in the light of spectroscopic studies, has been formulated as the A-frame complex, $Rh_2(CO)_3L_2$. A quite different type of product forms when $Co_2(CO)_8$ is reacted with in dppm, dmpm or dmdpm.[398] The orange complexes so formed have both terminal and bridging CO groups and ^{31}P n.m.r. spectra show the phosphines to be bridging in the proposed arrangement shown in Fig.90. The dppm complex

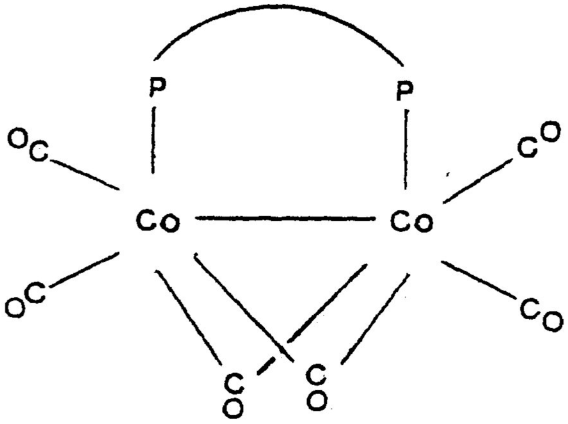


Fig. 90.

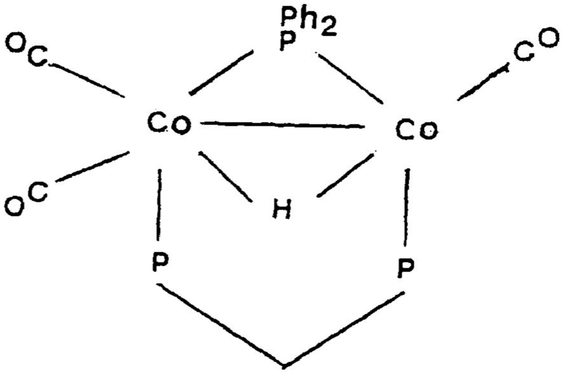


Fig. 91.

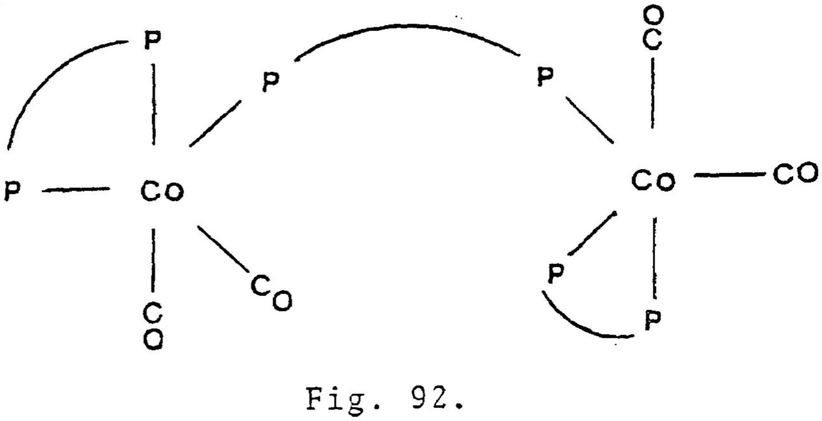


Fig. 92.

reacts with H_2 at 70 atm. and at elevated temperatures resulting in the cleavage of a P-C bond of a dppm ligand. Thus, the green complex so formed has been shown by X-ray crystallography to contain two bonded cobalt atoms bridged by three different groups, a PPh_2, a dppm and a hydride, resulting in a relatively longer Co-Co bond at 2.637Å. The structure is shown in Fig.91.

In contrast, when $Co_2(CO)_8$ is treated with dppe or <u>cis</u>-dppee followed by the addition of $NaBPh_4$, the result is the formation of the tetra carbonyl complexes,[401] $[Co_2(CO)_4(P-P)_3][BPh_4]$ (P-P=dppe,<u>cis</u>-dppee). On the basis of i.r. spectroscopy, it has been suggested that these complexes have a structure in which two $Co(CO)_2(P-P)$ units are bridged by a P-P ligand as shown in Fig.92. More will be said about this later in the thesis.

Only a few bimetallic complexes have been reported from this subgroup. For example, Hutton, Pringle and Shaw[406] have reported that treatment of $[Ir(CO)(dppm)_2]Cl$ with CuC≡CPh in boiling acetone gives the red complex $IrCu(CO)(PhC{\equiv}C)(dppm)_2Cl$. Low temperature ^{31}Pn.m.r. spectra show an AA´BB´ pattern consistent with dppm ligands bridging two different metal atoms. The i.r.

spectrum exhibits two bands assigned to terminal νCO and $\nu(C\equiv C)$ respectively. X-ray diffraction confirms[406] that the metal-metal bond is supported by two bridging dppm ligands and that the coordination positions around the iridium atom are occupied by the acetylenic and CO groups while a Cl ligand is terminally bonded to the copper as shown in Fig.93. The analogous gold complex is also prepared similarly. In related work[406], the iridium complex $[Ir(CO)(dppm)_2][Cl]$ reacts with AgOAc/PhC≡CH to give $IrAg(CO)Cl(PhC\equiv C)(dppm)_2$, which further reacts with $NaBPh_4$ to give $[IrAg(CO)(PhC\equiv C)(dppm)_2][BPh_4]$. It has also been reported that d^{10} metal ions in these complexes can readily be displaced with other metals, in transmetallation reactions. Thus $IrM(CO)(PhC\equiv C)Cl(dppm)_2$ [where M=Cu,Ag] reacts readily with $Rh_2(CO)_4Cl_2$ in methylene chloride to give $IrRh(CO)_2Cl(PhC\equiv C)(dppm)_2$. In addition, $[Ir(CO)(dppm)_2Cl][Cl]$ reacts with $AuCl(PPh_3)$ in boiling acetone to give the deep red $[IrAu(CO)Cl(dppm)_2][Cl]$ which is isolated as the chloride salt. Neutral complexes are formed with $[AgCl(PPh_3)]_4$ and CuCl.

The same authors have also reported[406] that on treating $IrAg(CO)Cl_2(dppm)_2$ with $Rh_2(CO)_4Cl_2$, two complexes are formed which can also be obtained from the reaction of $[Ir(CO)(dppm)_2][Cl]$ with $Rh_2(CO)_4Cl_2$.

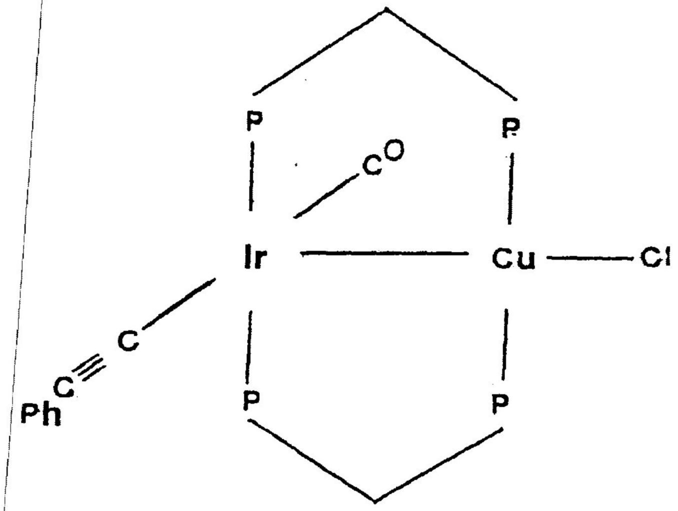


Fig. 93.

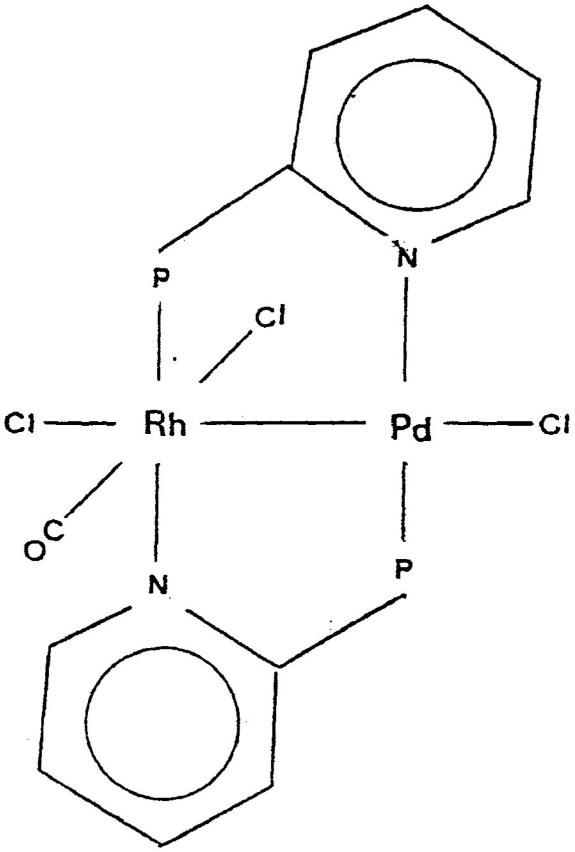


Fig. 94.

However, when CO gas is passed through a solution of this mixture, two products are obtained, the major product has been formulated as $[IrRh(CO)_3Cl(dppm)_2][Cl]$ while the minor product is proposed to have the chemical formula $[IrRh(CO)_2Cl(dppm)_2][Cl]$ which has an 'A frame' structure, where Cl is in the bridging position. This has been formed probably by the loss of a CO group from $[IrRh(CO)_3Cl(dppm)_2][Cl]$.

It has also been reported[406] that $[Rh(CO)(dppm)_2]Cl$ reacts with $[AgCl(PPh_3)]_4$ giving a complex formulated on the basis of elemental analysis, i.r. and n.m.r. results as $RhAg(CO)Cl_2(dppm)_2$.

Farr <u>et.al</u>.[407] have reported another interesting bimetallic complex, $RhPd(CO)Cl_3(PPh_2py)_2$, which is formed when $Rh(CO)Cl(PPh_2py)_2$ is treated with $Pd(COD)Cl_2$ [where PPh_2py=diphenylphosphinopyridene]. An X-ray diffraction study shows that the Rh atom is six-coordinated by two terminal chlorides, a carbonyl and, in addition, is bonded to each of the two bridging PPh_2py units. The second metal is approximately square planar, and the metal-metal distance of 2.594Å is consistent with a direct metal-metal bond as shown in Fig.94. It has been suggested that the formation of this complex involves the oxidative addition of a d^8 Pd(II) complex to an isoelectronic d^8 Rh(I) complex.

In another recent paper, Farr *et.al.*[408] have reported that when $Rh_2(CO)_4Cl_2$ is treated with *cis*-$Pt(PPh_2py)_2Cl_2$, a yellow complex formulated from spectroscopic and analytical results as $Pt[(PPh_2py)_2Cl][Rh(CO)_2Cl_2]$ is formed. On heating this is converted into $RhPt(CO)Cl_3(PPh_2py)$ but, when treated with halide ions, it gives $RhPt(CO)X_5(PPh_2py)_2$ [where X=Cl,Br]. It has been noted that oxidative addition occurs only at the Pt site and that the rest of the binuclear complex remains intact.

1.3.8. Ni, Pd and Pt:

A large variety of phosphine-substituted carbonyl complexes has been prepared from this subgroup. These are listed in Table [8], and can conveniently be generalized by the formula $[M(CO)_{n-x}Y_x]_z$. (where Y= phosphine; x=1-3; n=4; z=1,2). The majority of the nickel complexes have been prepared by the direct reaction of the metal carbonyl with the ligand, although other routes which mainly involve reactions of substituted carbonyl complexes have also been explored. It is interesting to

Table [9].

Complex	Metal	Condition of syntheses and comments		ref
$ML(PR_3)_3$	Ni,Pd,Pt	A,B,C F,G	R=Me,$MePh_2$,p-MePh,Ph_2CH_2;OEt;OPh	409-417, 7
$MLPF_3(PPh_3)_2$	Pd	B		418
$MLX_2(PMe_3)$	Ni	C	X=Cl,Br,I	419
$MLX_2(PMe_3)$	Ni,Pt	C	R=Me,Et,Bu,Cy,Ph,Me_2Ph;$MePh_2$, Ph_2Cy,X=Cl,Br,I	419,420
$[MLX(PR_3)_3][Z]$	Ni	C	X=Cl,Br;Z=BF_4 R=Me	 419
$[MLX(PEt)_2][Z]$	Ni,Pd,Pt	C,H^e	X=Cl,NO;Z=BF_4;PF_6;ClO_4	421-423, 155,424
$MLX(PR_3)R'$	Ni,Pd,Pt	C	R=Bu,Cy,Ph,$MePh_2$,$Bu^t{}_2Ph$; R'=H,allyl,aryl;X=Cl,Br,I	 431
$[MLX(PR_3)_2][Z]$	Ni,Pt	C^b,F	R=Ph,$PhMe_2$,Ph_2Me;Z=ClO_4,PF_6 X=Me,Et,PF_6,C_6Cl_5;$MeOC_6H_4$;p-MeC_6H_4 p-$O_2NC_6H_4$	432,433
$ML(PR_3)(CF_3C{\equiv}CCF_3)$	Ni	D	R=Ph	434
$MLXR'(PR_3)$	Pt	C	X=Aryl;R'=R=Ph	428
$MLX(PR_3)_2R'$	Pt	C	R=p-$Me_2NC_6H_4$;X=Cl;R'=?	431
$ML(PR_3)_3$	Ni	F^d	R=(Ph_2)(p-PhOMe);$(p\text{-}PhOMe)_3$	435
$[ML(PR_3)_2R'][Z]$	Pt	C,H^b	R=Et;Ph;R'=H;Me;Ph Z=ClO_4,SnCl,BPh_4	7,417-419 422,424 436,437
$M_2LS(PPh_3)_3$	Pt	$B^{b,d}$		427,438

$ML_2(PR_3)_2$	Ni,Pd,Pt	A^b,B F^b,G	R=Ph	7,439- 442,444 -446 472,477
$ML_2(PR_3)_2$	Ni	A^b,B	R=Me,Et,Bu^n,EtCN,NMe$_2$,F;Cl; OEt,OPh	413,447 450
$ML_2(PXR_2)_2$	Ni,Pt	A,F^b	X=PhCH$_2$,Et,Pr^1,Cl	413,447 450
$M_2L_2X(PR_3)_2$	Pt	B,H	R=Bu$_2{}^t$Ph;Ph;X=Cl$_2$;C_6H_8	427,451
$ML_3(PR_3)$	Ni,Pd,Pt	A,B, G	R=Ph	412,413,7 444,446, 446,449, 472,478
$ML_3(PR_3)$	Ni	A^b,C	R=Bu^t,OEt,OPh;Cy,4-FC$_6$H$_4$;3-FC$_6$H$_4$; 3-ClC$_6$H$_4$;F,Cl	416,7,449 452,453, 454
$ML_3(PXR_2)$	Ni		X=Bu^t,SiMe$_3$,GeMe$_3$,SnMe$_3$ R=Bu^t,SiMe$_3$;GeMe$_3$;SnMe$_3$	453
$[M_2L_6(PR_2)][Z]$	Ni	Fe	Z=Li(THF)$_4$;R=Ph,Cy	455
ML(dppe)dppee	Ni	A,B^d		446,456
$M_2L(dppm)_2$	Pd	C^c		457
$M_2LX_2(P\text{-}P)_2$	Pd,Pt	C,D	P-P=R$_2$PYPR$_2$;R=Me,Ph Y=CH$_2$;X=Cl,Br,NCO;OH,OPh	26,458, 459
$[M_2LX(P\text{-}P)_2][Z]_n$	Pt	C^e	X=H,D,Me$_2$Py;Z=PF$_6$BF$_4$,I;n=1,2 P-P=dppm,dppe,dppp,dppb	458,460, -462 463

$[M_2L_2(dppm)_2][Z]_2$	Pt	C	$Z=PF_6$	464
$[M_2L_2X(dppm)_2][Z]_2$	Pt	C	$X=Me_2;Z=BF_4$	461
$ML_2(P-S.Et)_2$	Ni	B	$P-SEt=Ph_2P(CH_2)SEt$	448
$ML_2(P-P)$	Ni	A^b,B,	P-P=dmpm,dmpe,depe,dppe,dppee	439,446,
		C	dppp,dppb,bppp	465,466
		also	$P-P=R_2PYPR_2;R=Me,C_2H_5,Ph,CH_2CHCN,$	469,472
			$F,Y=CH_3N,C_6H_4,o-C_6H_4;n=1,2,3,4$	474,162
$M_2L_2(dmpm)_3$	Ni	D^b		162
$M_2L_3(P-P)_2$	Ni	A	$P-P=R_2PXPR_2;R=CF_3;F;Ph$	467,468
			$X=NH,NCH_3;S,O,CH_2$	469,475,
				476
$M_2L_4(P-P)_2$	Ni	A^a	$P-P=R_2PXPR_2;X=O,(CH_2)_2$	466,468,
			$R=CF_3,C_2H_5$	470,472
$M_2L_6(P-P)$	Ni	A	$P-P=R_2PXPR_2;R=C_2H_5;CH_2CH_2CN$	466
			$X=(CH_2)$	

Bimetallics Complexes:

Complexes	Comments	Ref
$[MM'LX_2(dppm)_2][Z]_a$	$M=Pt=Pt;M'=Pd;X=Cl$	496,497
	$M=Pd;M'=Rh,Ir;X=(C\equiv CPh)$	501
	$Z=Cl,a=1$	
$MM'LX_2(PPh_3)_3$	$M=Pt,Pd;M'=Pt,Pd;X=Cl$	482
$[MM'LX_aR(dppm)_2][Z]_b$	$M=Pt;M'=Rh;R=C_2Me,(C_{10}H_7)_2,$	483,494,
	$NCBu^t;Z=PF_6;BPh_4,Rh(CO)_2Cl_2$	495
	$b=0$	

$MM'L_3(Cp)R(Y)$	$M=Ni;M'=Mo,W,Fe;R=PPh_3,C_2X$ $X=H,Ph,CO_2Me,Bu^n,Y=PPh_3$	485,487
$MM'L_3X(dppm)_2$	$M=Pd,Pt;M'=Mn,X=Cl,$ $Cr,Mo,W;(PhC\equiv C)_2$	228,500, 501
$MM'L_4X(Cp)(dppm)$	$M=Ni;M'=Mo;X=CN,SPh$	488
$MM'L_4X(Y)$	$M=Pd;M'=Co,Fe;X=Cl;$ $Y=PPh_2,PPh_3$	489,490 300
$MM'L_4(R)(dppm)(\eta^1\text{-}dppm)$	$M=Pt;M'=W;R=C(OMe)X$ $X=Me,C_6H_4Me\text{-}_4$	491, 492
$[MM'L_4X_aR(dppm)]$	$M=Pt;M'=W;R=C(Cp)A,CA;C(OMe)A$ $X=Br;a=0,1;A=C_6H_4\text{-}Me\text{-}_4$	491
$MM'L_5(Cp)(PMe_2)$	$M=Ni;M'=Fe$	493
$[MM'L5(R)(dppm)][Z]_a$	$M=Pt;M'=W;R=C(OMe)Me;CMe;C_2H_2$ $Z=BF_4;a=0,1$	492
$MM'L_5(R)(dppe)$	$M=Pt;M'=W;R=C(OMe)C_6H_4Me\text{-}_4$	499

note that nickel and platinum dominate the chemistry of phosphine-substituted carbonyl complexes in this subgroup. This is consistent with the reluctance of Pd to form carbonyl complexes as discussed in the previous section.

The highly substituted complexes $M(CO)(PPh_3)_3$ (M=Ni,Pd,Pt) have been synthesized by a variety of methods. For example $Ni(CO)(PPh_3)_3$ was prepared as a yellow solid[409] by treating $Ni(COD)_2$ with PPh_3 in the presence of phenyl propionate. It was suggested that the actual mechanism involves the initial cleavage of the $C_2H_5CO-OC_6H_5$ bond followed by decarbonylation. The analogous cream-coloured Pd complex can be prepared either by the reduction of $Pd^{II}(acac)_2$ with $AlEt_3$ or by the reduction of $PdCl_2(PPh_3)_2$ with $NaBH_4$ in the presence of PPh_3 under a CO atmosphere[411]. The Pt analogue was earlier reported by Malatesta and Cariello[471] and later isolated and characterized by Chini and Longoue[413] and also Albano <u>et.al</u>[412]. On treating $Pt(PPh_3)_4$ or $Pt(PPh_3)_3$ with CO, two isomeric complexes were isolated by Chini <u>et.al</u>[413] as pale yellow and colourless solids respectively. An X-ray study showed[417] that the latter has a more deformed tetrahedral structure resulting in a greater back donation from metal to CO as shown in the i.r. spectra[413]. All these complexes were characterized on the basis of analytical and spectroscopic results.

Similar complexes with other monodentate phosphine and phosphite ligands have also been reported. Thus $Ni(CO)\{P(OPh)_3\}_3$ was isolated[417] when $Ni(acac)_2$ was treated with $P(OPh)_3$ in the presence of $AlEt_3$ under a CO atmosphere at elevated temperatures. This complex can also be prepared by reacting $Ni\{P(OPh)_3\}_4$ with CO gas in 1,5-cycloctadiene (COD), again at elevated temperature. A structure analogous to that of the PPh_3 complexes has been assigned on the basis of elemental analyses and i.r. data.

Several halide derivatives of these complexes have also been prepared. Thus Saint-Joly et.al.[417] reported that $[Ni(CO)X(PR_3)_3][Z]$ and $Ni(CO)X_2(PR_3)_2$ type complexes can be prepared either by reacting $NiX_2(PR_3)_2$ compounds with CO or by replacing the PR_3 ligand from the pentacoordinate complexes $NiX_2(PR_3)_3$ and $[NiX(PR_3)_4][Z]$ with CO under normal conditions. These complexes (where R=Me,Et,Ph,Me_2Ph,$MePh_2$; Z=BF_4 and X=Cl,Br,I) were characterized by analytical and spectroscopic data to be five-coordinated with trigonal bipyramidal geometry. An X-ray diffraction study[419] on $Ni(CO)I_2(PMe_3)_2$ shows that the PMe_3 groups are in the axial positions while CO occupies an equatorial position as do the two iodide ligands. The most interesting feature of the structure is the Ni-C bond distance which, at, 1.728Å, is the shortest such distance reported so far. These authors found that the experimental stability order towards CO dissociation of $Ni(CO)X_2(PR_3)_2$ is I > Br > Cl and R = Me > Et ≈ Me_2Ph > $MePh_2$ > Ph with the exception of $Ni(CO)Br_2(PEt_3)_2$ which is very unstable. Four-coordinated platinum complexes of similar structure have also been reported[420].

A large number of complexes of the type $[M(CO)X(PR_3)R']$,[425,431] are known for all three metals. These complexes are generally prepared either by reacting halophosphine complexes with CO or by halogenating the phosphine-substituted carbonyl complexes.

Disubstituted complexes of the type $M(CO)_2(PR_3)_2$ have been reported for all three metals. These are generally prepared by reacting either the metal carbonyl with phosphine or by the action of CO on zero valent metal-phosphine complexes. In addition, halo-substituted complexes have also been reduced in the presence of phosphine and CO. Thus, the platinum complex $Pt(CO)_2(PPh_3)_2$ has been prepared by treatment of $PtCl_2$ with CO in the presence of PPh_3 using zinc dust under refluxing conditions. This complex can also be prepared by treating $Pt_3(CO)_3(PPh_3)_4$ with CO. The Pd analogue has been prepared[477] by the reaction of $Pd_3(CO)_3(PPh_3)_3$ with CO while $Ni(CO)_2(PPh_3)_2$ was isolated as a crystalline complex, when $Ni(CO)_4$ is treated with PPh_3[472]. These complexes were largely characterized on the basis of elemental analyses, dipole moment data and i.r. spectra. Both the Pd and Pt complexes are unstable and decompose in the absence of CO. More will be said about this later in the discussion section.

A number of other disubstituted complexes are also known. For example Baird and Wilkinson[327] have reported that when $Pt(PPh_3)_3$ is reacted with carbonyl sulfide, a complex $Pt(COS)(PPh_3)_2$ is formed which is very labile. When heated in chloroform, it is converted into a yellow complex which, on the basis of analytical and i.r. data, was formulated as $Pt_2(CO)_2S(PPh_3)_3$. However, later a single crystal X-ray[435] study showed that this complex is really $Pt_2(CO)S(PPh_3)_3$ having a Pt-Pt bond and a three-membered ring containing sulfur. The complex exists in two isomeric forms and the difference between the two isomers is mainly confined to one PPh_3 group in which the phenyl rings adopt two quite different conformations with respect to the rest of the molecule. This results in a slightly different orientation of the adjacent carbonyl group for each isomer. The two i.r. bands observed by Baird and Wilkinson[327] are consistent with the presence of one CO group having a different environment in the two forms.

Monosubstituted derivatives for all three metals have also been reported. The white, crystalline $Ni(CO)_3(PPh_3)$ forms on treatment of $Ni(CO)_4$ with PPh_3 at low temperature.[7,478] It can also be prepared by starting with $Ni(PPh_3)_4$ and reacting it with CO.[446] However, the Pd analogue was prepared by passing CO gas through a solution containing $Pd_3(CO)_3(PPh_3)_3$, while the analogous Pt complex can be prepared by treating either $Pt_3(CO)_3(PPh_3)_4$ or $Pt(CO)_2(PPh_3)_2$ with CO gas. The Pd and Pt complexes are unstable in the absence of CO and decompose readily to give either dicarbonyl or polymeric complexes. These compounds were characterized largely on the basis of their i.r. spectra, except for the Ni complex which was more fully characterized on the basis of analytical data together with i.r. spectra.

A large number of bisphosphine complexes have been synthesized from this subgroup. Davis and Sneeden[457] have reported that when $PdCl_2(dppm)$ is treated with $NaBH_4$ in the presence of CO gas, two complexes are obtained which were formulated, on the basis of analytical and i.r. data, as $Pd_2(CO)Cl_2(dppm)_2$ and $Pd_2(CO)(dppm)_2$. However, no structural details were given. The former complex can also be prepared by passing CO gas into a solution containing $Pd_2Cl_2(dppm)_2$.[26] This palladium derivative, has been characterized analytically and spectroscopically as a dimeric complex (Fig.95) having a single νCO band assigned to a bridging CO ligand at 1705 cm^{-1} in the i.r. spectrum. Similar complexes in which Br, I, and NCO replace Cl have also been reported and analogous structures have been assigned.[26]

The platinum analogue has been prepared either by bubbling CO gas into a solution containing $Pt_2X_2(dppm)_2$ or by the reaction of $[Pt_2(CO)_2X_4]^{2-}$ with dppm[458,479] (X=Cl). This complex exhibits a νCO band in the i.r. spectrum at 1638cm^{-1} and, in solution, it readily isomerizes to another species, $[Pt_2(CO)X(dppm)_2]^+$, which can be isolated as the PF_6^- salt. The unusually low νCO frequency led these authors to suggest that CO acts as a four-electron donor and as a

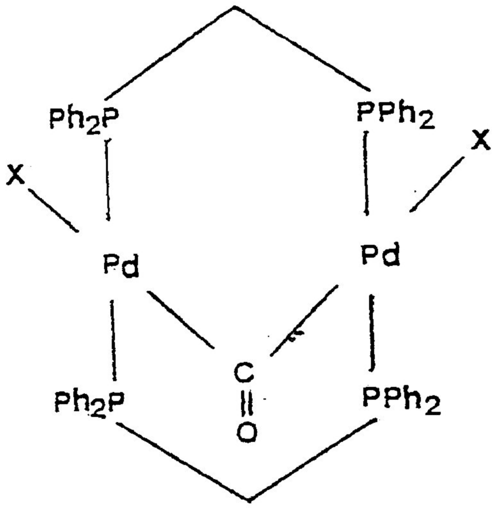


Fig. 95.

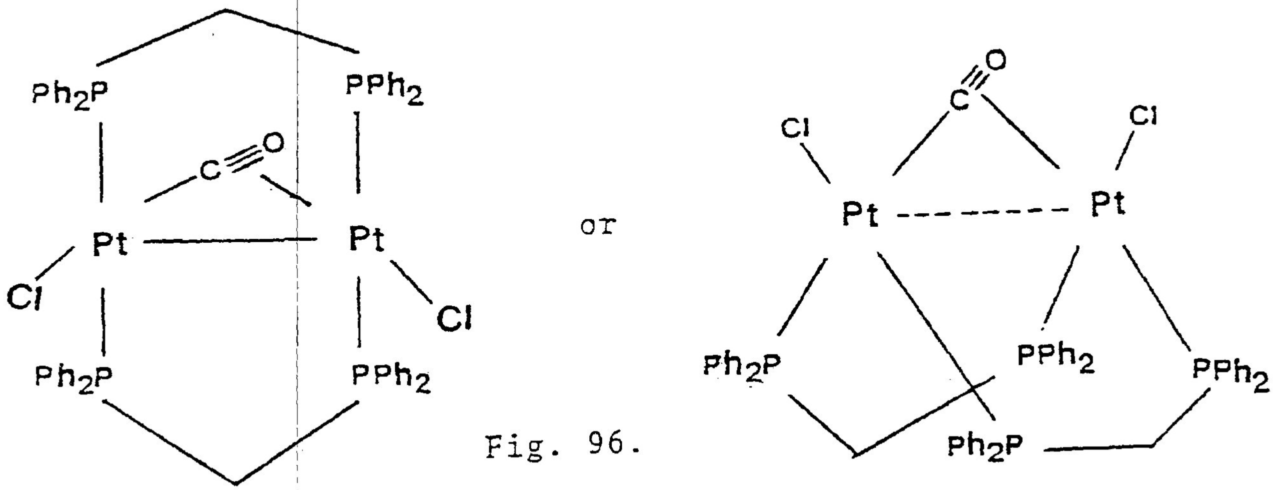


Fig. 96.

(a)

(b)

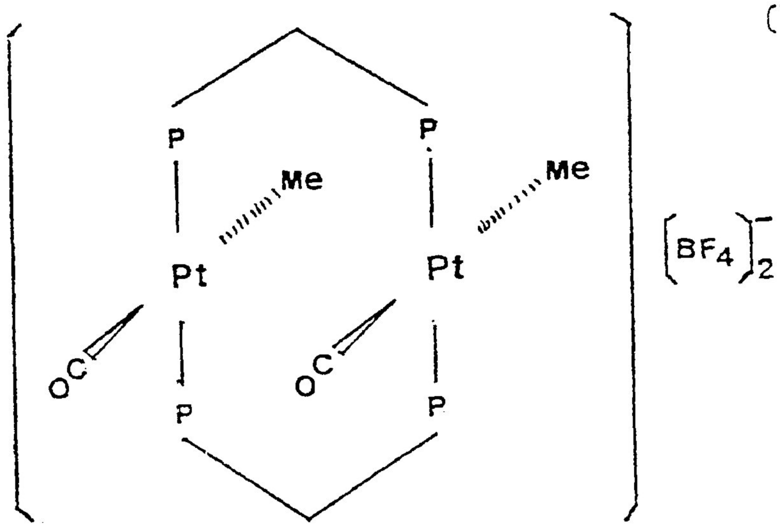


Fig. 97.

bridging ligand in this complex in a manner similar to that observed for a Mn complex reported earlier by Commons and Hoskins.[460] The structures shown in Fig.96(a and b) were proposed for the Pt complex. However, single crystal X-ray diffraction studies on analogous palladium complexes, $Pd_2(CO)X_2(P-P)_2$ (where (P-P)=dpam,[461] dmpm[459]), have been reported and these have been shown to have bridging CO groups acting as more conventional two-electron donors. These results prompted a reconsideration[462] of the structures shown in Fig.96 and a structure analogous to that of $[Pd(CO)X_2(dppm)_2]$, shown in Fig.95, has now been assigned.

Hutton <u>et.al</u>.[461] reported that the A-frame complex $[Pt_2(\mu\text{-}CO)(Me)_2(\mu\text{-}dppm)_2][BF_4]_2$ can be prepared on treatment of $[Pt_2(Me)_2(NCMe)_2(\mu\text{-}dppm)_2][BF_4]_2$ with CO. However, on further treatment with CO gas this complex gives, reversibly, the dicarbonyl complex $[Pt_2(CO)_2(Me)_2(\mu\text{-}dppm)_2][BF_4]_2$ which exhibits a single νCO band at $2100cm^{-1}$ in the i.r. spectrum. An X-ray study showed that this complex has the structure shown in Fig.97.

Kullberg and Kubiak[459] have reported that on treatment of $Pd_2(OH)_2(\mu\text{-}dppm)_2$ with ^{13}CO, the A-frame complex $Pd_2(\mu-^{13}CO)(OH)_2(\mu-dppm)_2$ is formed and this was characterized as a structure analogous to that shown in Fig.95 by comparing its ^{31}P and ^{13}C n.m.r. spectra with those of $Pd_2(\mu-CO)Cl_2(\mu-dppm)_2$.

In contrast to dppm or dmpm, when bisphosphine ligands with longer back bone carbon chain lengths were used, products of entirely different structural types were obtained. Thus, Minghetti et.al.[463] reported that when CO gas is passed through a solution containing $[Pt_3H_3(P-P)_2][BF_4]$ (where P-P=dppe,dppp,dppb), green to violet complexes are obtained which were characterized from analytical and spectroscopic data. In addition, a single crystal X-ray diffraction study[463] on the dppe complex shows that both dppe ligands in this complex are coordinated in a chelating fashion, the hydrogen and CO are bridging ligands and there is a Pt-Pt bond. The structure is shown in Fig.98. Related complexes obtained using dppp or dppb were assigned analogous structures.

Corian et.al.[464] have reported that on treatment of $Ni(P-P)_2$ (where P-P=dppe, dppp, dppb) with CO gas in C_6H_6 or CH_2Cl_2, mono and dicarbonyl complexes are obtained. Analytical and i.r. data indicated that these complexes are $Ni(CO)(P-P)(\eta^1-P-P)$ and $Ni(CO)_2(P-P)$

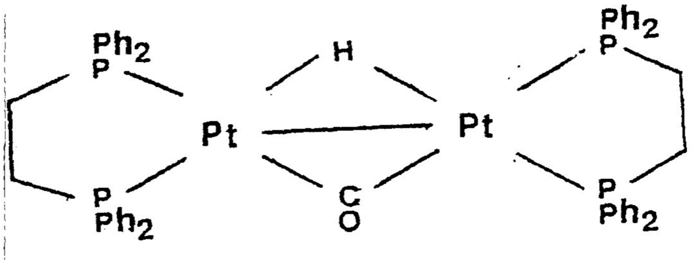


Fig. 98.

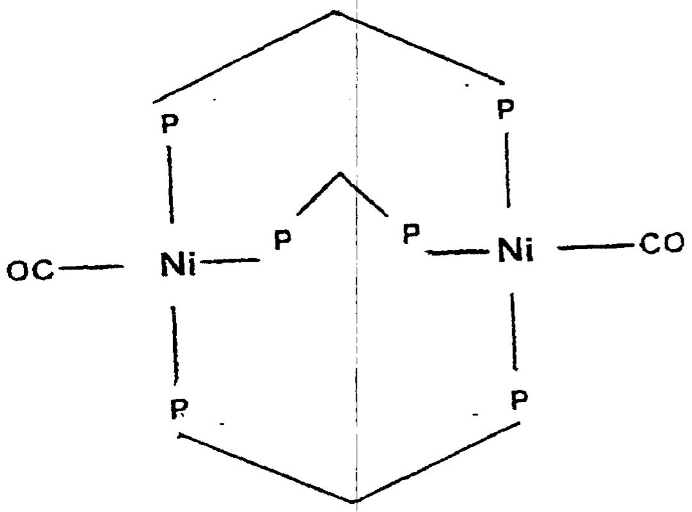


Fig. 99.

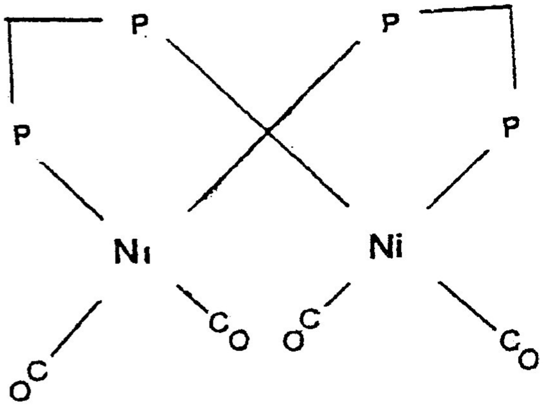


Fig. 100.

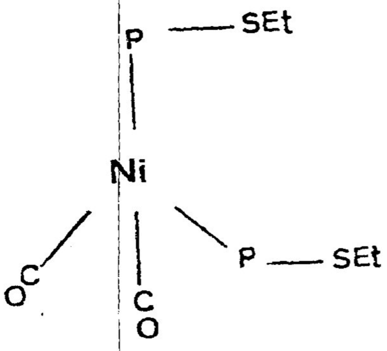


Fig. 101.

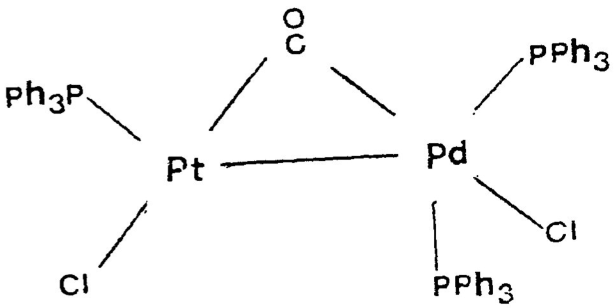


Fig. 102.

respectively. Complexes of the former type, where P-P=dppp and dppb, have been reported when compounds of the type $Ni(P-P)_2$ are treated with acyl halides.[456] The latter type of complex has also been reported to form with the ligands dppee[437]; depe[466]; dmpm[162] and dmpe.[474] More will be said about this later in the discussion section.

Organic ligands such as cyclopentadiene have also been displaced in some instances. Thus, King and RaghuVeer[162] reported that treatment of $[Ni(CO)(Cp)]_2$ with dmpm in boiling THF results in displacement of the Cp ring and the formation of a yellow complex which, on the basis of analytical, spectroscopic and molecular weight determination data, has been characterized as a dimeric system with three dmpm ligands coordinated in a bridging fashion as shown in Fig.99.

In contrast, when dmpm is treated with $Ni(CO)_4$, a white complex is formed which was originally characterized as monomeric $Ni(CO)_2$(dmpm). However, a single crystal X-ray diffraction study by Porschke _et.al_.[470] revealed that this complex is actually dimeric and has the structure shown in Fig.100.

A very interesting Ni-CO complex has been reported by Rigo et.al.[448] It forms when Ni(P-SEt)$_2$ {where P-SEt=1-(thioethyl)-2(diphenylphosphino)ethane} is treated with CO at 1 atmosphere pressure. The solution immediately decolorizes and a white crystalline solid is obtained. This was characterized by analytical and spectroscopic data as Ni(CO)$_2$(P-SEt)$_2$, where both P-SEt units act as monodentate ligands forming a tetrahedral structure around the nickel atom as shown in Fig.101. Mention of this will be made again in the discussion section.

Bimetallic complexes with various metals have been prepared from this subgroup using a variety of methods which are listed in Table [8]. For example, Bender et.al.[482] reported that, on treatment of either Pt(CO)(PPh$_3$)$_3$ with the labile PdCl$_2$(PhCN)$_2$ or of Pd(CO)(PPh$_3$)$_3$ with PtCl$_2$(PhCN)$_2$, a bimetallic complex is formed. This has been characterized (analysis,i.r. and ^{31}P n.m.r. spectra) as the dimeric system shown in Fig.102. It exhibits a single νCO band in the i.r. spectrum at 1823cm^{-1} which was assigned to the CO ligand bridging two different metals.

Pringle and Shaw[496,497] reported that

when $Pd(PPh_3)_4$ is treated with the labile Pt(II) complex $Pt_2Cl_2(NCBu^t)_2$ in the presence of dppm, an orange complex $PtPdCl_2(\mu\text{-dppm})_2$ is formed. When CO gas is passed through the solution containing this bimetallic compound, a red crystalline complex can be isolated. Due to the low solubility of this complex, it was characterized mainly from elemental, analytical and i.r. spectral data as $PtPd(\mu\text{-CO})Cl_2(dppm)_2$. The single νCO band exhibited by this complex in the i.r. spectrum at 1680 cm^{-1} is almost average in frequency between νCO for $Pt_2(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$ (1638cm^{-1}) and for $Pd_2(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$ (1705 cm^{-1}). It was also noted that the mixed complex does not lose its CO as readily as does the dipalladium analogue but probably more readily than does the diplatinum analogue. Furthermore, it was also observed that CO can be readily displaced by SO_2 which ,in turn, is easily and completely displaced by N_2,Ar or CO (to regenerate the μ-CO complex). Thus, a small amount of SO_2 can be used to catalyse the reversible uptake of CO by $PtPdCl_2(\mu\text{-dppm})_2$. More will be said about this in the discussion section.

In other reactions, when $Pt(dppm)Cl_2$ is treated with AgOAc-MeC≡CH, it gives $PtAgCl_2C{\equiv}CMe(\mu\text{-dppm})_2$ which, on transmetallation with $Rh_2(CO)_4Cl_2$ forms a complex isolated as the PF_6 salt. This was originally thought to be a dimeric system with the acetylide ligand symmetrically bonded to both Pt and Rh atoms[483,498] as shown in Fig.103. However, a single crystal X-ray diffraction study[493] later revealed that the acetylide group is σ-bonded to Pt and forms an unsymmetrical side-on π- bond to Rh as shown in Fig.104. Similar complexes have also been reported for Pd.[501] In addition, complexes of the type $MM'(CO)_3(\mu\text{-}C{\equiv}CPh)(\mu\text{-}dppm)_2$ (where M=Pd,Pt and M'=Cr,Mo or W) have also been prepared and similarly characterized.[500,501]

The brown complexes $NiFe(CO)_3(Cp)(PPh_3)$-(C_2R) [where $R{=}H,Ph,CO_2Me$] have been prepared by treatment of $Ni(Cp)(PPh_3)(C_2R)$ with $Fe_2(CO)_9$. These were characterized initially from mass and i.r. spectral evidence. In addition, a single crystal X-ray diffraction study on the complex where R=H showed that the ethynyl triphenylphosphonium group acts as a bridging ligand, and that the phosphorus atom is closer to the nickel atom than to the iron atom. An intramolecular triphenylphosphonium salt type of structure was suggested with the formal negative charge distributed between the nickel and the iron atoms[485,486] as shown in Fig.105.

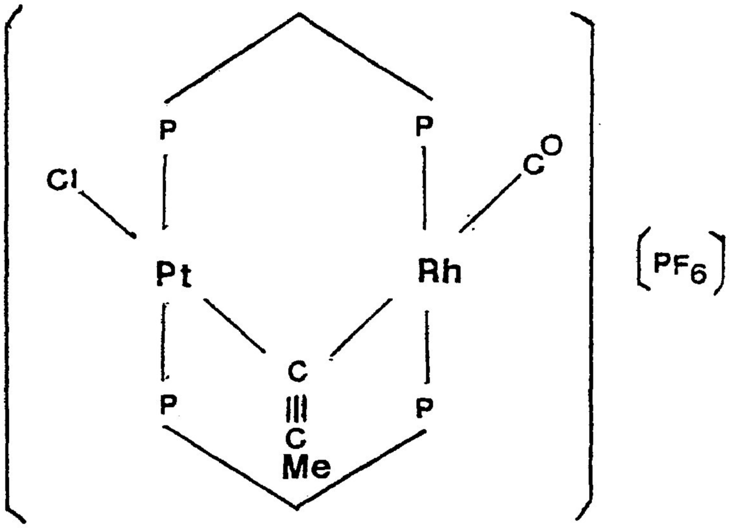


Fig. 103.

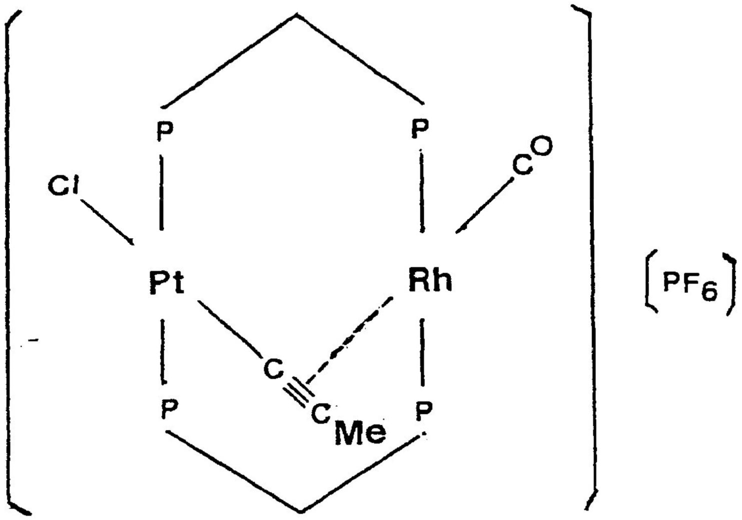


Fig. 104.

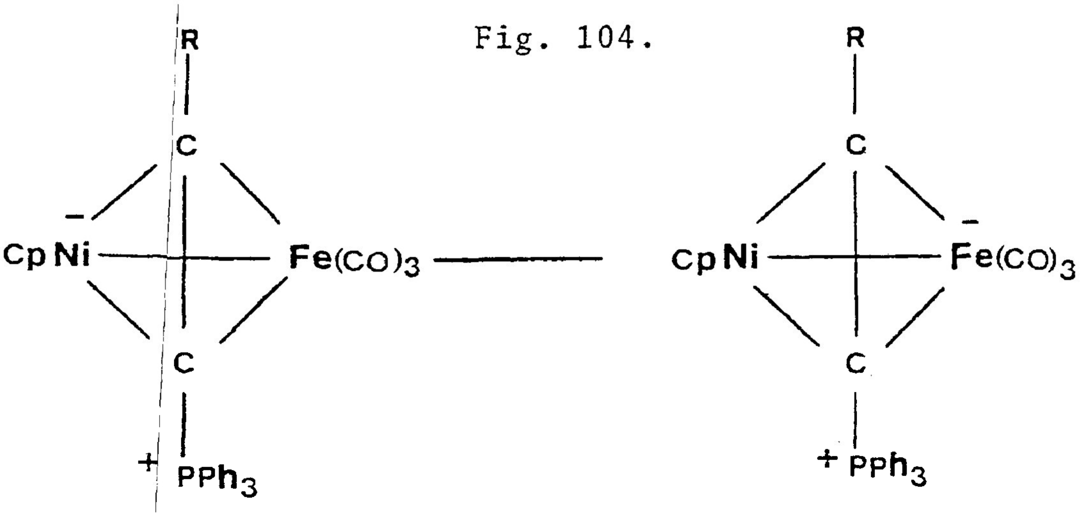


Fig.105.

Several other bimetallic systems containing nickel have been described. Thus, Carlton et.al.[487] have reported that when Na[M(CO)$_3$(Cp)] (M=Mo,W) are treated with NiCl$_2$(PPh$_3$)$_2$ in THF at room temperature, followed by the addition of water and careful washing of the resulting solid with acetone, a moderately stable deep green crystalline complex formulated as NiM(CO)$_3$(Cp)(PPh$_3$)$_2$, is formed. The i.r. spectrum suggested the presence of both bridging and terminal carbonyl groups n.m.r. studies indicated it to be a paramagnetic species. X-ray diffraction studies, however (on M=W), revealed that one of the CO ligands is terminally coordinated to W while the other two CO groups interact with nickel and may be considered as semibridging.

In other studies, Ehrl and Vahrenkamp[498] reported that reactions between Fe(CO)$_4$, PMe$_2$Cl and Ni(CO)$_3$(PMe$_2$Cl), produce a bimetallic complex, NiFe(Cp)(CO)$_5$(PMe$_2$). Spectroscopic data suggested that the PMe$_2$ unit bridges the two metal atoms and, in addition to the Cp ring, two of the carbonyl groups are terminally coordinated to the iron atom while three are attached to the nickel atom as shown in Fig.106.

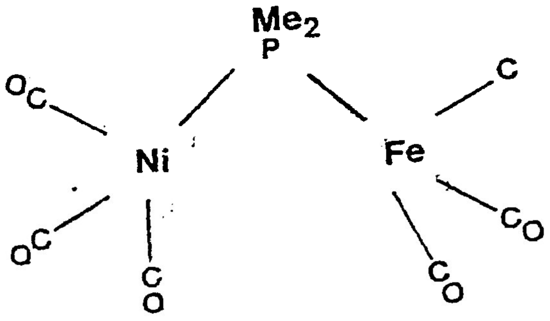


Fig. 106.

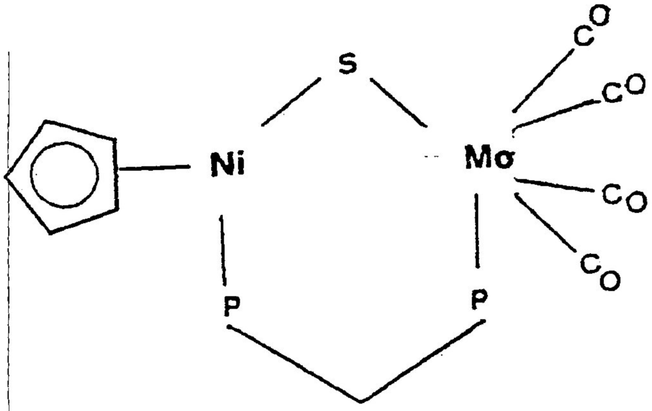


Fig. 107.

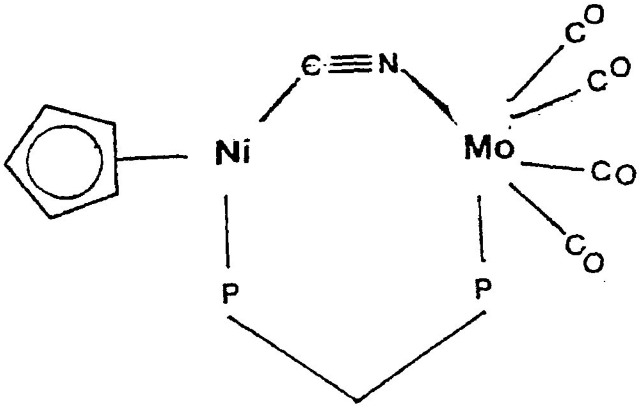


Fig. 108.

In another interesting reaction, Sato *et.al.*[425] isolated both black and brown complexes when an ether solution containing $Mo(CO)_4(C_7H_8)$ was treated with Ni(Cp)(SPh)(η^1-dppm) or Ni(Cp)(CN)(η^1-dppm) respectively. Molecular weight data for the black complex suggested a monomeric species. However, the ^{31}P n.m.r. spectra of the two complexes show two doublets indicating the presence of non equivalent phosphorus atoms which suggested bridging dppm as shown in Fig.107 and 108.

A number of other bimetallic complexes have also been prepared and these are listed in Table[8].

1.4. Objectives:

From the preceding introductory discussion, it is clear that reactions of metal carbonyls, or substituted metal carbonyls, with phosphine ligands is by far the most widely used route to metal-CO-phosphine complexes. Of mech less importance are reactions of metal-phosphine complexes with carbon monoxide. The prefered route to these complexes, therefore, makes extensive use of metal carbonyls as starting inateials. This may not always be convenient for a number of reasons. For example, some carbonyls may not be readily available, many are air sensitive, very volatile and extremely toxic and therefore great care must be practiced when handling them (0.001 p.p.m of $Ni(CO)_4$ is the daily threshold limit and longer exposures may be fatal.[506] Several metal carbonyls are liquid at room temperature.

In the past several years, extensive research has been done in these laboratories to investigate the properties of $NaBH_4$ and $NaBH_3CN$ as reducing agents and as coordinating ligands in reductions of higher oxidation state metal salts in the presence of a variety of phosphine ligands. Much valuable information has been obtained from these reactions and the results have, for the most part, already been published.[502-504] These studies have shown that interactions of transition metal salts with $NaBH_4$ and $NaBH_3CN$ in the presence of phosphine ligands produce a wide range of new products. This is particularly true when $NaBH_3CN$ is used. In general, possible to isolate several intermediate products in these reactions simply by adjusting the conditions of the reactions.[505] There is clearly the potential to extend these reactions by introducing CO.Apart from two or three instances,[335,345] however, phosphine-substituted carbonyl complexes have not been prepared by this route, and there is no report in the literature of the production of complexes using $NaBH_3CN$, a milder reducing agent than $NaBH_4$, as a regent in such syntheses.

It is also well known, that most of metal carbonyls are extremely toxic and great care must be practiced when handeling these results. Thus, 0.001 P.P.M. of $Ni(CO)_4$ is the threshold limit set for one day exposures. Exposures longer than this may cause severe damage to the body system and can be fatal in most cases.[5] Several metal carbonyls are liquid at room temperature and are highly volatile. They must therefore be handled with especial care routine laboratory work.

Bearing these facts in mind, this project was started with the following objectives.

(a). To establish a convenient route for the formation of zerovalent, phosphine-substituted nickel carbonyl complexes Ni(II) salt thereby avoiding the direct use of the extremely toxic and voltile $Ni(CO)_4$.

(b). To study under a wide variety of conditions the interactions of BH_4 and BH_3CN^- as reducing agents for Ni(II) in the presence of mono-and bisphosphine ligands under a CO atmosphere. In particular,the objective of this study was to investigate the influnce of reaction conditions (amount of phosphine, temperature, rate of addition of reducing agent and duration of reaction etc) and the nature of the phosphine ligand upon the types of product formed and the bonding modes adopted by CO in complexes containing that ligand.

(c). To compare the behaviour of $NaBH_4$ with that of $NaBH_3CN$ as a reducing agent in the above reactions and to note any additional stabilization due to CO ligand in the complexes formed(compared to products pbtained when CO is absent from the reaction).

(d). To determine the reactivities of any Ni(O)-CO phosphine products towards a variety of ligands.

(e). In the course of this work, unexpected products containing monocoordinated bisphosphines were obtained. This led to a last objective, to investigate the nature of these as precursors homo and heteronuclear bimetallic systems.

The results of these studies which involve the careful control of reaction conditions and the use of a wide variety of physical methods for the structural characterisation of the compounds which were isolated are described in the nest chapter.

2. Experimental:

2.1. Material:

The phosphines dppm, dppe, dppp, dppb, and dpppe were purchased from Strem Chemicals incorporated and PPh_3 from Alfa Products Ventron Division, $NaBH_4$ and $NaBH_3CN$ were obtained from the Aldrich Chemical Company and, due to their hygroscopic nature, were stored over anhydrous $CaCl_2$. Reagent grade $NiCl_2.6H_2O$ and iodine were was purchased from BDH Chemicals Limited. Reagent grade $Mo(CO)_6$ and $Ni(CO)_4$ were purchased from Strem Chemicals. Aqueous HBr(48%) and aqueous HCl(37%) were obtained from Alfa Products and American Scientific and Chemicals respectively. CP grade carbon monoxide and UPH grade hydrogen gases were purchased from Canadian Liquid Air Ltd. Sulfur dioxide and nitric oxide gases were purchased from Matheson Gas Products. All the above chemicals were used without further purification.

$Pt(COD)Cl_2$ and $[Rh(CO)_2Cl]_2$ were synthesized according to publiched methods.[507-509] All solvents were reagent grade and were degassed with oxygen free dry nitrogen and stored in a N_2 filled glove box or degassed by dry nitrogen gas prior to use in fume hood. All glassware used was dried at 100°c.

Initial synthetic work was done in a well ventilated fume hood using the apparatus shown in Fig.109 under completely controlled conditions to avoid any contact of atmospheric oxygen with the reactions. All other manipulations were carried out in a glove box (unless otherwise mentioned) which was constantly flushed with dry nitrogen.

2.2. Analyses and Physical measurements:

All air sensitive samples were suitably protected from atmospheric oxidation or hydrolysis during analyses and physical measurements.

The infrared spectra of the samples were recorded as Nujol mulls pressed between sodium chloride plates for the 4000cm^{-1} to 600cm^{-1} region or between polyethylene plates between the region 600cm^{-1} to 200cm^{-1} on a Beckman IR 4250 spectrophotometer (Calibrated periodically with a polystyrene refrence film). Electronic spectra (usully reflectance) were recorded on a Cary-14 recording spectrophotometer in the 18,00 to 300

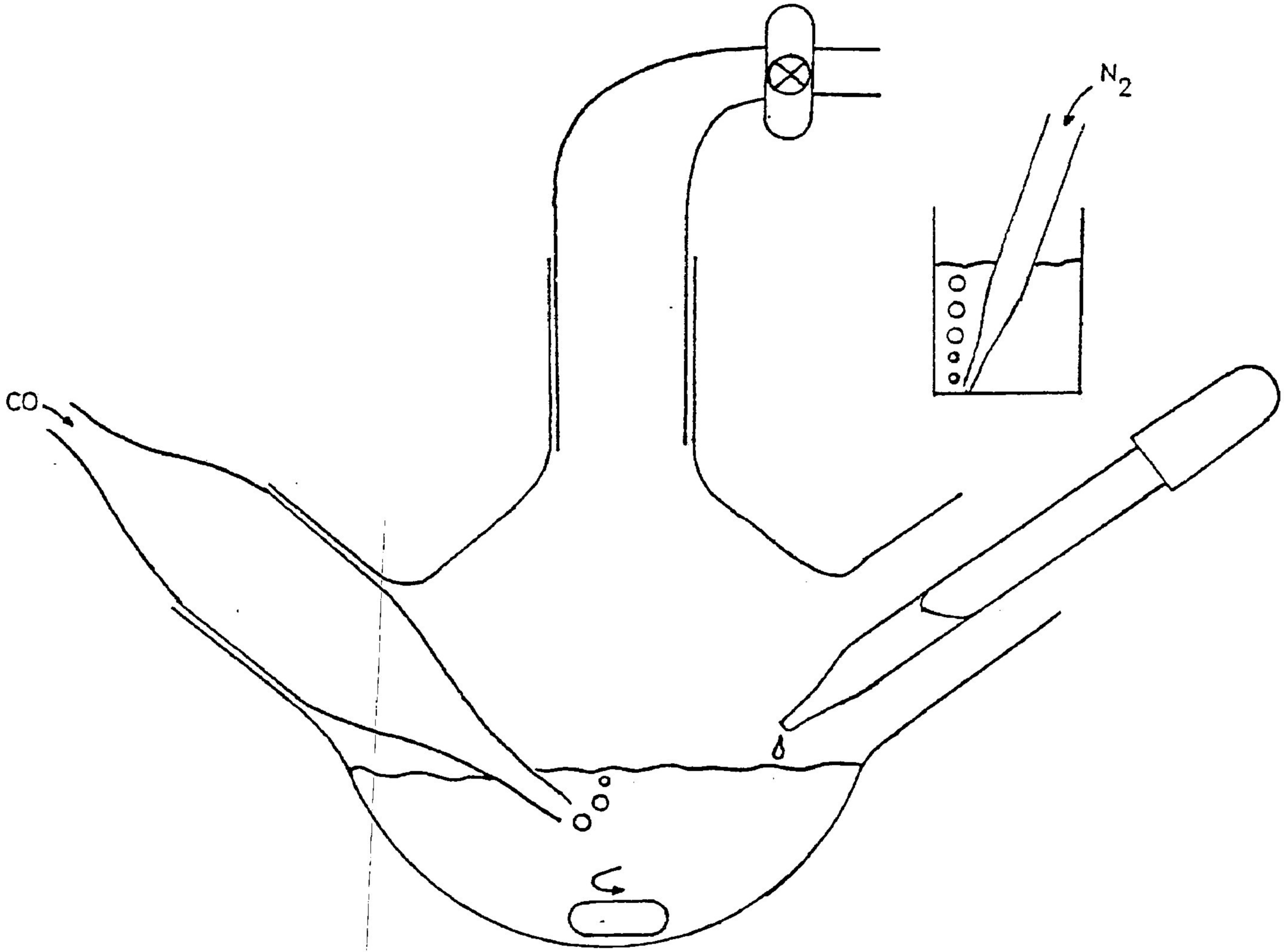


Fig. 109. Apparatus used for syntheses.

nm range.

^{31}P and ^{1}H n.m.r. spectra were recorded on a Bruker WP 80 Fourier transform instrument equipped with an automatic temperature control device (B-VT 1000) at 32.3 mHz and 80 mHz respectively. The chemical shifts were measured relative to internal tetramethylsilane (TMS) and external H_3PO_4(85%) for ^{1}H and ^{31}P n.m.r. respectively but, in practice, the direct use of H_3PO_4 during routine ^{31}P n.m.r. spectra was avoided to eliminate saturation of the spectra by H_3PO_4. The position of the H_3PO_4 signal was first recorded against either D_2O or $(CD_3)_2CO$ which were used as external frequency lock systems, and which were sealed in thin glass capillaries coaxically fitted to the ^{31}P n.m.r. sample tubes through a vortex plug. The position of H_3PO_4 against these frequency locking solvents was found to be 2800Hz (D_2O) and 2910Hz $(CD)_3CO$. Hence chemical shifts of other ^{31}P signals from the samples were calculated with reference to these frequencies. There are two main advantages in using this method. Firstly, if H_3PO_4 is used as an external reference, the H_3PO_4 signal can easily be saturated and thus weak signals in the sample may not be measured. By using the above method a sample may be scanned over a longer period of time and this is particularly useful for sparingly soluble samples where pulsing for longer period become feasible. Secondly, solutions of reaction mixtures could be scanned without contamination by and possible reaction with H_3PO_4 (if added as an internal standered). The ^{31}P n.m.r. spectra were normally recorded at ambient temperatures (unless otherwise specified) in the proton decoupled mode. The chemical shift(s) are positive if down field from the refrence signal. ^{31}P n.m.r. spctra were simulated using Bruker's BNC-28 ITRCAL simulation and interation program.

The X-ray crystallographic results to be referred to later were obtained by colleagues at the Department of Chemistry University of Minnesota at Duluth USA. Crystals were grown for this purpose according to the methods to be described later. Suitable crystals were carefully selected under a microscope in a N_2 filled glove bag and were sealed in 0.3 mm Lindeman capilaries.

The X-ray powder diffraction data were aquired on a Phillps P.W.1050 diffractometer equipped with a P.W.1010 generator.

Mass spectra were recorded on a Hitachi-Perkin Elmer model RMU-7 double focusing mass spectrometer (usually to find the solvent of crystallization).

Approximate analysis for some samples were obtained on a Hitachi 570 scanning electron microscope, equipped with a Tracor Northen X-ray micro analysis system. Crystals were glued by carbon on carbon stubs and coated with carbon.

A Phillps P.W.1540 X-ray fluorescence spectrometer equipped with a PW1130 generator and 2.7. KW Cr anode X-ray tube was used generally to establish the presence of halide in samples.

Micro analytical data for carbon, hydrogen and nitrogen were acquired on a Perkin Elmer model 240 analyzer and on a Control Equipment Corporatation's elemental analyzer model 240-XA equipped with an automotic computor control system. For samples where combustion was incomplete under normal conditions, either V_2O_5 or a mixture of V_2O_5 and WO_3 were used as combustion aids. Metal and phosphorus analyses were obtained from an Allied Analytical System's Jarrel-Ash ICAP 9000 spectrometer with simultaneous elemental determination using an argon plasma.

Molecular weights were determined either in $CHCl_3$ or in C_6H_6 solution at ambient temperature using a Wescor 5500 vapor pressure osmometer calibrated with PPh_3. Accuracy was checked periodically by measurements of the molecular weight of either PPh_3, dppm or dppe in $CHCl_3$ or in C_6H_6.

Melting points were recorded on Gallenkamp melting point apparatus.

2.3. Syntheses:

A general pattern was followed for most of the syntheses which will be described in this chapter. This involved the addition of the reducing agents, $NaBH_4$ or $NaBH_3CN$, to the CO-saturated Ni(II) chloride solutions in the presence of the appropriate phosphine ligand. Usually, the reaction medium was either ethanol/benzene or ethanol/toluene. Mixed solvent systems were used because most of the phosphines used are completely soluble in benzene or toluene whereas the nickel salt is soluble in ethanol. The reactions were studied under a wide range of conditions and the more important factors which were found to affect the course of the reactions are:

(a) the amount of $NaBH_4$ / $NaBH_3CN$ used.
(b) the rate of addition of $NaBH_4$ / $NaBH_3CN$.
(c) the reaction time.
(d) the temperature.
(e) the ratio of metal to ligand (phosphine).
(f) the nature of the phosphine used.
(g) the solvent system.
(h) the rate of stirring.

2.3.1. Dicarbonylbis(triphenylphosphine)nickel(0) $Ni(CO)_2(PPh_3)_2$.

(a). From $NaBH_4$:

A stirred mixture of $NiCl_2.6H_2O$ (0.50g; 2.10mmol) in ethanol (20mL) and PPh_3 (2.20g; 8.41mmol) in toluene (30mL) was saturated with CO gas for 40 minutes. To this light greenish black solution was added a suspension of $NaBH_4$ (0.24g; 6.32mmol) in ethanol (15mL). The solution immediately turned to reddish then yellow. CO gas was constantly bubbled at a rate of ~2-3 bubbles/second for a further 1.5 hours during which time a cream coloured precipitate formed. This was filtered off, washed with ethanol (~10mL) and diethyl ether (~10mL), redissolved in benzene (~25mL) and left at room temperature over 12 hours. The light cream crystals which formed were filtered off and washed with ethanol (~10mL) dietheyl ether (~10mL) and dried under reduced pressure.

yield: 20% M.P. 180°C

Analysis

Calcd. for $Ni(CO)_2(PPh_3)_2$:

C = 71.39% H = 4.70%

Found : 71.06 4.63

(b). From $NaBH_3CN$:

$NiCl_2.6H_2O$ (0.5g; 2.1mmol) and PPh_3 (2.20g; 8.44mmol) were mixed and stirred in benzene/ethanol (1:1; 60mL) under a slow stream of CO gas for about one hour. An ethanolic (30mL) solution of $NaBH_3CN$ (0.53g; 8.4mmol) was then added to this greenish black solution. CO gas was allowed to pass at a slow rate (2-3 bubbles/sec.) through this solution for a further 2 hrs while it was stirring. The light greenish-cream coloured suspension so formed was filtered off, the residue was washed with ethanol (~10mL) and redissolved in benzene (~25mL) and ethanol (~10mL) was added. This mixture was then kept aside for four weeks during which time light cream crystals were formed, filtered off and washed with enthanol (~10mL), hexane (~10mL) and, finally dried under reduced pressure.

Yield : 40%

2.3.2. Reactions of Ni(II),dppm,$NaBH_4$ or $NaBH_3CN$ and CO.

This system has been studied under a range of reaction conditions and several interesting products have been isolated. The reactivities of some of these products has been investigated. Details of these reactions are described below.

2.3.2.1. μ-Carbonyl-μ-bis[bis(diphenylphosphino)methane] bis{monocarbonylnickel(0)}.

$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$.

(a) From $NaBH_4$:

$NiCl_2.6H_2O$ (0.50g; 2.10mmol) and dppm (1.62g; 4.21mmol) were mixed in ethanol/toluene (1:1; 55 mL) under a slow stream of CO gas. Then a suspension of $NaBH_4$ (0.24g; 6.32mmol) in ethanol (15mL) was added dropwise to the stirred mixture over a period of 10 minutes while CO gas was still passing through the solution. The solution turned first to green then greenish grey , forming some solid suspension. CO gas was bubbled slowly (~2-3 bubbles/sec.) for another two hours during which time the suspension changed to orange. This was filtered off and the filtrate allowed to stand at room temperature for two days during which time orange crystals formed. These were filtered off, washed with ethanol (~ 10 mL) and then ether (~ 10 mL) and dried under reduced pressure.

Yield: 40% M.P. 240°C (decomp.)

Analysis:

Calcd. for $Ni_2(CO)_3(dppm)_2$

C=65.61% H=4.53%

Found: 65.78 4.69

(b) From $NaBH_3CN$:

A mixture of $NiCl_2.6H_2O$ (0.50g; 2.10 mmol.) and dppm (2.83g; 7.36mmol.) in ethanol/benzene (1:1; 60mL) was stirred and saturated with a slow stream of CO gas over 25 minutes. An ethanolic solution (15mL) of $NaBH_3CN$ (0.49g; 7.77mmol.) was then added to this solution over a period of 15 minutes while CO gas was still passing through it slowly. The mixture was stirred for a further 3 hours under a slow stream of CO gas (~2-3 bubbles/sec.), during which time the solution turned to

green, then grey until finally a white precipitate formed. This was filtered off, washed with hexane (~10mL) and ether (~10mL). The solid was redissolved in benzene (~20mL) and hexane (~10mL) added. Crystallization occurred over ~12 hours at room temperature. The orange crystals were filtered off, washed with ethanol (~10mL) and dried under reduced pressure.
Yield : 37%

2.3.2.1.0. Reactions of $Ni(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$:

A number of rections were carried out to study the reactivity of the metal-metal bonded $Ni(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$ complex. The details of these reactions are summarized here:

2.3.2.1.1. μ-sulfurylbis-μ[bis(diphenylphosphino)methane] bis{monocarbonylnickel(O)}

$Ni_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$

Dry sulfur dioxide was passed for ~5-7 seconds into a stirred orange solution containing $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ (0.20g; 0.22mmol) in dichloromethane (20mL). The solution immediately turned dark brown. A layer of ethanol (~8mL) was carefully added and the solution was left for five days at room temperature. The dark brown needles so formed were filtered off, washed with ethanol (~10mL) and hexane (~10mL), then dried under reduced pressure.

yield: 13% M.P. 230°C

Analysis:

Calcd. for $Ni_2(CO)_2(SO_2)(dppm)_2 \cdot 0.33CH_2Cl_2$.

C = 60.07% H = 4.25%

Found: 60.01 % 4.48 %

2.3.2.1.2. Bis(nitroso)-μ-bis[bis(diphenylphosphino)methane]-bis{monocarbonylnickel(0)} chloride.

$[Ni_2(CO)_2(NO)_2(\mu\text{-dppm})_2][Cl_2]$

Into a stirred orange solution of $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ (0.20g; 0.20mmol) in dichloromethane (20mL) nitric oxide gas was passed for ~8-10 seconds, resulting immediately in a dark brown colour. To this dark brown solution, a layer of ethanol (~8mL) was added carefully and the mixture was left for one week at room temperature. A dark brown microcrystalline product formed and was filtered off washed with ethanol (~8ml), and hexane (~10mL), and dried under reduced pressure.

Analysis: M.P. 278°C

Calcd. for $[Ni_2(CO)_2(NO)_2(dppm)_2][Cl]_2$

	C= 58.19%	H= 4.10%	N= 2.61%
Found:	58.69	4.52	2.73

2.3.2.1.3. μ-Carbonyl-μ-bis[bis(diphenylphosphino)methane]bis{bromonickel(I)}.

$Ni_2(\mu\text{-}CO)Br_2(\mu\text{-}dppm)_2$

$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ (0.19g; 0.19 mmol) was dissolved in dichloromethane (10mL) and stirred for about 10 minutes. To this orange solution aqueous hydrobromic acid (20 drops; 48%) was added slowly. CO gas was evolved and the resulting green solution was stirred for a further five minutes. The aqueous layer was then removed, and a layer of ethanol (~5mL) was carefully added to the remaining solution which was then left for four days at room temperature. The deep green crystalline product so formed was filtered off, washed with ethanol (~10mL) and hexane (10mL) and then dried under reduced pressure.

yield: 11% M.P. 228°C

Analysis:

Calcd. for $Ni_2(CO)Br_2(dppm)_2.0.66CH_2Cl_2$

	C = 55.11%	H = 4.20%
Found:	55.05	4.25

2.3.2.1.4. μ-carbonyl-μ-bis[bis(diphenylphosphino)methane]bis{iodonickel(I)}

$Ni_2(\mu\text{-}CO)I_2(\mu\text{-}dppm)_2$

An orange solution containing $Ni_2(CO)_3(dppm)_2$ (0.46g; 0.47mmol) in dichloromethane (~20mL) was stirred for about 10 minutes. Iodine (0.12g; 0.473mmol), dissolved also in dichloromethane (~8mL), was added dropwise to this solution over ~6-8 minutes, resulting in the formation of a maroon coloured solution and the evolution of CO gas. The resulting solution was stirred for a further five minutes. A layer of ethanol or hexane (~8-10 mL) was then carefully added and the solution was left at room temperature for four days. The maroon microcrystalline product so formed was filtered off, washed with ethanol (~5mL) and hexane (~5mL) and then dried under reduced pressure .

Yield: 13% M.P. 228°C

Analysis:

Calcd: for $Ni_2(CO)I_2(dppm)_2.0.25CH_2Cl_2$.		
	C = 51.74%	H = 3.74%
Found:	51.93	3.88

2.3.2.1.5. bis-μ-[bis(diphenylphosphino)methane]bis{iodo

nickel(I)}.

$Ni_2I_2(\mu\text{-dppm})_2$

To a stirred solution of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$ (0.062g; 0.064mmol) in dichloromethane (~20mL) was added iodine crystals (0.008g; 0.032mmol). The resulting green solution was stirred for a further 10 minutes while CO gas was evolved. Ether was then allowed to diffuse slowly into the solution over a period of four days at room temperature. The greenish-gray powder which formed was filtered off, washed with ethanol (~10mL) and dried under reduced pressure.

Yield: 9% M.P. 230°C

Analysis:

Calcd. for $Ni_2I_2(dppm)_2\cdot 1.5CH_2Cl_2$

	C	H
Calcd.	C=48.79%	H=3.71%
Found:	48.76	3.76

2.3.2.1.6. Bis-μ-[bis(diphenylphosphino)methane]bis{dicarbonylnickel(0)}

$Ni_2(CO)_4(\mu\text{-dppm})_2$

This complex could not be isolated due to its instability at room temperature in the solid state. However, it was characterized on the basis of i.r. and ^{31}P n.m.r. data (see discussion). The complex was prepared when carbon monoxide was passed through a dichloromethane solution (20mL) of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ (0.32g; 0.33mmol) over a period of ~5-7 minutes. The original orange solution turned pale yellow in colour, forming the required complex. This can be stablized in solution in the presence of an excess of CO or if the reaction vessel is placed on an ice bath. All attempts to isolate this complex by adding hexane or by evaporating the solvent under reduced pressure were, however, unsuccessful and only the starting $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ complex was obtained.

2.3.2.1.7. Reactions of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ with HCl:

To a stirred orange solution containing $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ (0.371g; 0.383mmol) in dichloromethane (~25mL) was added dropwise aqueous HCl (30 drops; 37%). CO gas was evolved and the orange solution turned green. This was stirred for a further 5 minutes and the aqueous layer was then removed. A layer of ethanol (~8mL) was then carefully added to this green solution which was then left over a week at room temperature. The bright green crystalline compound which formed, was filtered off, washed with ethanol (~10mL) and dried under reduced pressure.

Analysis:

Found: C=62.48% H=4.74%

2.3.2.1.8. Reactions of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ with S_8:

$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ (0.22g; 0.23mmol) was dissolved in dichloromethane (25mL) and stirred for about 10 minutes under N_2. To this orange solution was added a suspension of S_8 (0.06g; 0.23mmoL) in dichloromethane (7mL) dropwise over a period of 5 minutes. The resulting mixture turned black. This was stirred for a further 5 minutes. The black suspenssion was filtered off and a layer of ethanol (~10mL) was added carefully to the filtrate which was then left aside for two weeks. The black crystalline product so formed was filtered off and washed with hexane (~10mL) and dried under reduced pressure.

Analysis: M.P. 400°C (decomp.)

Found: C=33.15% H=2.65% S=25%

2.3.2.1.9. Reactions of $Ni(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ with other metals.

Few exploratory reactions of $Ni(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ with $Pt(COD)Cl_2$, $HgCl_2$, $ZnCl_2$ and $CdCl_2$

were carried out. No solid product could be isolated in these reactions. All these reactions were carried out under identical conditions, therefore, only details of one reaction [i.e. Pt(COD)Cl_2] will be given. Thus, to a stirring dichloromethane solution (25mL) of $Ni_2(\mu$-CO)$(CO)_2(\mu$-dppm$)_2$ (0.16g; 0.16mmol) was added Pt(COD)Cl_2 (0.06g; 0.16mmol) in dichloromethane (10mL). The orange solution immediately turned dark purple, this was stirred for a further 10 miutes and a layer of ethanol (10mL) was then added over a period of one week. The solvent was then removed under reduced pressure and the mixture was redissolved in dichlorometane (20mL) and hexane was slowly diffused over one week, no solid could be obtained.

2.3.2.2. Dicarbonyl-bis-η^1[bis(diphenylphosphino)methane] nickel(0)

$Ni(CO)_2(\eta^1$-dppm$)_2$

A solution of $NiCl_2.6H_2O$ (0.5g; 2.10 mmol) in ethanol (35mL) and dppm (2.82g; 7.26mmol) in benzene (25mL) were mixed together, stirred and saturated with a slow stream of CO gas for 25 minutes. To this dark brown suspension, an ethanolic solution (10mL) of $NaBH_3CN$ (0.5g; 7.94mmol) was added dropwise over a period of 10 minutes while CO gas was still passing at a slow rate. This was stirred under a constant flow of CO gas for a further 1.5 hours, during which time the initial dark brown colour changed to purple, then blue, then red and finally a cream coloured precipitate formed. This was filtered off. A layer of hexane (~15mL) was added carefully to the filtrate which was then allowed to stand at room temperature over 12-hours. The colourless crystals which formed were filtered off, washed with hexane (~20mL) and dried under reduced pressure.

Yield: 39% M.P.=150°C

Analysis:

Calcd. for $Ni(CO)_2(dppm)_2$

C = 70.69% H = 4.99%

Found : C = 70.59 H = 5.22.

2.3.2.2.0. Reactions of $Ni(CO)_2(\eta^1\text{-dppm})_2$:

Several reactions of $Ni(CO)_2(\eta^1\text{-dppm})_2$ were performed to make hetro- and homobimetallic complexes. The details of these reactions are given here:

2.3.2.2.1. μ-Carbonyl-μ-bis[bis(diphenylphosphino)methane]-chloronickel(0)chloroplatinum(II).

$NiPt(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$

Solid $Ni(CO)_2(\eta^1\text{-dppm})_2$ (0.10g; 0.12 mmol) was added to a solution of $Pt(COD)Cl_2$ (0.44g; 0.12 mmol) in dichloromethane (15mL). The Ni complex readily dissolved and the resulting solution immediately turned dark purple. A layer of ethanol (~6-8mL) was carefully added and the solution was left for four days at room temperature. The dark purple coloured crystals which formed were filtered off washed with ethanol (~10mL) and ether (~10mL) and then dried under reduced pressure.

Yield: 25% M.P. 205°C

Analysis:

Calcd. for $NiPt(CO)Cl_2(dppm)_2.0.33CH_2Cl_2$

	C	H
Calcd.	53.61%	3.88%
Found:	53.72	4.16

2.3.2.2.2. μ-Carbonyl-μ-bis[bis(dipheylphosphino)methane] chloronickel(0)chloropalladium(II). $NiPd(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$.

A suspension of $PdCl_2$ (0.04g; 0.2mmol) in acetone (~10mL) and water (~2mL) was added to solid $Ni(CO)_2(\eta^1\text{-dppm})_2$ (0.17g; 0.2mmol). Benzene (~10mL) was added to the resulting mixture which was then shaken manually for about ~20 minutes forming a dark greenish-purple suspension. This was filtered off and a layer of hexane (~8mL) was carefully added to the filtrate which was allowed to stand at room temperature over a period of two weeks. The intensely green crystals so formed were filtered off, washed with hexane (~10mL) and dried under reduced pressure.

Yield : 19%

Analysis:

	Calcd. for $NiPd(CO)Cl_2(dppm)_2.H_2O$	
	C=58.28%	H=4.38%
Found:	58.01%	4.49%

2.3.2.2.3. μ-carbonyl-μ-bis[bis(diphenylphosphino)methane]chloronickel(0)chloronickel(II) $Ni_2(\mu-CO)Cl_2(\mu-dppm)_2$

$NiCl_2.6H_2O$ (0.07g, 0.31mmol) was dissolved in ethanol (10mL) and added to solid $Ni(CO)_2(\eta^1-dppm)_2$ (0.27g, 0.31mmol). To this suspension, benzene (6mL) added and the resulting mixture shaken manually for about 10 minutes forming a dark green solution. A layer of hexane (~8mL) was added to this solution which was then left aside for two days, during which time dark green microcrystals were formed. These were filtered off, washed with hexane (~10mL) and dried under reduced pressure.

Yield : 35% M.P. 210°C.

Analysis:

Calcd. for $Ni_2(CO)Cl_2(dppm)_2$

C=62.16% H=4.47%

Found: 61.93 4.65

2.3.2.2.4. μ-Carbonyl-μ-chloro-bis-μ-[bis(diphenylphosphino)methane]carbonylnickel(0)carbonylrhodium(I) $NiRh(\mu\text{-}CO)(CO)_2(\mu\text{-}Cl)(dppm)_2$

To a stirred ice cold toluene (15mL) solution of $Ni(CO)_2(\eta^1\text{-}dppm)_2$ (0.17g; 0.19mmol) under N_2 gas was added quickly, a dichloromethane (~7mL) solution of $Rh_2(CO)_4Cl_2$ (0.04g, 0.09mmol) forming an orange red solution. Carbon monoxide gas was passed through this solution for ~2-3 minutes forming yellow microcrystals. These were filtered off, washed with hexane (~15mL) and dried under reduced pressure.

Yield: 11% M.P. 220°C.

Analysis:

Calcd. for $NiRh(CO)_3Cl(dppm)_2.1.25CH_2Cl_2$

C=56.5% H=4.0%

Found: 56.3 4.0

2.3.2.2.5. Bis-μ-[bis(diphenylphosphino)methane]-bis{dicarbonylnickel(0)}

$Ni_2(CO)_4(\mu\text{-dppm})_2$.

This apparently different isomer of the complex described earlier, was also characterized in solution by ^{31}P n.m.r. spectroscopy. The complex was prepared when $Ni(CO)_4$ is passed through an ice cold toulene solution (20mL) containing $Ni(CO)_2(\eta^1\text{-dppm})_2$ (0.28g; 0.32mmol) forming a light-yellow solution. Attempts to isolate the complex by removing solvent under reduced pressure resulted in the formation of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$.

2.3.2.3. Unidentified Complex:

$NiCl_2.6H_2O$ (0.55g; 2.31mmol) in ethanol (40mL) and dppm (2.04g; 5.31mmol) in toluene (15mL) were mixed and stirred under N_2 for about 10 minutes. An ethanolic suspension (10mL) of $NaBH_4$ (0.21g; 5.53mmol) was added quickly over a period of 2-3 minutes to the stirred mixture, forming a deep green solution. This was filtered off and CO gas was passed through the filtrate for about 10 minutes resulting in the formation of a purple coloured solution which ^{31}P n.m.r. shows to contain a mixture of complexes with at least one species containing a phoshido ligand as a major product (see discussion section). The solvent was removed under reduced pressure after two days and the residue redissolved in benzene (20mL) and hexane allowed to diffuse in slowly. This did not result in the isolation of this complex.

2.3.3. Reactions of Ni(II),dppe,$NaBH_4$ or $NaBH_3CN$ and CO:

Several interesting products have been produced under a variety of reaction conditions from this system. Details of these reactions are summarized below.

2.3.3.1. {μ-Bis(diphenylphosphino)ethane}-bis[carbonyl-η^2-{bis(diphenylphosphino)ethane}nickel(0)].

$Ni_2(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$.

(a). From $NaBH_4$:

$NiCl_2.6H_2O$ (0.5g; 2.1mmol) in ethanol (25mL) and dppe (1.67g; 4.2mmol) in toluene (30mL) were mixed together and sirred under a slow stream of CO gas for about 40 minutes. $NaBH_4$ (0.16g; 4.2mmol) in ethanol (15mL) was added dropwise over a period of 15 minutes to this dark brown mixture. The resulting mixture was stirred for a further 2 hours while CO gas was still passing at a slow rate (~2-3 bubbles/sec.). The yellow suspension so formed was filtered off, and the solid residue was redissolved in dichloromethane (20mL), ethanol (10mL) added and this was kept aside for a period of two days during which time yellow crystals formed. These were filtered off, washed with hexane (10mL) and dried under reduced pressure.

Yield: 13%

(b). From $NaBH_3CN$:

A stirred mixture of $NiCl_2.6H_2O$ (0.500g; 2.10mmol) in ethanol (35mL) and dppe (1.62g; 4.06mmol) in benzene (35mL) was saturated with a slow stream of CO gas for 1 hour. To this dark brown solution was added dropwise an ethanolic solution (15mL) of $NaBH_3CN$ (0.33g; 5.25mmol) over a period of 15 minutes. The resulting suspension was stirred for a further two hours while CO gas was bubbled at a constant rate of ~2-3 bubbles/sec, during which time it turned first to red then to orange and, finally, a bright yellow precipitate formed. This was filtered off, washed with ethanol (~10mL) and hexane (~15mL) then redissolved in dichloromethane (30mL) and allowed to stand for two days at room temperature. The bright yellow hexagonal crystals which formed were filtered off, washed with hexane (~10mL) and dried under reduced pressure.

Yield: 15% M.P.= 210^{o}C (decomp.)

Analysis:

Calcd. for $Ni_2(CO)_2(dppe)_3$

	C= 70.21%	H= 5.26%	Ni= 8.58%	P= 13.59%
Found	70.10	5.35	7.93	14.63

2.3.3.2. Carbonyl{η^2-bis(diphenylphosphino)ethane}{η^1-bis(diphenylphosphino)ethane}nickel(0)

$Ni(CO)(\eta^2\text{-dppe})(\eta^1\text{-dppe})$

$NiCl_2.6H_2O$ (0.50g; 2.10mmol) in ethanol (45mL) and dppe (2.51g; 6.30mmol) in benzene (25mL) were mixed and sirred under a slow stream of CO gas, passing at a rate of ~2-3 bubbles/sec., for about an hour. $NaBH_3CN$ (0.35g; 5.48mmol) in ethanol (10mL) was added dropwise over a period of 10 minutes to this dark brown solution. The resulting yellow precipitate was filtered off and the filtrate concentrated by vacuum evaporation to ~5mL. The resulting orange coloured substance was filtered off, washed with hexane (~5mL), then with ether (~5mL), and dried under reduced pressure forming a cake.

Yield: 89% M.P.= 98-99°C

Analysis:

Calcd. for $Ni(CO)(dppe)_2$

C= 72.05% H = 5.44%

Found 72.09 5.70

2.3.3.2.0. Reactions of $Ni(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})$:

Several reactions of $Ni(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ were carried out to make bimetallic systems. Details of these reactions are summarized below:

2.3.3.2.1. Bis-μ-[bis(diphenylphosphino)ethane]-bis{dicarbonylnickel(0)}

$Ni_2(CO)_4(\mu\text{-dppe})_2$

This complex could not be isolated in a pure form, and has been tentatively formulated largely on the basis of ^{31}P n.m.r. spectroscopy. The complex was obtained from two different reactions, as described below.

(a) From $Ni(CO)_4$:

To an stirred dichloromethane solution (25mL) containing $Ni(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ (0.31g;

0.35mmol), $Ni(CO)_4$ was bubbled for a period of 10 minutes forming an orange-yellow solution. Attempts to isolate this complex by adding ethanol or hexane were unsuccessful. When the solvent was removed under reduced pressure an orange solid was obtained which decomposed on recrystallization.

(b) From $Mo(CO)_6$:

$Mo(CO)_6$ (0.08g, 0.30mmol) in THF (40mL) was stirred and irradiated under a constant flow of N_2 gas. To this light yellow solution was added solid $Ni(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ (0.26g; 0.29mmol) and the resulting solution was stirred and irradiated by UV light for a further 5 minutes forming an orange solution. Again all attempts to isolate this complex by adding ethanol or hexane were unsuccessful.

2.3.3.2.2. Reactions with $Pt(COD)Cl_2$:

$Ni(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ (0.15g; 0.17mmol) was dissolved in C_6H_6 (15mL) and stirred for about 10 minutes. To this orange solution was added dropwise $Pt(COD)Cl_2$ (0.06g; 0.16mmol) in dichloromethane (10mL) and the resulting orange-purple solution was stirred for a further 10 minutes. This was then filtered and hexane was slowly diffused to the filtrate over a period of four days. The solvent was then removed under reduced pressure and the resulting mixture was redissolved in dichloromethane and a layer of ethanol was added. This was then left aside for a period of one week. No solid product could be isolated.

2.3.3.2.3. Reactions with Fe(CO)$_5$:

To a stirred solution of Ni(CO)(η^1-dppe)(η^2-dppe) (0.22g; 0.25mmol) in C_6H_6 (25mL) was added Fe(CO)$_5$ (8mL) and the resulting orange-red solution was stirred for a further 10 minutes. This was then refluxed for 15 minutes and was filtered. All attempts to isolate any solid product from the reaction filtrate by slow diffusion of ether over a period of one week were unsuccessful. When the solvent was removed under reduced pressure, decomposition occurred.

2.3.3.3. Bis(cyano)-[η^2-bis(diphenylphosphino)ethane]carbonylnickel(II).

Ni(CO)(CN)$_2$(dppe)

$NiCl_2.6H_2O$ (0.5g, 2.1mmol) and dppe

(1.67g, 4.21mmol) were mixed and stirred in toluene/ ethanol (1:1, 60mL) under a slow stream of CO gas for about 40 minutes. An ethanolic solution of $NaBH_3CN$ (0.27g, 4.2mmol) in ethanol (15mL) was added dropwise over a period of 15 minutes to the dark brown solution, while CO gas was still passing at a slow rate (2-3 bubbles/sec.) through the solution. CO gas was passed for another hour. The resulting yellow precipitate was filtered off. After one week of room temperature standing the filtrate was concentrated by passing a stream of nitrogen gas, forming a small amount of orange solid which was also filtered off. The remaining solution was concentrated to a minimum volume by nitrogen gas, forming red microcrystals which were filtered off, washed with hexane and dried under reduced pressure.

Yield: 7%

Analysis:

	C	H	N
Calcd. for $Ni(CO)(CN)_2(dppe).0.25EtOH$	C=64.6%	H=4.7%	N=5.1%
Found:	64.8	5.6	5.0

2.3.3.4. Bis(cyano)[η^2-bis(diphenylphosphino)ethane]nickel(II)

$Ni(CN)_2(dppe)$

To an ethanolic solution (30mL) containing $NiCl_2.6H_2O$ (0.5g, 2.1mmol) was added dppe (2.51g; 6.3mmol) in benzene (30mL) and the resulting dark brown mixture was stirred under a slow stream of CO gas for about 40 minutes. An ethanolic solution (20mL) of $NaBH_3CN$ (0.66g; 10.48mmol) in two equal portions was added dropwise to this mixture over a period of 20minutes (10 minutes each). Immediately after the addition of the first portion, the reaction vessel was transferred to an ice bath. CO gas was bubbled (at a rate of 2-3 bubbles/sec.) for a further 4.5 hours. The red-brown suspension so formed was filtered off, washed with ethanol (~10mL) and redissolved in CH_2Cl_2(~30mL). A layer of ethanol (~15mL) was carefully added to this solution which was then allowed to stand at room temperature over a period of two days. Some more yellow crystals formed which were filtered off and the filtrate was allowed to stand three weeks at room temperature during which time well shaped red crystals were formed. These were filtered off and washed with ethanol (~10mL) and hexane (~10ml) and then dried under reduced pressure.

Yield: 9% M.P. 250°C (decomp.)

Analysis:

Calcd. for $Ni(CN)_2(dppe).EtOH$

C=64.90% H=5.41% N=5.05%

Found: 64.72 5.51 4.54

2.3.3.5. Dicarbonyl-η^2-[bis(diphenylphosphino)ethane]nickel(O).

$Ni(CO)_2(\eta^2\text{-dppe})$

This complex has not been isolated, but was characterized in solution by ^{31}P n.m.r.spectroscopy. The complex can be prepared either from $Ni(CO)_2(PPh_3)_2$ or from $Ni(CO)_2(\eta^1\text{-dppm})_2$ as described below.

(a) From $Ni(CO)_2(PPh_3)_2$:

To a stirred solution of benzene (25mL) containing $Ni(CO)_2(PPh_3)_2$ (0.42g; 0.66mmol) was added dppe (0.26g; 0.66mmol) in benzene (10mL) and the resulting solution was stirred for about 10 minutes forming a pale yellow solution. All attempts to isolate this complex by adding a layer of ethanol or hexane were unfortunately fruitless and only very small amount of a mixture was obtained which could not be further purified even after repeated crystallization.

(b) From $Ni(CO)_2(\eta^1\text{-dppm})_2$:

dppe (0.11g; 0.26mmol) was dissolved

completely in benzene (15mL). This was then added to solid $Ni(CO)_2(\eta^1\text{-dppm})_2$ (0.23g; 0.26mmol) and the resulting solution was shaken manually for about 10 minutes forming a pale yellow solution. Again all attempts to isolate a pure complex by adding hexane or ethanol were unsuccessful.

2.3.4. Reactions of Ni(II),dppp,$NaBH_4$ or $NaBH_3CN$ and CO:

Although this system has not been as thoroughly investigated as the corresponding dppm and dppe systems, several exploratory reactions were carried out, and some interesting Ni(0) complexes have been obtained. Details of these reactions and the methods of isolation of these complexes are described below.

2.3.4.1. μ-{Bis(1,3-diphenylphosphino)propane}-bis[carbonyl-η^2-{bis(1,3-diphenylphosphino)propane}nickel(0)]

$Ni_2(CO)_2(\mu\text{-dppp})(\eta^2\text{-dppp})_2$

A stirred mixture of $NiCl_2.6H_2O$ (0.50g; 2.10mmol) in ethanol (50mL) and dppp (1.73g; 4.21 mmol) in toluene (10mL) was saturated with CO gas for 2 hours. After 5 minutes, the dark brown solution changed to wine red and a solid started to form. A suspension of

$NaBH_4$ (0.16g; 4.21mmol) in ethanol (15mL) was added dropwise over a period of 20 minutes while a slow stream of CO gas was still passing through the suspension. The colour of this suspension changed to lighter brown and then yellowish brown. CO gas was passed for a further 15 minutes. The resulting yellow precipitate was filtered off, washed with ethanol (~10mL) and redissolved in benzene (~35mL). Ethanol (~35mL) was added and the mixture was allowed to stand at room temperature for 12 hours. The yellow microcrystalline product was filtered off, washed with ethanol (~10mL) and diethyl ether (~15mL) and dried under reduced pressure.

Yield: 17% M.P.= 126°C

Analysis:

Calcd. for $Ni_2(CO)_2(dppp)_3.2EtOH$

	C	H
Calcd.	C= 69.63%	H= 5.87%
Found:	69.65	5.94

2.3.4.2. Dicarbonyl[bis(1,3-diphenylphosphino)propane]nickel(0)

$Ni(CO)_2(\eta^2\text{-}dppp)$

A mixture of $NiCl_2.6H_2O$ (0.50g; 2.10mmol) in ethanol (25mL) and dppp (1.73g; 4.20mmol) in benzene (35mL) was saturated with a slow stream of CO gas and stirred for 1.5 hours. After five minutes the dark brown solution turned to wine red and a solid started to form. An ethanolic solution (15mL) of $NaBH_3CN$ (0.13g; 2.1mmol) was then added and the CO gas was allowed to bubble at a rate of ~2-3 bubbles/second for a further 1.5 hour while the suspension was stirred. During this time it turned into a wine red solution. This was left at room temperature for 10-days. It was then concentrated by vacuum evaporation to ~10mL and allowed to stand at room temperature over 12 hour. The pink microcrystalline product so formed was filtered off washed with ethanol (~10mL) and dried under reduced pressure.

Yield: 18% M.P. 149°C

Analysis:

	C	H
Calcd. for $Ni(CO)_2(dppp)$	C = 66.1%	H = 4.94%
Found	66.08	4.79

2.3.5. Reactions of Ni(II),dppb,$NaBH_4$ or $NaBH_3CN$ and CO:

This system was briefly explored, and the interesting results obtained are summarized here.

2.3.5.1. Bis-η^2-[bis(1,4-diphenylphosphino)butane]nickel(O).

$Ni(dppb)_2$

To a stirred mixture of $NiCl_2.6H_2O$ (0.5g; 2.1mmol) and dppb (1.79g; 4.2mmol) in toluene/ ethanol (2:1, 60mL) under a slow stream of CO gas was added dropwise and ethanolic (15mL) suspension of $NaBH_4$ (1.12g, 29.5 mmol) over a period of 40 minutes. CO gas was slowly passed through the resulting suspension for an additional two hours during which time several colour changes took place until, finally, an orange-red suspension was formed. This was filtered off and ethanol (~20mL) was added to the filtrate, which was then allowed to stand at room temperature for a period of four days. The bright red crystals so formed were filtered off, washed with ethanol (~5mL) and hexane (~10mL) and dried under reduced pressure.

Yield: 14% M.P. 175°C (decomp.)

Analysis:

Calcd. for $Ni(dppb)_2.0.5EtOH$

	C	H
Calcd.	C=73.29%	H=6.32%
Found:	73.31	6.28

2.3.5.2. Dicarbonyl-η^2-[bis(1,4-diphenylphosphino)butane] nickel(0)

$Ni(CO)_2(\eta^2\text{-dppb})$.

$NiCl_2.6H_2O$ (0.5g; 2.1mmol) and dppb (1.79g; 4.2mmol) were mixed together and stirred in benzene/ethanol (2:1; 60mL) for about one hour under a slow stream of carbon monoxide gas. An ethanolic solution (15mL) of $NaBH_3CN$ (0.26g; 4.2 mmol) was added dropwise to this mixture over a period of 20 minutes, while CO gas was still passing at a rate 2-3 bubbles/sec. Carbon monoxide gas was passed for an additional two hours during which time the colour of the suspension changed from redish-brown to yellowish-brown to darker brown and finally, a yellowish-brown suspension was formed. This was filtered off and ethanol (20mL) was added to the filtrate. This was allowed to stand at room temperature for four weeks. The pale yellow microcrystalline product so formed was filtered off, washed with ethanol (~15mL) and dried under reduced pressure.

Yield: 17% M.P. 190°C.

Analysis:

Calcd. for $Ni(CO)_2(dppb).75C_6H_6$

	C	H
Calcd.	C=69.09%	H=5.42%
Found:	69.06	5.33

2.3.6. Reactions of Ni(II),dpppe,$NaBH_4$ and CO:

Only a few reactions of an exploratory

nature were carried out on this system, and only one complex was isolated which is tentatively identified as follows.

2.3.6.1. Chloro-bis-η^2[bis(1,5-diphenylphosphino)pentane] nickel(I)

$NiCl(\eta^2\text{-dpppe})_2$

Carbon monoxide gas was passed slowly through a stirred mixture of $NiCl_2.6H_2O$ (0.5g; 2.1mmol) and dpppe (1.91g; 4.3mmol) in toluene/ethanol (1:1; 50 mL) for about 35 minutes. A suspension of $NaBH_4$ (0.16g; 4.21mmol) in ethanol (15mL) was added dropwise over a period of 15 minutes to this mixture, while CO gas was still passing at a slow rate (~2-3 bubles/sec.). The CO was passed for a further 4 hours. The resulting greenish-gray suspension was filtered off, washed with ethanol (~10mL) and redissolved in DMF (25mL). Ether (100mL) was added and pink microcrystals formed over a period of 4 months in a freezer. These were filtered off, washed with ether (~20mL) and dried under reduced presure.

Yield: 15% M.P. 144°C.

Analysis:

Cald. for $NiCl(dpppe)_2.1.75DMF$

C=65.9% H=6.27%

Found: 65.71 6.08

2.3.7. Reactions of Ni(II),cis-dppe,$NaBH_3CN$ and CO:

Again this system has been explored only very briefly explored and only one comlex was isolated. The formulation of this complex is tentative.

2.3.7.1. Bis-η^2-cis-[bis(1,2-diphenylphosphino)ethylene] nickel(0)

Ni(η^2-cis-dppee)$_2$.

A mixture of $NiCl_2.6H_2O$ (0.5g; 2.1mmol) and cis-dppee (1.66g; 4.19mmol) in benzene/ethanol (1:1; 60mL) was stirred and saturated with CO gas for 40 minutes. To this was added an ethanolic solution (15mL) containing $NaBH_3CN$ (0.4g; 6.4mmol) over a period of 10 minutes. The resulting mixture was allowed to stirr for a further 2 hours under a slow stream of carbon monoxide gas (~2-3 bubbles/sec.). The red solution so formed was filtered, hexane (15mL) was added to the filtrate and a red crystalline product formed over a period of 4 days. This was filtered off, washed with ethanol (~5mL) and hexane (~10mL) and dried under reduced pressure.

Yield: 12% M.P. 216°C.

Analysis:

Calcd. for $Ni(dppee)_2$

	C	H
Calcd.	C=73.17%	H=5.39%
Found:	73.47	5.53

3. Results and Discussion:

3.1. Introduction:

From the introductory section it is quite clear that phosphine substituted metal carbonyl complexes present a very interesting area of chemical research. These complexes possess unique structural and chemical properties. It is also equally evident from the previous section that these complexes have been prepared by several routes which may be summarized as follows.

(i). **Direct substitution:** Carbonyl groups in metal-carbonyls can be replaced by phosphines directly either by heating the metal carbonyls with phosphine ligands, or by refluxing in a suitable solvent. The degree of substitution may be controlled by adjusting the metal to ligand ratio.

(ii). **Photolytic methods:** U.V. radiation can also effect the substitution of metal carbonyls, usually in donor solvents in the presence of phosphines.

(iii). **Substituted metal carboyls:** Substituted metal carbonyl derivatives containing weakly bonded ligands such as THF, acetonitrile, olefins, arenes etc. provide one very convenient route for the syntheses of phosphine substituted metal carbonyl complexes.

(iv). Catalytic methods: In some cases, substitution of CO group(s) with tertiary phosphines have been achieved rather conveniently under catalytic conditions, for example by using $NaBH_4$. This method also reduce the voltalization of metal carbonyls.

(v). Electrochemical methods: Electrochemical methods have also been used to replace CO groups with phosphine ligands.

Only first three routes have been used routinely and extensively to prepare these complexes and in most cases the highly toxic binary carbonyls are the main starting materials.

Preliminary results in these laboratories have shown that reactions between metal ions and $NaBH_4$ in the presence of CO lead to the production of metal carbonyls.[510] Also, reactions between metal ions, $NaBH_4$ and phosphines lead to the production of low valent metal phosphine complexes. It was therefore expected that reactions between metal ions and $NaBH_4$ in the presence of both CO and phosphines would lead to phosphine-substituted metal carbonyls. These would presumably form in solutions in which low valent metals are being produced and for which both CO and phosphine can compete for coordination sites.

The investigation to be described in the following pages is, therefore, a detailed study of the behaviour of Ni(II) towards $NaBH_4$ (and $NaBH_3CN$) in the presence of variety of phosphine ligands under CO atmospheres and under a variety of reaction conditions.

The seven phosphines which were initially chosen for the study are PPh_3, dppm, dppe, cis-dppee, dppp, dppb and dpppe. Reactions involving dppm or dppe with $NiCl_2.6H_2O$ in the presence of $NaBH_4$ or $NaBH_3CN$ under CO atmospheres were more thoroughly studied while the reactions with the remaining phosphines were of an exploratory nature. The details of these reactions will now be described.

3.2. Ni(II)/PPh_3/$NaBH_4$ or $NaBH_3CN$/CO:

The ligand PPh_3 is the only monophosphine used in this study, with most of the work involving the less bulky bisphosphine ligands. Usually upon coordination, monophosphines tend to form monomeric complexes, while dimeric complexes are often obtained from bisphosphine ligands. With monophosphines, the degree of substitution largely depends upon the steric bulk of the ligand.

This system, Ni(II) salt, $NaBH_4$ or $NaBH_3CN$, PPh_3 and CO, is the simplest one investigated in this study. One complex has been isolated and fully characterized and n.m.r evidence for the formation of at least two more complexes has been obtained. However, all attempts to isolate these other two complexes were unsuccessful.

In a typical synthesis, $NiCl_2.6H_2O$ is reduced in-situ with $NaBH_4$ in the presence of PPh_3 under a slow stream of CO. The reaction goes smoothly to completion within two hours of $NaBH_4$ addition, and forms a pale, cream coloured solid. This, on recrystallization from benzene and hexane, gives colourless or light cream coloured crystals which chemical analyses have shown to be $Ni(CO)_2(PPh_3)_2$. The same complex is obtained as the major product when $NaBH_3CN$ is used instead of $NaBH_4$.

Furthermore varying the ratio of metal to ligand or increasing the quantity of $NaBH_4$ or $NaBH_3CN$ does not appear to affect the reaction pathway.

This is a well known complex and has been used as a catalyst since the 1940's. Rose and Statham[441] have synthesized it from the reaction of $Ni(CO)_4$ and PPh_3 in ether under refluxing conditions, but were unable to recrystallize the product. The same authors further reported that this complex catalyzes violently the polymerization of phenyl acetylene, unless the compound is diluted with a large volume of alcohol. Even in 10% alcoholic solutions, polymerization is vigorous and exothermic. Moreover this complex also catalyzes the conversion of 1-phenyl propargyl alcohol to 1,3,5-tri(α-hydroxybenzyl)benzene.

This complex has also been prepared by other routes, such as treating $Ni(PPh_3)_4$ with CO gas in benzene or dichloromethane[446], or by treating either $Ni(PPh_3)_2\{SeC(O)NEt_2\}_2$ or $NiCl_2(PPh_3)_2$ with CO gas[437].

The i.r. spectrum is shown in Fig.110, and the frequency values, together with the literature values, are recorded in Table [10]. The spectrum reported

Table (10):

I.r. and n.m.r. data of $Ni(CO)_2(PPh_3)_2$.

Complex	νCO c.m.$^{1-}$	^{31}Pn.m.r. δ	^{1}Hn.m.r. δ (p.p.m.)	ref.
$Ni(CO)_2(PPh_3)_2$	2000(s), 1990(sh), 1942(s), 1915(m)	32.7(a)	7.17, 7.22	a
	1998, 1936			439
	1995, 1940			446
		32.6		466

(a) Our work.

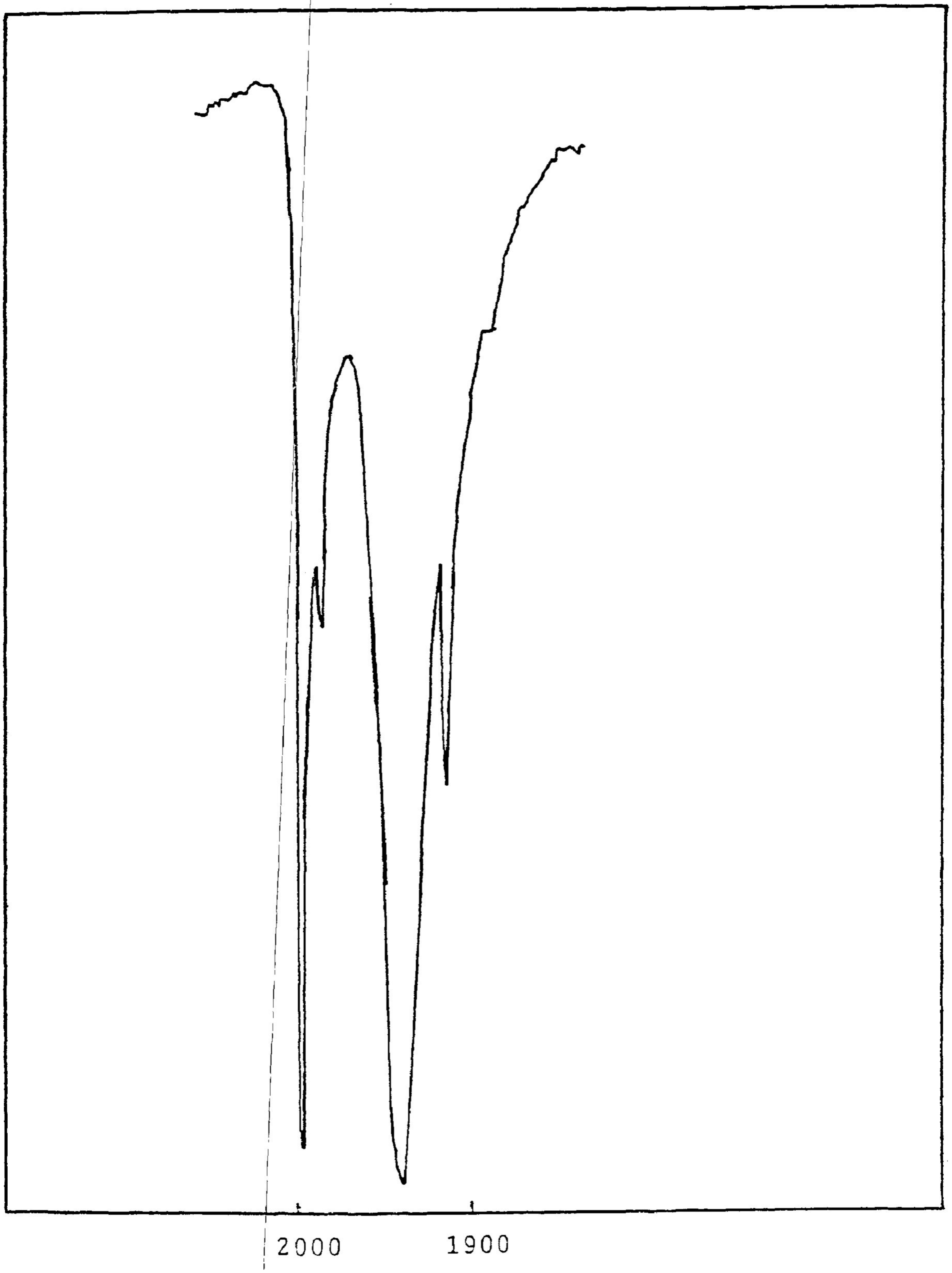


Fig. 110. Selected Features of the Infrared Spectra of $Ni(CO)_2(PPh_3)_2$.

here contains two additional weak νCO bands at 1990 and 1915 cm^{-1}. However, this was recorded in the solid state (Nujol) in which distortions may lower the symmetry from that found in solution. The analogous palladium and platinum derivatives, prepared from $M(PPh_3)_4$ {M=Pd,Pt} and CO at high temperature and pressure, also exhibit two strong νCO bands in their solution i.r. spectra[477] (see Table [10]).

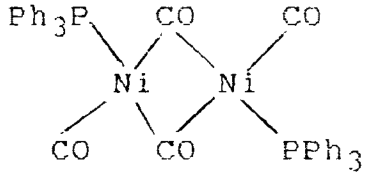
The ^{31}P n.m.r. spectrum of $Ni(CO)_2(PPh_3)_2$ in benzene solution shows a singlet at δ=32.7 ppm which is consistent with the value reported by Meriwether at 32.6 ppm[466]. Thus, the two coordinated PPh_3 groups are in a magnetically equivalent environment. The ^1H n.m.r. spectrum shows resonances due to phenyl protons at δ=7.17 and 7.22 p.p.m. as broad signals.

In benzene solution, a molecular weight determination shows a value of 558 which is close to the value of 638.7 for the monomeric complex.

All this evidence supports the formulation of this complex as a tetrahedral structure as proposed earlier by Chatt and Hart[472], although some distortion from the idealized tetrahedral geometry may have occurred due to the bulky PPh_3 ligands.

The other two complexes which are formed from these reactions were identified only by ^{31}P n.m.r. spectroscopy. Thus, when the reaction filtrate (containing an excess of free phosphine) after $Ni(CO)_2(PPh_3)_2$ has been filtered off, is allowed to stand at -15°C (in a freezer) over a period of two weeks, a new strong singlet appears at δ=30.6 p.p.m. Periodic monitoring of the ^{31}P n.m.r. spectrum shows that this new species appears at the expense of $Ni(CO)_2(PPh_3)_2$ (δ 32.7) and of free phosphine (δ=5.6) which suggests that the new species is most likely to be $Ni(CO)(PPh_3)_3$.

Furthermore, when a benzene solution of $Ni(CO)_2(PPh_3)_2$ with a small amount of free phosphine is allowed to stand at room temperature over a two week period, a new strong singlet occurs in the ^{31}P n.m.r. spectrum at δ=24.6 p.p.m. Again, evidence from the periodic monitoring by ^{31}P n.m.r. shows that this new species appears as the signal due to $Ni(CO)_2(PPh_3)_2$ decreases. At the same time the free phosphine content increases. No solids were isolated from these solutions, but it is possible to speculate that the new species could be $Ni(CO)_3(PPh_3)$, $Ni_2(CO)_2(\mu\text{-}CO)_2(PPh_3)_2$ or $Ni(CO)_2(PPh_3)(C_6H_6)$ which could have been formed according to following equation.

$2Ni(CO)_2(PPh_3)_2 \longrightarrow$  $+2PPh_3$

or

$$Ni(CO)_2(PPh_3)_2 \xrightarrow[C_6H_6\ \text{room temp}]{+PPh_3\ 2\ \text{weeks}} Ni(CO)_2(PPh_3)(C_6H_6)+2PPh_3$$

3.3. Reactions of Ni(II), dppm, $NaBH_4$ or $NaBH_3CN$ and CO.

The reader will recall from the objective that reactions of Ni(II) salts with $NaBH_4$ and $NaBH_3CN$ in the presence of dppm have been investigated in some detail in these laboratories.[502,505] For example Khan has studied the interactions of $NiCl_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$ with $NaBH_3CN$ in the presence of a variety of bidentate phosphine ligands. With dppm, it was reported[505] that at least four major Ni(II) and Ni(I) products, $[Ni(BH_3CN)(dppm)_2][ClO_4]$, $Ni_2(BH_3CN)(CN)(dppm)_2$, $Ni_2(CN)_2(dppm)_3$ and $Ni_2(CN)_2(dppm)_2$ can be obtained by the careful control of reaction conditions.

It will be clear from the following

discussion that the addition of CO into these rections results in the production of profoundly different species. Thus, from the many reactions carried out in this investigation between $NiCl_2.6H_2O$, dppm and $NaBH_4$ or $NaBH_3CN$ under a CO atmosphere, at least three major products are known to be formed. At the present time, only two of these have been isolated and fully characterized. The syntheses of these Ni(0) systems are very sensitive to such factors as the ratio of metal to phosphine, the temperature and whether $NaBH_4$ or $NaBH_3CN$ is used. Furthermore, not only are these complexes very air sensitive in solution, but two of them are also very unstable in solution at room temperature. This made charaterization work quite difficult and extensive work with solutions kept at low temperatures in inert atmospheres was required.

Details of the syntheses and characterizations of the first two complexes, $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$ and $Ni(CO)_2(\eta^1\text{-dppm})_2$ will now be discussed. However the third complex, $Ni_2(CO)_4(\mu\text{-dppm})_2$, will be discussed later with the reaction chemistry of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$ because it can be more conveniently synthesized from the latter.

3.3.1. $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$

This orange complex is produced under a wide range of conditions. It is best made from the reaction of $NiCl_2.6H_2O$, dppm and $NaBH_4$ under a CO atmosphere in a mixed (benzene or toluene and ethanol) solvent system. Details are given in the experimental section. The course of the reaction is dependent upon whether $NaBH_4$ or $NaBH_3CN$ is used, their amounts and also on the Ni:dppm ratio. Thus, a high yield is obtained when the $NiCl_2.6H_2O$:dppm:$NaBH_4$ ratio is 1:2:>5. If the amount of dppm is increased or if $NaBH_3CN$ is used then the product is formed along with varying amounts of a white complex. This (see later) is slowly converted into the orange complex when the mixture is dissolved in dichloromethane.

The orange complex is stable indefinitely in the solid state under an oxygen free atmosphere, but decomposes within ~12 hours when exposed to air. In solution it is even less stable if exposed to air.

Analytical data are in excellent agreement with the formulation $Ni_2(CO)_3(dppm)_2$. This compound is not new and was recently the subject of a brief conference presentation by Stanley et.al.[475] who reported its preparation by fragmentation of $HC(PPh_3)_3$ from the complex $Ni(CO)_2[HC(PPh_3)_3]$. No further details were however given. In addition, its surprising structure, established by X-ray crystallography, is a "cradle" type with both bridging dppm ligands on the same side of the molecule as compared to the expected A-frame type of structure shown by the closely related $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}P\text{-}P)_2$ complexes [where P-P= R_2PYPR_2; R= CF_3,F and Y= NH,NMe,S] prepared from the reaction of $Ni(CO)_4$ with the appropriate phosphine ligands.[467-469] In fact, the complex $Ni_2(\mu\text{-}CO)(CO)_2\ [S\{P(CF_3)_2\}_2]_2$ has been shown by X-ray crystallography to have an A-frame structure.[511] Also, while this thesis was being written, DeLaet et.al.[474] reported that when the cradle $Ni_2(\mu\text{-}CNMe)(CNMe)_2(\mu\text{-}dppm)_2$ complex is treated with carbon dioxide at 1500-2200 psi over 48 hours it results in the formation of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$. The same authors have also prepared this complex by treating $Ni(COD)_2$ with dppm and carbon monoxide gas.

The infrared spectrum is shown in Fig.[111] and the carbonyl frequencies are recorded in Table [11]. Five carbonyl absorptions occur in the νCO region and it is quite clear that the molecule contains both terminal and bridging carbonyl groups. The lowest

Table [11]:

I.r. and n.m.r. data of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}P\text{-}P)_2$, its derivatives and related complexes.

Complex	$\nu(CO)$ c.m.$^{-1}$	^{31}Pn.m.r. δ	^1Hn.m.r. δ(p.p.m.)	ref.
$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2{}^a$	2000(W),1972(s),1955, 1915(W),1790(s)	22.7	2.58,3.40 (m)	x
	1967(sh),1947(s),1784(m)			476
$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}Lf)_2{}^b$	2070(s),2055(s),1891(s)			469
$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}Lm)_2{}^a$	2074.5(vs),2052(vs), 1912.5(s)			468
	2019*,2018*,1868*			
$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}Ls)_2{}^a$	2088(vs),2075(vs),2033*, 1894(vs),1854			468
$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}Ln)_2$	2085(vs),2080(vs), 2065(vs), 2033*,2025*,1870(sh), 1865,1825*			467
$Ni(CO)_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$	1995(m),1982(s),1038(m), 1045(m),1173(w),1195(w)	17	2.6,4.15, 7.0,7.5	x
$Pd_2(\mu\text{-}SO_2)Cl_2(\mu\text{-}dppm)_2$	1028,1041,1157,1165			514
$PtPd(\mu\text{-}SO_2)Cl_2(\mu\text{-}dppm)_2$	1031,1157	27.2,23.8 (c.m)	4.15,2.6	496
$PtPd(\mu\text{-}SO_2)(C_6F_5)_2(\mu\text{-}dppm)_2$	1145(s),1025(s)			515
$Pt_2(\mu\text{-}SO)_2(C\equiv CPh)_2(\mu\text{-}dppm)_2$	1160,1030			516
$Ni_2(CO)_4(\mu\text{-}dppm)_2$	2080(m), 2018(sh), 2004(vs), 1955(s)	17.9		
$Ni_2(\mu\text{-}CO)Br_2(\mu\text{-}dppm)_2$	1775	23.5	1.25 3.7(cm)	
$Ni_2(\mu CO)I_2(\mu\text{-}dppm)_2$	1775	25	1.25,3.0 7.4(br)	
$Ni_2I_2(\mu\text{-}dppm)_2$		25		
$Ni_2(CO)_2(NO)_2(\mu\text{-}dppm)_2$	1985(vs), 1965(sh) 1775(w,br),1558(s)	21.0 24(w)		

a= Nujol, b= Hexane, * Sharp spikes on the edges of the strong bands. V= Very, S= strong, W= Weak; M= Medium, Sh= Shoulder, x= our work, c=complex

m= multiplet lf= $F_2P(CH_3N)PF_2$,

lm= $(CF_3)_2(P(CH_3N)PCF_3)_2$, ls= $(CF_3)_2PSP(CF_3)_2$, ln=$(CF_3)_2P(CF_3)_2P(NH)P(CF_3)_2$.

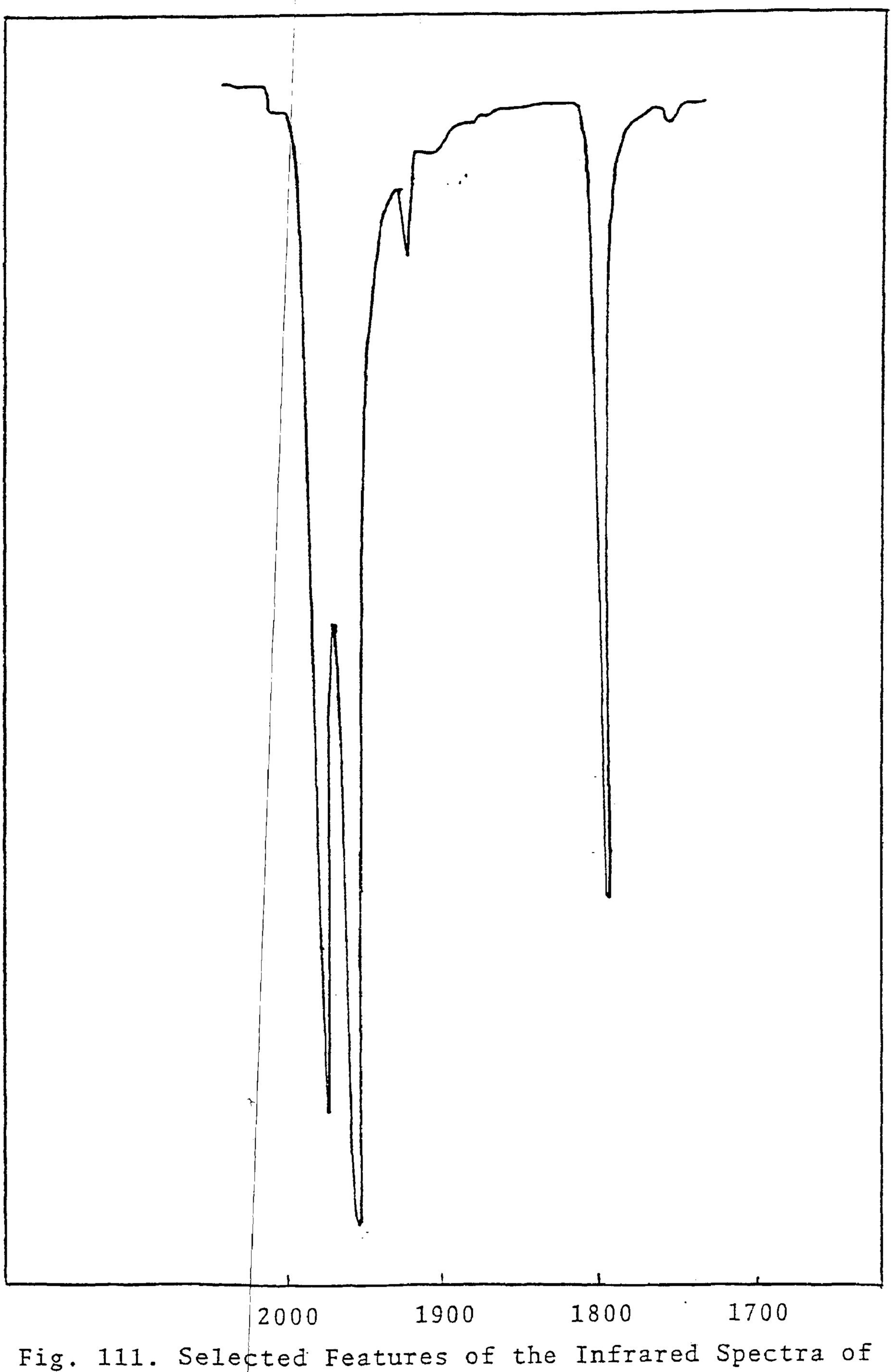


Fig. 111. Selected Features of the Infrared Spectra of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$.

frequecy absorption at 1790 cm^{-1} can be assigned to the bridging carbonyl group. This is 101 cm^{-1} and 104 cm^{-1} lower than the frequencies assigned to the bridging carbonyl groups in the related complexes $Ni_2(\mu\text{-}CO)(CO)_2[\mu\text{-}(F_2P)_2NMe]_2$[467] and $Ni_2(\mu\text{-}CO)(CO)_2[\mu\text{-}\{(CF_3)_2P\}_2]_2$[468] respectively.

As mentioned above, the presence of bridging carbonyl group in the latter has been established by X-ray crystallography.[511] The higher bridging and terminal carbonyl frequencies in the i.r. spectra of these complexes may be attributed to better π- acceptor properties of these bisphosphine ligands as compared to dppm, resulting in less π- electron donation from the metal `d' orbitals to the π^* orbitals of CO.

The two strong higher frequency absorptions at 1972 cm^{-1} and 1955 cm^{-1} in $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ are assigned to carbonyl groups coordinated terminally to each metal atom, while the remaining bands in the terminal carbonyl region at 2000 cm^{-1} and 1915 cm^{-1} probably result from distortions in the solid state structure which may cause a lowering of the symmetry. There are differences between this i.r. spectrum and that reported by Delaet et.al.,[476] as can be seen in Table

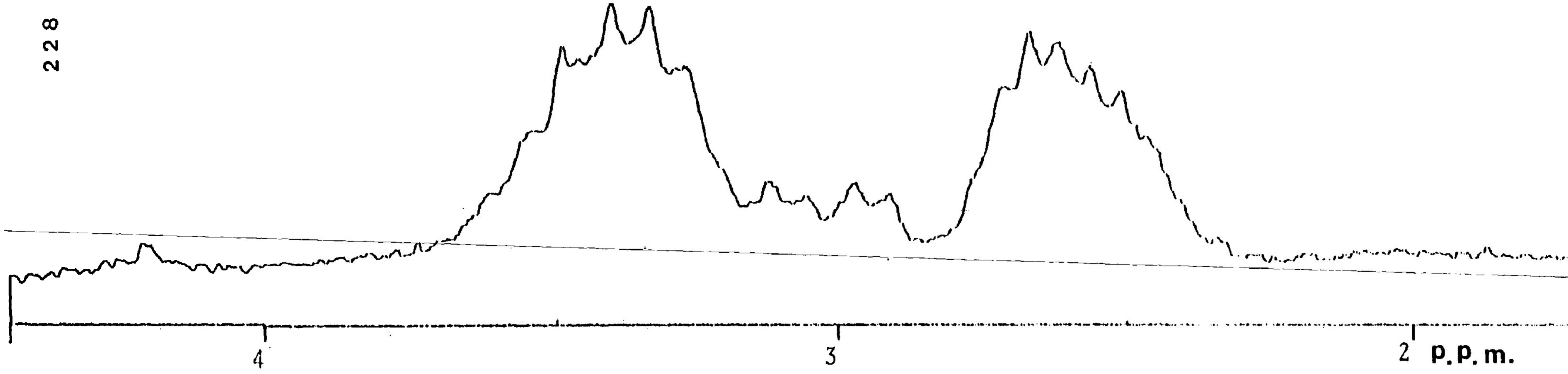


Fig. 112. ^{1}Hn.m.r. Spectrum of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$.

[11], in that only one strong band in the terminal carbonyl region has been reported by these authors, while this study shows at least two strong band occurs in this region, as shown in Fig.111. However, this difference may be attributed to the NaCl cells used in this study while KBr cells were used by Delaet and coworkers, which possibly resulted in pooerer resolution.

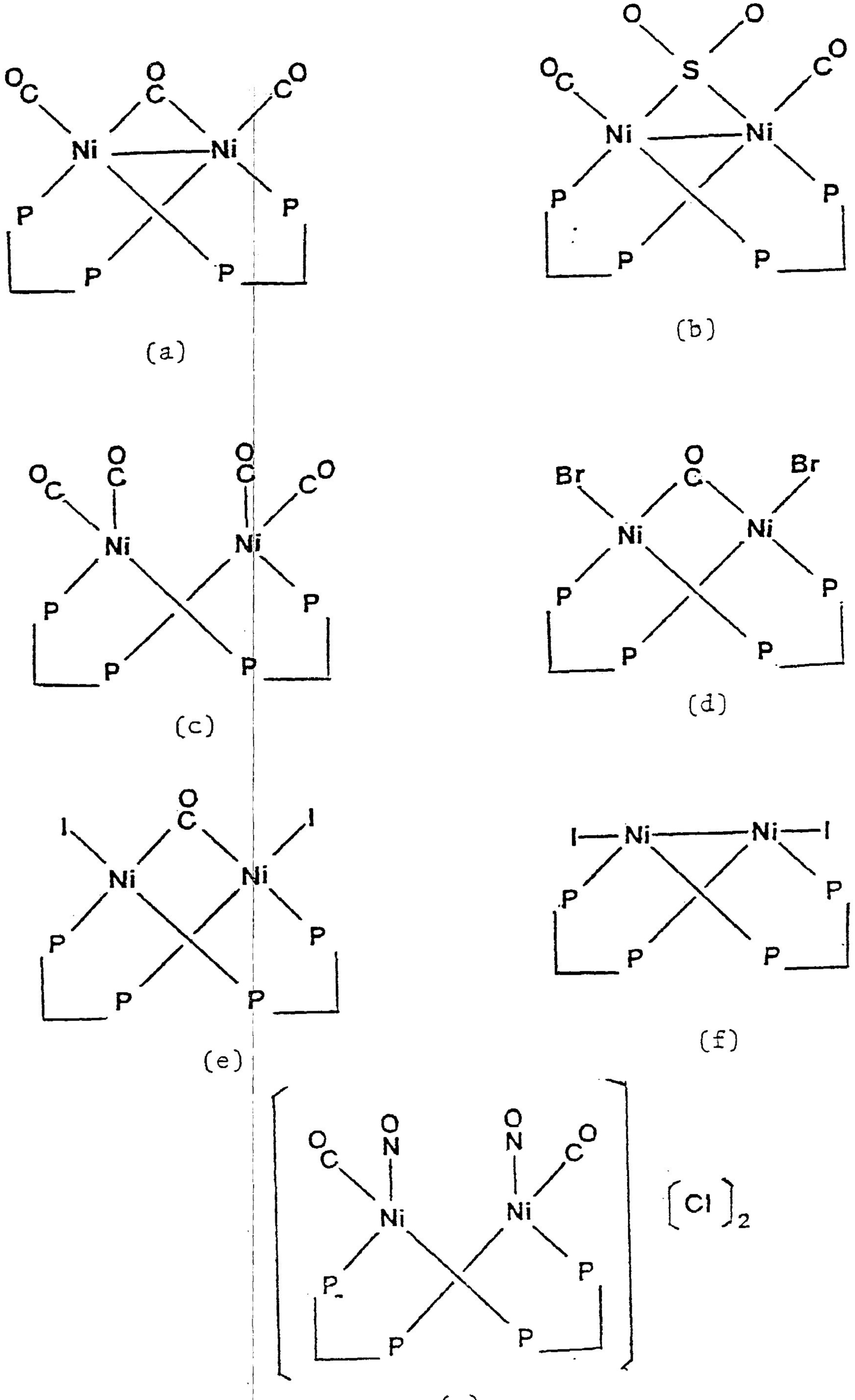
The ^{31}P n.m.r. spectrum in dichloromethane solution at room temperature shows a single sharp resonance at $\delta=22.7$. All phosphorus nuclei are, therefore, in magnetically equivalent environments and the position of the signal is consistent with the dppm ligands bridging the two metal centers. Similar ^{31}P n.m.r. chemical shifts, have been reported for closely related complexes such as $Rh_2(CO)_2(\mu\text{-dppm})_2$,[387] $Co_2(CO)_4(\mu\text{-dppm})_2$[512] and $[Pt_2(\mu\text{-MeC}\equiv\text{C})(Me)_2(\mu\text{-dppm})_2][BF_4]$[483] all of which involve bridging dppm ligands.

The ^{1}H n.m.r. spectrum of this complex at room temperature is quite complicated and shows two multiplets, shown in Fig.112, due to methylene protons of the dppm ligands, centered on $\delta=2.58$ and 3.40 p.p.m. respectively with J(H-H)=12.5 Hz. The signal at $\delta=2.58$

p.p.m. appears as two well defined overlapping quintets with a line separation [the apparent J(P-H), the average of ^{2}J(P-H) and ^{4}J(P-H)] of 4.32 Hz, while in the resonance at δ=3.40 p.p.m. the two overlapping quintets are less well defined and the line separation is ~5Hz. This is probably due to the non equvalent methylene protons of the coordinated dppm virtually coupled with the four magnetically equivalent phosphorus atoms in this complex to give a doublet of quintets in an ABXX'X"X"' spin system. In addition, signals due to protons on the phenyl rings appear as two broad, unresolved multiplets centered at δ=6.95 and 7.31 p.p.m.

Attempts to measure the molecular weight of the complex by osmometric methods were unsucessful due to limited solubility in the solvents used for this purpose (benzene and chloroform). In addition, no molecular ion was detected by mass spectrometry.

There seems to be no doubt, therefore, that this compound is the same molecule for which Stanley et.al.[475] determined the structure, although our method of preparation is very much simpler. It should be emphasised that reaction of Ni(CO)$_4$ with small-bite bisphosphine ligands such as dppm or dmpm give only



(a) (b) (c) (d) (e) (f) (g)

Fig. 113.

disubstituted either monomeric or dimeric complexes of the type $Ni(CO)_2(\eta^2\text{-dppm})$[518] and $Ni_2(CO)_4(\mu\text{-dmpm})_2$.[162,470] No other substituted nickel carbonyl complexes have been reported from the direct reaction of $Ni(CO)_4$ with dppm. The Ni-Ni bond is shown in Fig.113(a) to satisfy the 18 electron requirements of the nickel atoms.

3.3.1.0. Reactions of $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$.

Complexes containing metal-metal bonds are well known for their reactivities.[26,386,388] For example, in reactions with SO_2,CO,NO,Cl^-,Br^- and I^- etc., the metal-metal bond may be cleaved, or small molecules may be inserted across the metal-metal bond. Moreover, the oxidation states of the metals may also be changed via oxidative addition reactions. Examples of some typical metal-metal bonded complexes and their reaction chemistry which have been reported in the last decade are $Rh_2(CO)_2(\mu\text{-dppm})_2$[397], $Ir_2(CO)_2(\mu\text{-dppm})_2$[386,389], $Pd_2Cl_2(\mu\text{-dppm})_2$[26] and $PtCl_2(\mu\text{-dppm})_2$.[479]

Some of the reactions described in this section are preliminary studies and in some cases much more work is needed to identify positively all the products.

Thus, it was expected that $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$, discussed above, would show similar behaviour and, indeed, it reacts with a variety of molecules, such as SO_2,NO,HCl,HBr,I_2 and S_8 etc. These reactions are summarized in scheme [III] and will be discussed in the following pages.

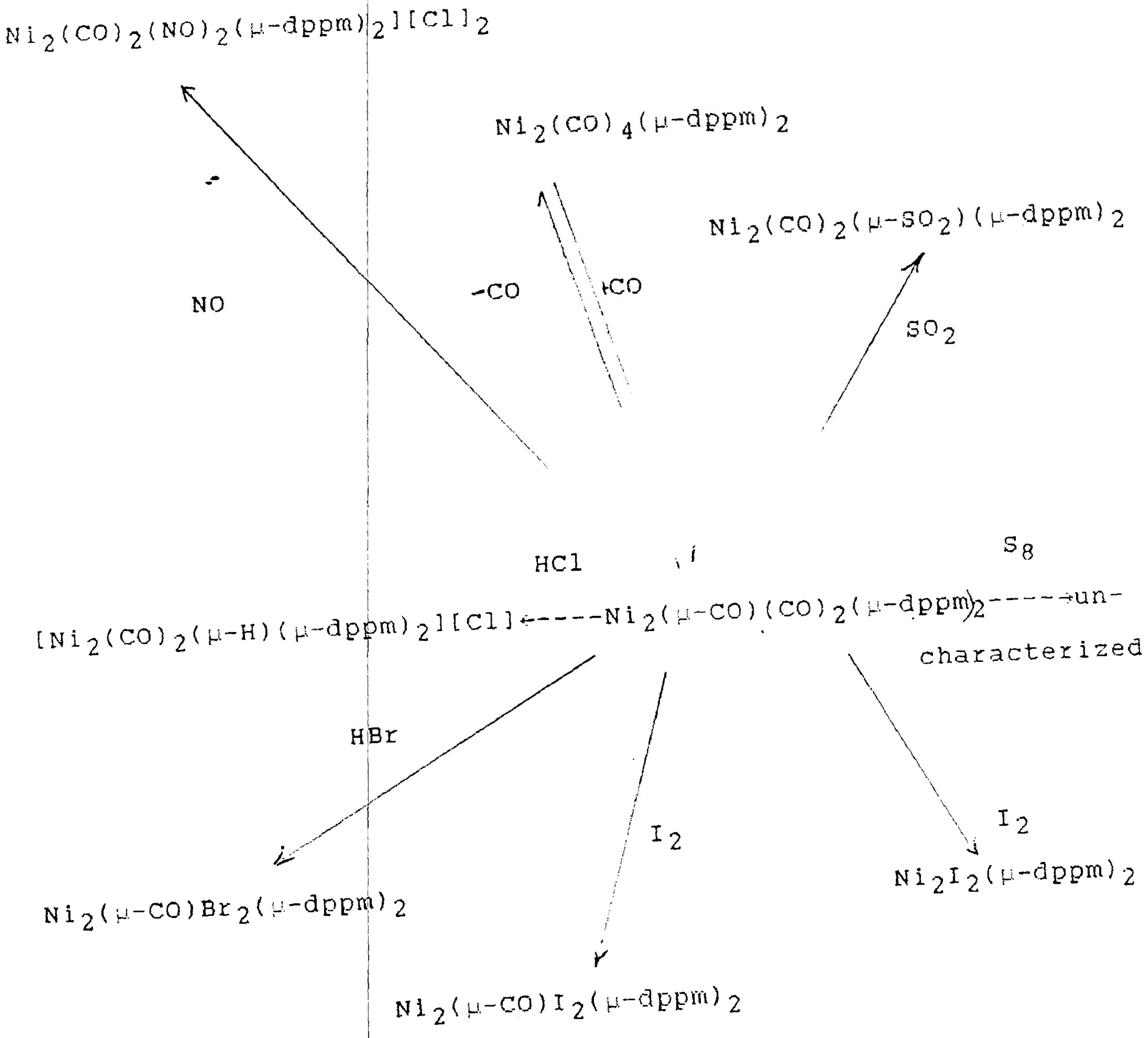
3.3.1.1. $Ni_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$.

This complex is prepared from reactions between dichloromethane solutions of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ and SO_2, which form dark brown solutions (for details see experimental). The reaction is rapid and appears to be complete within 10 seconds. On adding a layer of ethanol to the reaction filtrate, dark brown crystals formed over a period of five days.

The diamagnetic dark brown crystals are air stable but, in solution, decomposition occurs within a few hours on exposure to atmospheric oxygen.

Chemical analyses are consistent with the empirical formula $Ni_2(CO)_2(SO_2)(dppm)_2.0.33CH_2Cl_2$.

Reaction chemistry of $Ni(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$



scheme [III].

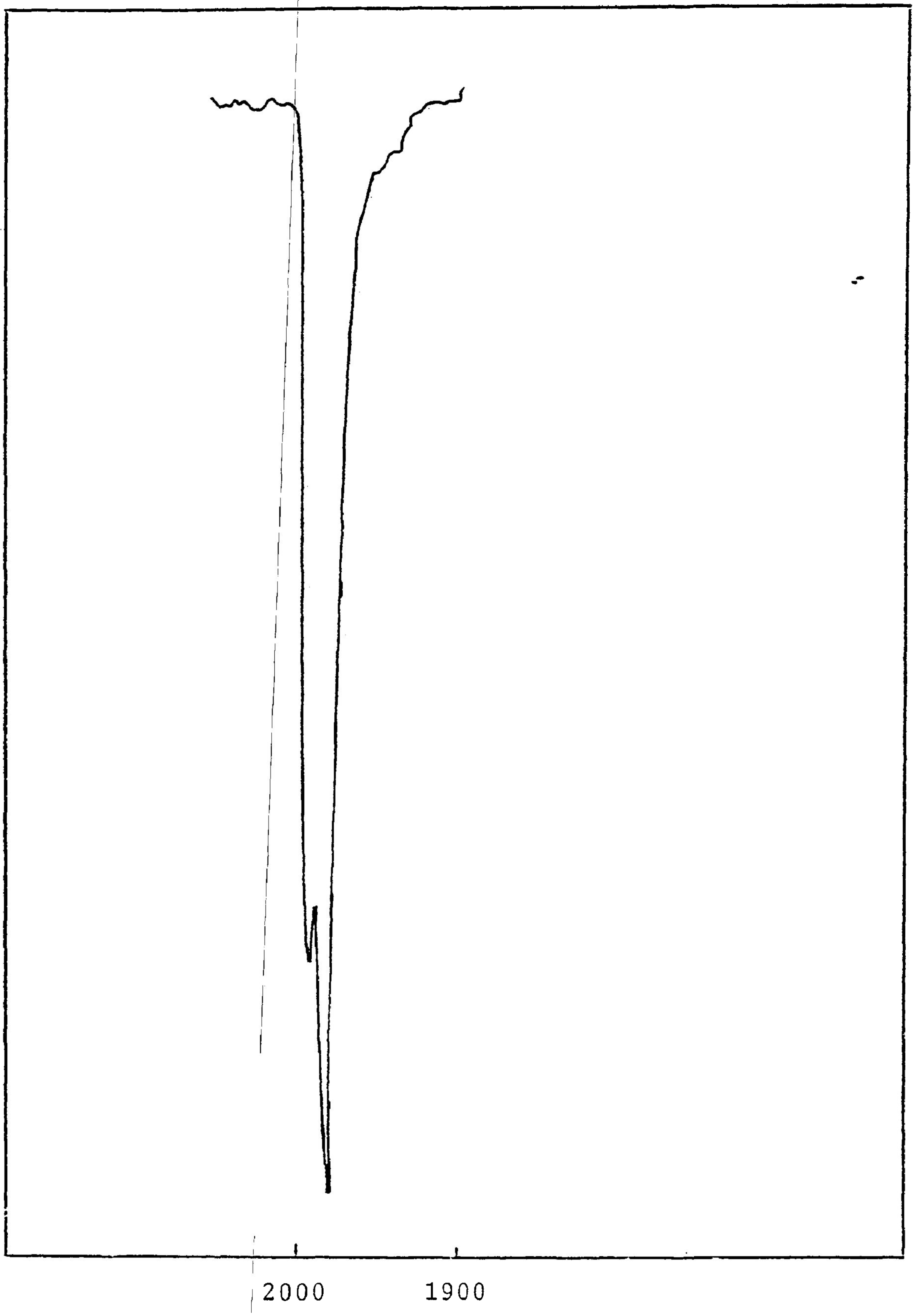


Fig. 114. Selected Features of the Infrared Spectra of $Ni_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$.

The presence of dichloromethane was confirmed by the ^{1}H n.m.r. spectrum (see below).

The i.r. spectrum in dichloromethane solution shows a strong band at 1990 cm^{-1} consistent with terminal carbonyl groups. There is no longer absorption due to μ-CO. In the solid state (Nujol), the 1990 peak appears as a doublet at 1995(m) and 1982(s) cm^{-1} as shown in Fig.114. This may be attributed to the distortions in the solid state. In addition, the i.r. spectrum shows absorptions at 1038(m), 1045(m),1173(w) and 1195(w) cm^{-1} which may be assigned to the ν(S-O) frequencies. Similar values for the bridging SO_2 group have been reported for $Pd_2(\mu\text{-}SO_2)Cl_2(\mu\text{-}dppm)_2$[514], $PtPd(\mu\text{-}SO_2)Cl_2(\mu\text{-}dppm)_2$,[496] $PtPd(\mu\text{-}SO_2)(C_6F_5)_2(\mu\text{-}dppm)_2$[515] and $Pt_2(\mu\text{-}SO_2)(C{\equiv}CPh)_2(\mu\text{-}dppm)_2$[516] which are recorded in Table [11].

The ^{31}P n.m.r. spectrum in dichloromethane solution shows a single resonance at δ=17.0 p.p.m., consistent with bridging dppm ligands and magnetically equivalent phosphorus atoms in solution.

The ^{1}H n.m.r. spectrum shows two unresolved multiplets centered at δ=1.87 and 3.75 p.p.m., which are attributed to the nonequivalent methylene protons of the dppm ligands. The related PtPd(μ-

$SO_2)Cl_2(\mu\text{-dppm})_2$ shows[496] resonances due to the methylene protons of the dppm ligands at δ=2.6 and 4.15 p.p.m. Similar values were observed for $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ discussed earlier. In addition, it shows two broad, unresolved resonances due to the phenyl protons of the dppm ligands at δ=7.0 and 7.5 p.p.m. and a resonance at δ=5.3 p.p.m., attributed to the protons of CH_2Cl_2 present in the lattice.

The existence of sulfur (from SO_2) was further confirmed by X-ray fluorescence spectrometry. All the evidence, therefore, is consistent with the displacement of the bridging CO group by SO_2 to give the new species, shown in Fig.113(b). A Ni-Ni bond is required to satisfy an 18 electron count on each nickel atom.

3.3.1.2. $Ni_2(CO)_4(\mu\text{-dppm})_2$.

As mentioned earlier, some the complexes formed in this investigation are extremely unstable. This is example of such a molecule. Evidence for the formation of this complex was seen on several occasions (^{31}P n.m.r.), for example, in the filtrates of reactions to generate $Ni(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ and

$Ni(CO)_2(\eta^1\text{-dppm})_2$. It is also prepared when CO is passed through dichloromethane solutions of $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$, forming a pale yellow solution (details in experimental section). This rapidly turns back to the original darker yellow colour when passage of the CO is stopped. However, at low temperature, the colour of the solution does not change, but all attempts to isolate this complex were unsuccessful. The complex decomposes, even in the solid state as soon as it is brought to room temperature.

The i.r. spectrum, in dichloromethane solution at 0°C, shows νCO at 2080(m),2018(sh),2004(v.s.) and 1955(s) cm^{-1} (as shown in Fig.115), consistent with only terminal carbonyl groups. For local C_{2V} symmetry two bands of A_1 and B_1 symmetry are expected, and it is possible that the other weaker bands at 2080,2018 and 1960 cm^{-1} may be due to decomposition during the recording of the spectrum. In fact, two bands at 1991 and 1927 cm^{-1} were observed for the analogous $Ni_2(CO)_4(\mu\text{-}dmpm)_2$ complex,[470] the structure of which has been unambiguously determined by a single crystal X-ray diffraction study.

The low temperature ^{31}P n.m.r. spectrum

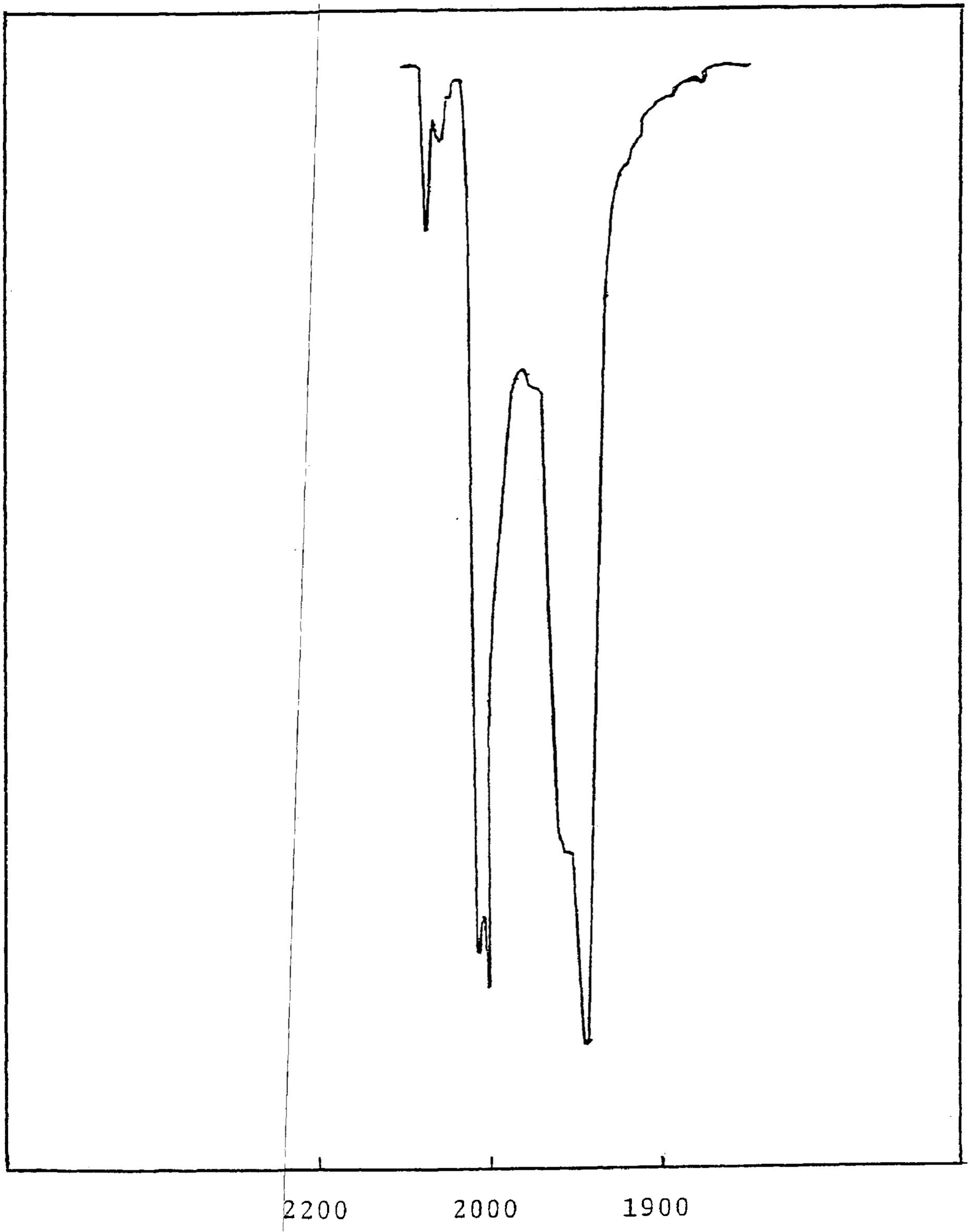


Fig. 115. Selected Features of the Infrared Spectra of $Ni_2(CO)_4(\mu\text{-dppm})_2$.

shows a single resonance at δ= 17.9, suggesting that both dppm ligands are coordinated in a bridging mode and that all the phophorus atoms are equivalent. However, when the sample is brought to room temperature the spectrum shows only a single resonance at δ=22.7 due to $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$.

On the basis of the above evidence, it is clear that the reversible reaction

$$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2 \underset{-CO}{\overset{+CO}{\rightleftarrows}} Ni_2(CO)_4(\mu\text{-}dppm)_2$$

occurs readily, and it is reasonable to assume that the pale yellow complex is a nickel(0) species with a structure analogous to that of $Ni_2(CO)_4(\mu\text{-}dppm)_2$[470], as shown in Fig.113(c), with dppm ligands cis to each other. This complex will be referred to again in the next section.

3.3.1.3. $Ni_2(\mu\text{-}CO)Br_2(\mu\text{-}dppm)_2$

This complex was isolated, when dichloromethane solutions of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ were treated with aqueous HBr, forming an intensely green solution from which, after adding ethanol, deep green crystals were obtained over a period of four days.

The diamagnetic crystals are stable indefinitely under nitrogen, but solutions slowly decompose on exposure to atmospheric oxygen.

Chemical analyses are in excellent agreement with the empirical formula $Ni_2(CO)Br_2(dppm)_2.0.66CH_2Cl_2$. The presence of CH_2Cl_2 is supported by ^1H n.m.r. and mass spectroscopy. The mass spectrum shows peaks at 88,86,84 and 51,49,47 due to CH_2Cl_2. The peaks at 88,86 and 51,49 are due to the presence ^{37}Cl and a combination of $^{37}Cl$and^{35}Cl isotopes. The presence of bromide was confirmed by X-ray fluorescence measurements.

The i.r. spectrum shows a single absorption at 1775 cm^{-1}, due to a bridging CO group [15 cm^{-1} lower in energy than the parent $Ni_2(\mu-CO)(CO)_2(\mu-dppm)_2$]. This lowering in the frequency may be rationalized in terms of increased back donation from the metal 'd' orbitals to the CO π^* orbitals due to coordination of halide groups.

The ^{31}P n.m.r. spectrum shows a single resonance at δ=23.5 p.p.m., consistent with bridging dppm. The down field shift from the parent complex may be attributed to the deshielding of the phosphorus nuclei by the halogen groups.

The ^1H n.m.r. spectrum shows two unresolved complex multiplets at δ=1.25 and 3.7 p.p.m. which are attributed to the methylene protons of the dppm. In addition, it shows a resonance at δ=5.32 p.p.m. assigned to the CH_2Cl_2 protons. Two broad resonances at δ=7.33 and 7.68 p.p.m. arise from the phenyl protons of the dppm ligands.

All the evidence is consistent with a dimeric molecule in which each nickel atom is bonded by a terminal bromide and bridged by a carbonyl and two dppm ligands in the manner shown in Fig.113(d).

3.3.1.4. $Ni_2(\mu\text{-}CO)_nI_2(\mu\text{-dppm})_2$. [n= 0,1]

In contrast to the HBr reactions, two products were isolated when $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$ is treated with iodine. Compound A is greenish-grey and compound B is maroon. The complex A is prepared from the green solution which results when iodine crystals are added in a 1:1 molar ratio to solutions of $Ni_2(\mu$-$CO)(CO)_2(\mu$-dppm$)_2$. Ether was slowly diffused into this over a period of four days. However, when dichloromethane solutions of iodine are slowly added to solutions of $Ni_2(\mu$-$CO)(CO)_2(\mu$-dppm$)_2$, (1:2 molar ratio), a maroon coloured solution is formed from which complex B is isolated over a period of four days after adding hexane.

Both of these complexes are stable over extended periods under nitrogen, but solutions decompose on exposure to oxygen within a few hours.

Elemental analyses are consistent with a chemical formula Ni_2I_2(dppm$)_2$.1.5CH_2Cl_2 for A and $Ni_2(CO)I_2$(dppm$)_2$.0.25CH_2Cl_2 for B. The presence of dichloromethane in both is supported by mass spectra which show peaks at 88,86,84 and 51,49,47.

The i.r. spectrum of B shows a medium intensity band at 1775 cm^{-1} which is assigned to the bridging carbonyl group and is in almost the same position as for $Ni_2(\mu$-$CO)Br_2(\mu$-dppm), again suggesting an increased back donation to the carbonyl group from the metal atoms. No carbonyl absorptions were observed for complex A.

Both of these complexes show a single resonance in ^{31}P n.m.r. spectra at δ=25, consistent with bridging dppm. The down field shift from the parent $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ again suggests deshielding of the phophorus nuclei has occurred due to coordination of two iodide groups.

The ^1H n.m.r. of A shows a resonance at δ=7.4 p.p.m. for the phenyl protons of the dppm ligand. No other structural information could be obtained. However, for B it shows two broad resonances at δ= 1.25 and 3.0 p.p.m. attributed to the methylene protons of the dppm ligands, and a broad resonance at δ= 7.5 p.p.m. which is assigned to the phenyl protons of the dppm. In addition, both complexes show a resonance at δ= 5.3 p.p.m. which arises from the CH_2Cl_2 protons.

The evidence suggests therefore, that these complexes are best represented by Fig.113(f) [A] and Fig.113(e) [B]. In each case the nickel(I) atoms have 16 electrons.

3.3.1.5. Other reactions of $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$:

In the following section, additional reactions of $Ni_2(\mu-CO)(CO)_2(\mu-dppm)_2$ are described, although the resulting products have not been fully characterised.

3.3.1.5.1. (a) Reactions with NO:

The reactions of dichloromethane solutions of $Ni_2(\mu-CO)(CO)_2(\mu-dppm)_2$ with nitric oxide gas result in the formation of dark coloured solutions, which after the addition of ethanol, deposit brownish-black needles over a period of one week (for details see experimental).

In the solid state, this diamagnetic complex is stable indefinitely under nitrogen. Decomposition occurs when solutions are exposed to atmospheric oxygen.

The i.r. spectrum shows absorptions at 1985(v.s),1965(sh),1775(w,br) and 1558(s)cm^{-1} (Fig.116). The first two bands are attributed to terminal carbonyl groups, while the absorption at 1558cm^{-1} is attributed to the νNO stretching frequency. Similar values were earlier

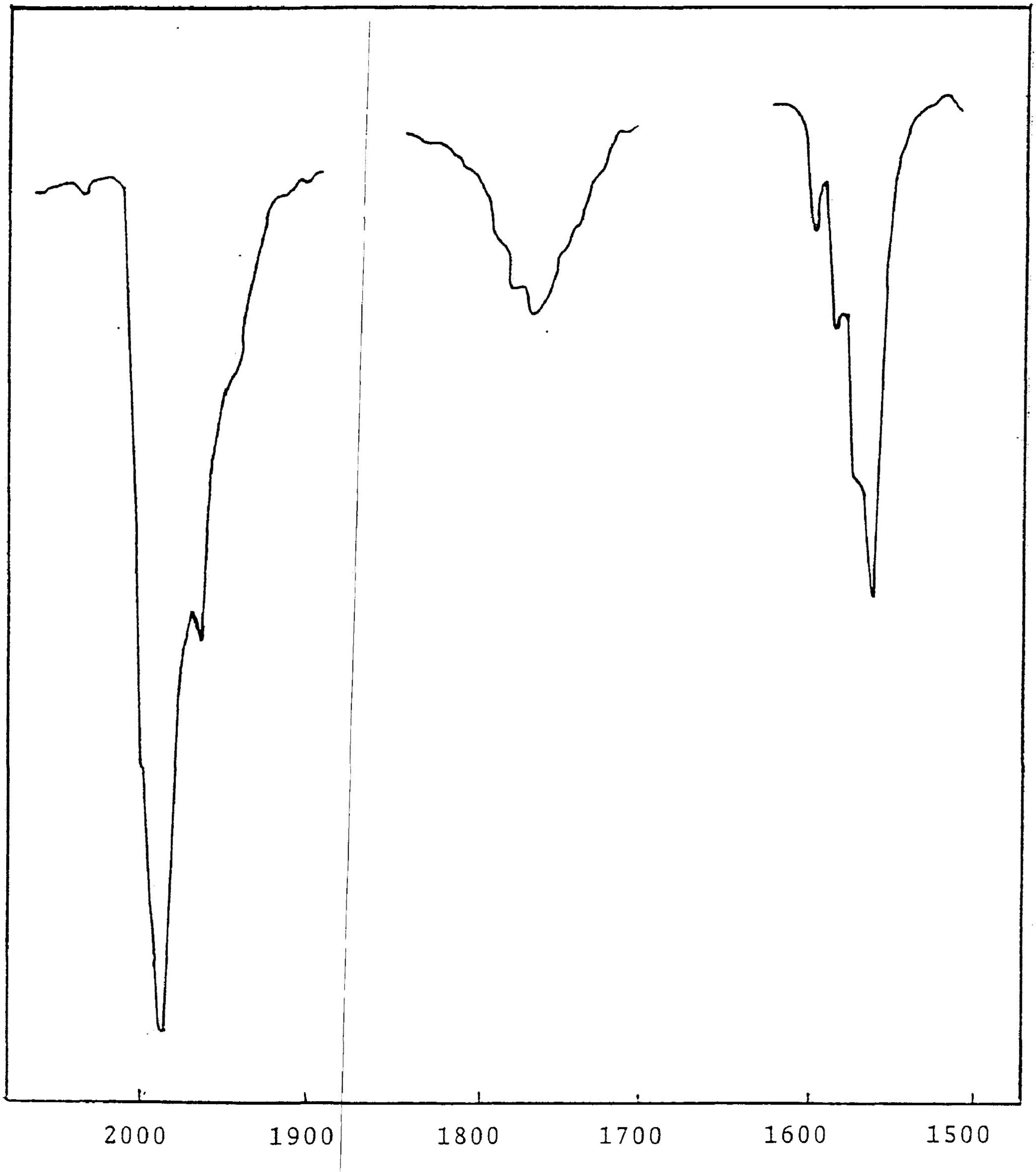


Fig. 116. Selected Features of the Infrared Spectra of $Ni_2(CO)_2(NO)_2(\mu\text{-dppm})_2$.

reported for the related $Ir(NO)Cl_2(PPh_3)_2$,[517] $V(CO)_3(NO)(PMe_3)_2$[123] and $V(CO)_3(NO)(dppm)$[123] complexes which exhibit νNO absorptions at 1560,1582 and 1580cm^{-1} respectively. The origion of the weak absorption at 1775cm^{-1} could be due to some impurity.

The ^{31}P n.m.r. spectrum shows a single resonance at δ= 21 (and a much smaller resonance at δ= 24 probably due to an impurity). The resonance at δ= 21 suggests that both dppm ligands are bridging. Furthermore, when CO is passed into this solution, a signal due to $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ appears at the expense of the signal at δ= 21. Thus, the reaction appears to be reversible.

The ^{1}H n.m.r. spectrum shows a broad resonance at δ=7.37 p.p.m. attributed to the phenyl protons of dppm. No other information could be obtained from the ^{1}H n.m.r. spectrum.

Reproducible chemical analyses have not yet been obtained, but the available data suggest an empirical formula $[Ni(CO)_2(NO)_2(\mu\text{-}dppm)_2][Cl]_2$, where Cl might have been abstracted from CH_2Cl_2, used as solvent. X-ray fluorescence indicates the presence of chlorine atoms which may or may not be due to CH_2Cl_2 in the lattice. The fact that a solution of this compound in ethanol reacts immediately with $NaBPh_4$ suggests that the chlorine atom(s) may well be present as Cl^-, and that the compound may contain a $Ni_2(CO)(NO)(\mu\text{-dppm})$ cation of some kind. Clearly more work is necessary before positive identification can be made, but one possibility is shown in Fig.6. When a large excess of nitric oxide is used in the reaction a resonance at $\delta = 27.4$ due to a new symmetrical species occurs. This species could not be isolated.

3.3.1.5.2. (b). Reactions with HCl.

This is another reaction in which the Ni atoms of $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$ appear to have been oxidized. Thus, when solutions are treated with aqueous HCl, green solutions are formed. Attempts to isolate a solid complex were largely unsuccessful, but in one instance a small amount of a green complex precipitated over a period of one week after the addition of ethanol [probably contaminated with unreacted $Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2$]. A similar green complex is also prepared by using dry HCl gas, but again a pure complex could not be isolated.

The impure complex appears to be stable indefinitely in the solid state under nitrogen, but solutions are extremely unstable at room temperature and in fact, decomposition occurs even at lower temperatures.

The i.r. spectrum shows absorptions at 2002(m),1972(m),1952(s),1788(w) and 1770(m) cm^{-1} (Fig.117). There are indictions (2002, 1778, 1770 cm.$^{-1}$) that either a hydride species is formed, among other complexes, which may have bridging dppm ligands, or a new carbonyl complex (other than that disscussed earlier) has been formed.

The low temperature ^{31}P n.m.r. spectrum shows a strong resonance at δ=25.5 and weaker resonances presumably due to impurities at δ=21.9, 26.2 and 27.6.

The ^{1}H n.m.r. spectrum shows resonances due to the methylene protons of the dppm ligand as two broad unresolved multiplets at δ= 2.55 and 3.25 p.p.m. In addition, it shows a broad resonance at δ= 7.18 p.p.m. due to the phenyl protons of the dppm ligand. Moreover,

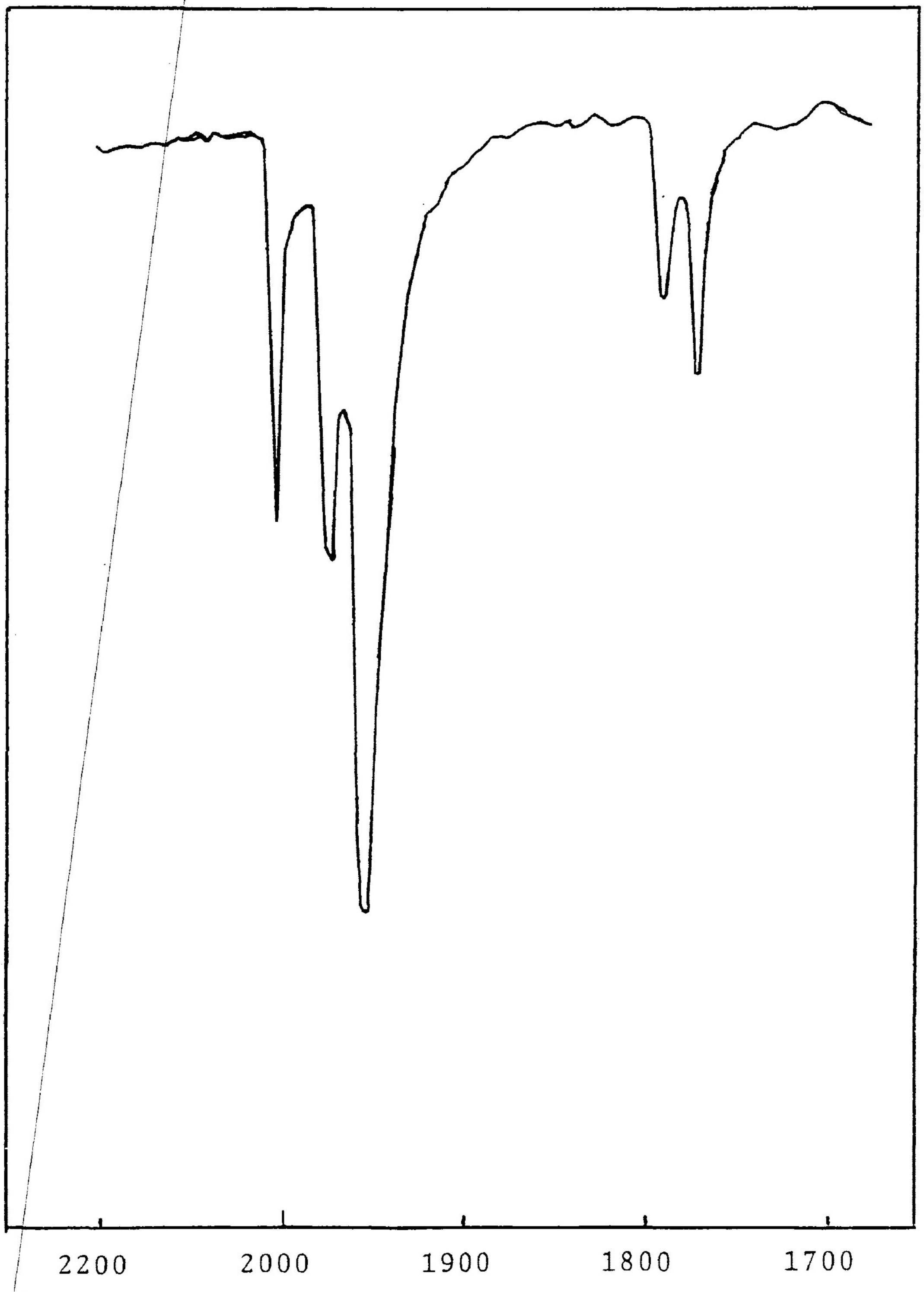


Fig. 117. Selected Features of the Infrared Spectra of the product from reaction of $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ with HCl.

it also shows broad unresolved resonances at δ= -8.2, 18.2 and -19.5 p.p.m. which may be attributed to hydride groups, which generally appear in the high field region.

Thus, on the basis of these data it is quite clear that at least one species with a hydride ligand(s) has formed in this reaction.

3.3.1.5.3. (c). Reactions with S_8.

$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ also reacts with elemental sulfur, forming a highly crystalline black complex. The i.r. spectrum shows no absorptions due to carbonyl group, and the ^{31}P n.m.r. spectrum shows a single resonance at δ=39.5 suggesting that dppm bridges two metals.

Chemical analyses reveal very low C (~33%), H (~2.6%) and a significant amount of S(~26%). This complex clearly needs more work but given its highly crystalline nature, the chemical analyses are probably valid. This means that the molecule contains only a small amount of phosphine compared to the amount of Ni and S present. There is a possibility, therefore that the complex may be related to the recently characterized

$Ni_8S_6(PPh_3)_n$ clusters.[518]

3.3.1.5.4. (d). Reactions with other metals-containing species.

In addition to the chemistry already described, several reactions were carried out to try to add a third metal across an existing metal-metal bond. To this author's knowledge, there is only one report[519] of a metal-metal bond being cleaved by the insertion of a third metal, thus forming a trimetallic system. It was therefore of interest to investigate the generality of this approach. For example, when $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ is treated with $Pt(COD)Cl_2$ in a 1:1 molar ratio the original orange solution rapidly turned intensely purple. Similar treatment with $HgCl_2$ resulted in the formation of a dark brown solution. Clearly some kind of reaction has occurred although no complex could be isolated.

Clearly the reactions described in sections (a)-(d) are best described as exploratory, and require additional work before firm conclusions can be drawn.

3.3.2. $Ni(CO)_2(\eta^1\text{-dppm})_2$.

Full details of the synthesis of this second dppm complex are given in the experimental section. However, briefly, $NiCl_2.6H_2O$, dppm and $NaBH_3CN$ were reacted in a molar ratio of 1:2:3.6 under a slow stream of CO in a mixed solvent (toluene or benzene and ethanol) system. The reaction goes smoothly to completion within 2-2.5 hours after the $NaBH_3CN$ addition, giving an off white suspension. This was filtered off and hexane was added to the filtrate which, after 12-16 hours in the freezer produced crystals of $Ni(CO)_2(\eta^1\text{-dppm})_2$ in ~38% yield. The yield can be further increased by concentrating the mother liquor under reduced pressure. The complex can also be obtained from reactions in which the metal to ligand ratio is increased to 1:3 and then allowing the reaction filtrate to stand at room temperature over a period of 12-16 hours. Alternatively, $NaBH_4$ can be used instead of $NaBH_3CN$, provided the higher metal to ligand ratio is maintained.

The colourless diamagnetic solid is stable indefinitely when stored under nitrogen gas, but in solution it oxidizes with in a few hours when exposed to air. As mentioned earlier, the stability of this complex in solution is temperature dependent which complicated the initial work on its isolation and characterization. It must be dissolved in cold solvents and the solutions must be kept at $0^{o}C$ or below under an inert atmosphere all the time. Solution decomposition at higher temperatures can be prevented by maintaining an excess of ligand, but this is not useful when studying the properties or the chemistry of this species.

Elemental analyses for carbon and hydrogen are in excellent agreement with the formulation of $Ni(CO)_2(dppm)_2$ and the complex has been unambiguously characterized as a tetrahedral nickel(0) complex in which both dppm ligands are coordinated through only one of their phosphorus atoms (i.e. in a monodentate fashion), as shown in Fig.118(a).

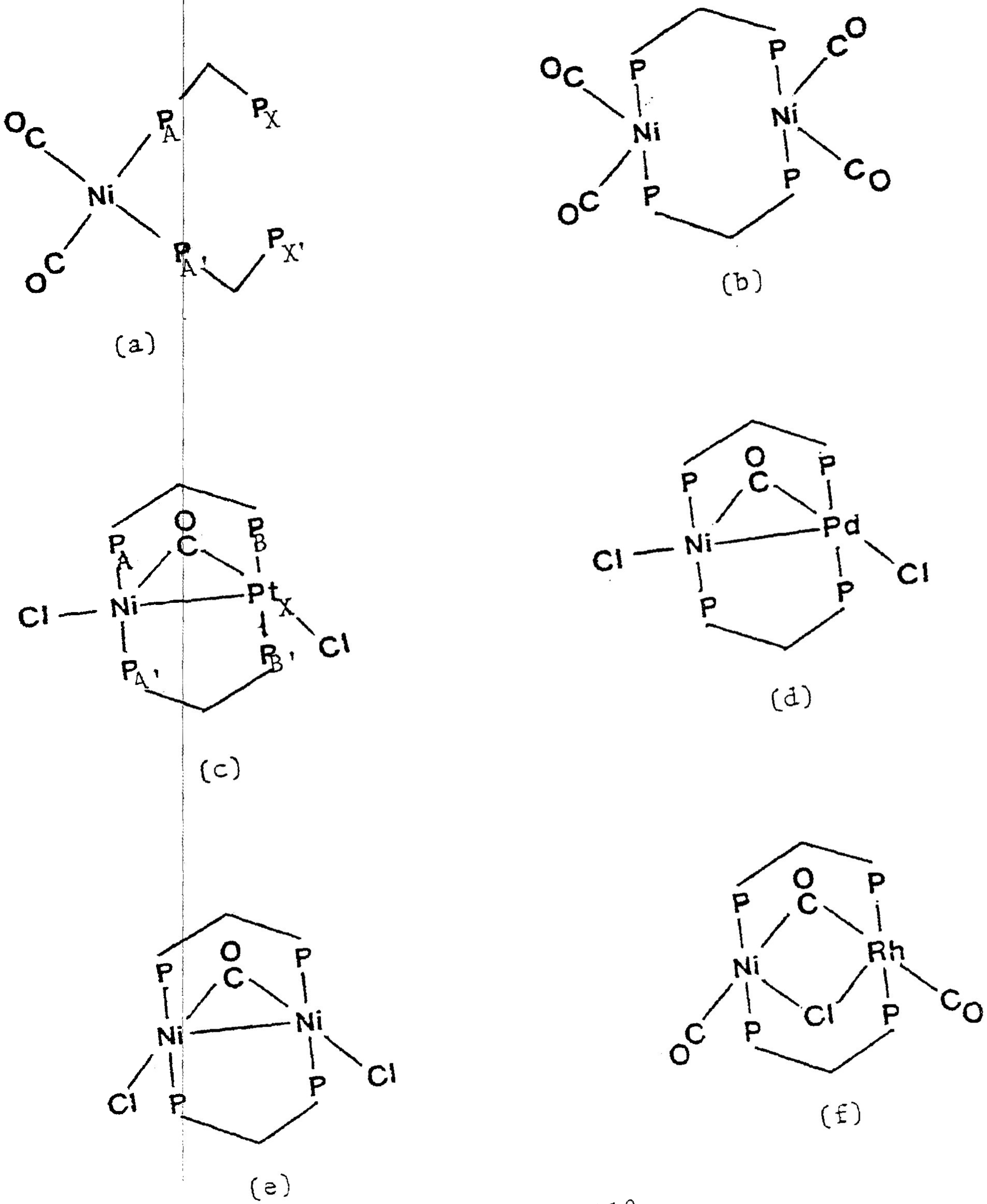
Thus, the i.r. spectrum shows two very strong bands in the terminal carbonyl region of A_1 and B_1 (C_{2V}) symmetry as shown in Fig.119. The frequency values of these carbonyl absorptions are recorded in Table [12]. The other three weak bands at 1978,1954 and 1900 cm^{-1} are probably due to the distortions in the solid state structure. This i.r. spectrum is very similar to that of the tetrahedral, monodentate phosphine complex

Table [12].

I.r. and n.m.r. data of $Ni(CO)_2(\eta^1\text{-dppm})_2$, its derivatives and related complexes.

complex	$\nu(CO)$ c.m.$^{-1}$	^{31}Pn.m.r$^+$. δP_A	δP_B	^1Hn.m.r. (δ p.p.m.)	ref.
$Ni(CO)_2\{\eta^1\text{-}Ph_2P(CH_2)_2S(Et)\}_2$	1995,1945				448
$Ni(CO)_2(\eta^1\text{-dppm})_2$	1992(vs),1978(sh) 1954(sh),1930(vs) 1900(v.w)	26.13	-2374	2.5 (d.d)	*
$Pt(CH_2CH_2CH_2CH_2)(\eta^1\text{-dppm})_2$		15.7	-24.6	2.90	523
$Pt(1\text{-naphthyl})_2(\eta^1\text{-dppm})_2$		7.2	-29.4	1.97 (c.m)	522
$Pt(C_6H_4Me\text{-}o)_2(\eta^1\text{-dppm})_2$		6.9	-27.7	2.23 (c.m)	522
$Ni(CO)_2(\eta^1\text{-dppm})_2$					
$Ni_2(CO)_2(\mu\text{-dppm})_2$	15.7				
$NiPt(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$,	1756	27.5	14.3	2.6-3.85 7.2-7.6(cm,br)	
$NiPd(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$	1712	26.3 3.69	20.3 4.25	20.4 7.25-8.10(c.m,br)	
$Ni_2(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$	1769	22.2		3.0,3.6 7.20 (cm,br)	

*= Our work, C= Complex, m=multiplet, d.d=doublet of doublet,+ In each case, P_A refers to the coordinated P atom and P_a the non coordinated P atom.



(a) (b) (c) (d) (e) (f)

Fig. 118.

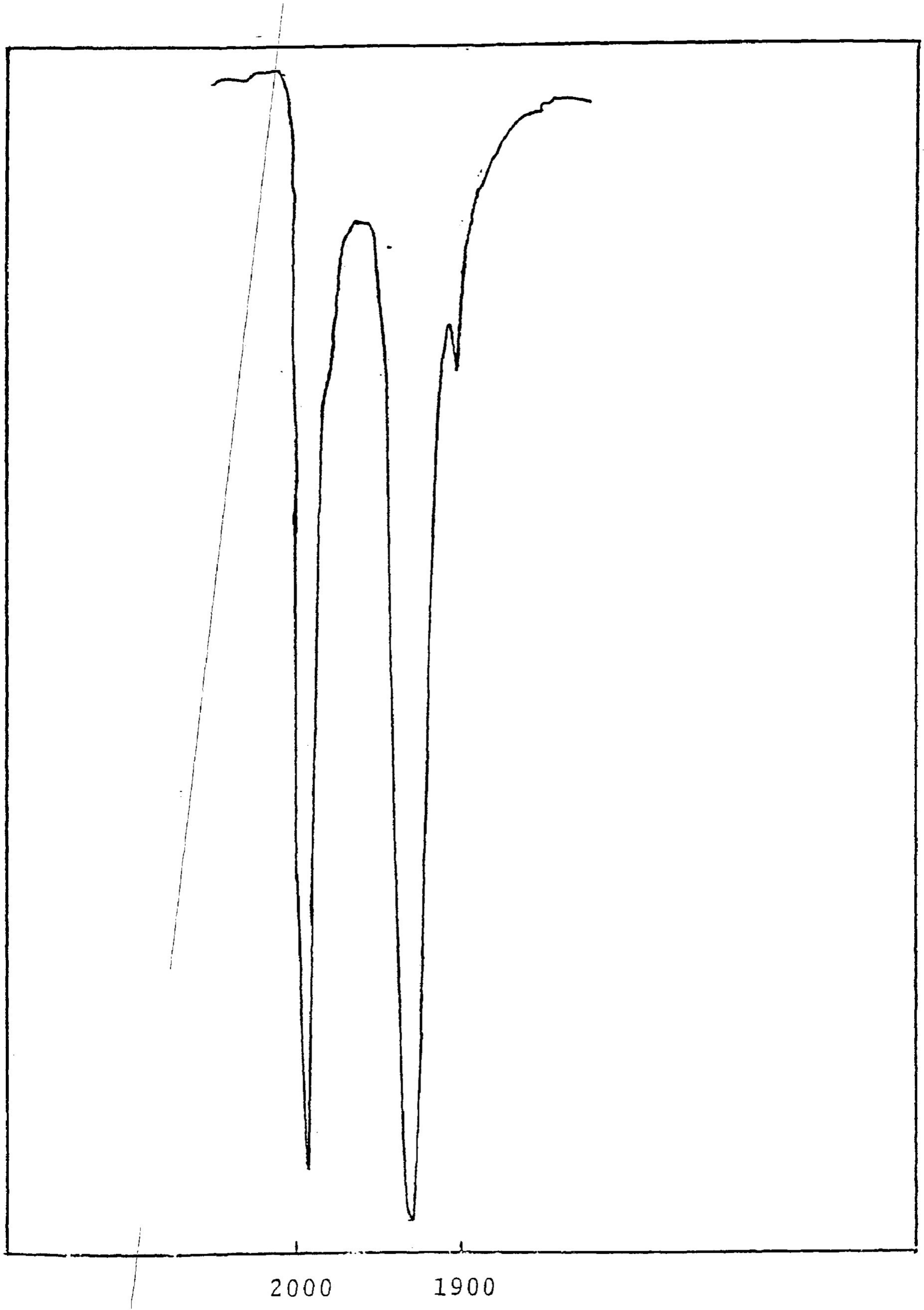


Fig. 119. Selected Features of the Infrared Spectra of $Ni(CO)_2(\eta^1\text{-dppm})_2$.

$Ni(CO)_2(PPh_3)_2$, shown in Fig.110, which was prepared during this study and discussed earlier in section 3.2. The related nickel(0) complex $Ni(CO)_2[\eta^1-Ph_2P(CH_2)_2S(Et)]_2$ has been prepared[448] from $Ni[\eta^2-Ph_2P(CH_2)_2S(Et)]_2$ by treating it with carbon monoxide gas. This also exhibits two bands in the i.r. spectrum in the terminal carbonyl region, the frequencies of which are also recorded in Table [12]. This complex has also been assigned a tetrahedral geometry, with each phosphine ligand coordinated through only one phosphorus atom. There is, thus, a close similarity between the spectra of these complexes.

The low temperature ^{31}P n.m.r. spectrum of $Ni(CO)_2(\eta^1-dppm)_2$ in toluene solution is shown in Fig.120(a). This clearly shows two well separated multiplets each with P-P coupling. The downfield resonances are centered at $\delta=26.13$, and are assigned to the coordinated P atoms of dppm , while the upfield resonances, which are centered at $\delta=-23.74$ and appear near the free phosphine region, are assigned to the uncoordinated P atoms of the dppm . The P atoms labelled AA' and XX' in Fig.118(a) signify two pairs of chemically equivalent nuclei which are magnetically non equivalent.[520,521] The ^{31}Pn.m.r. spectrum of $Ni(CO)_2(\eta^1-$

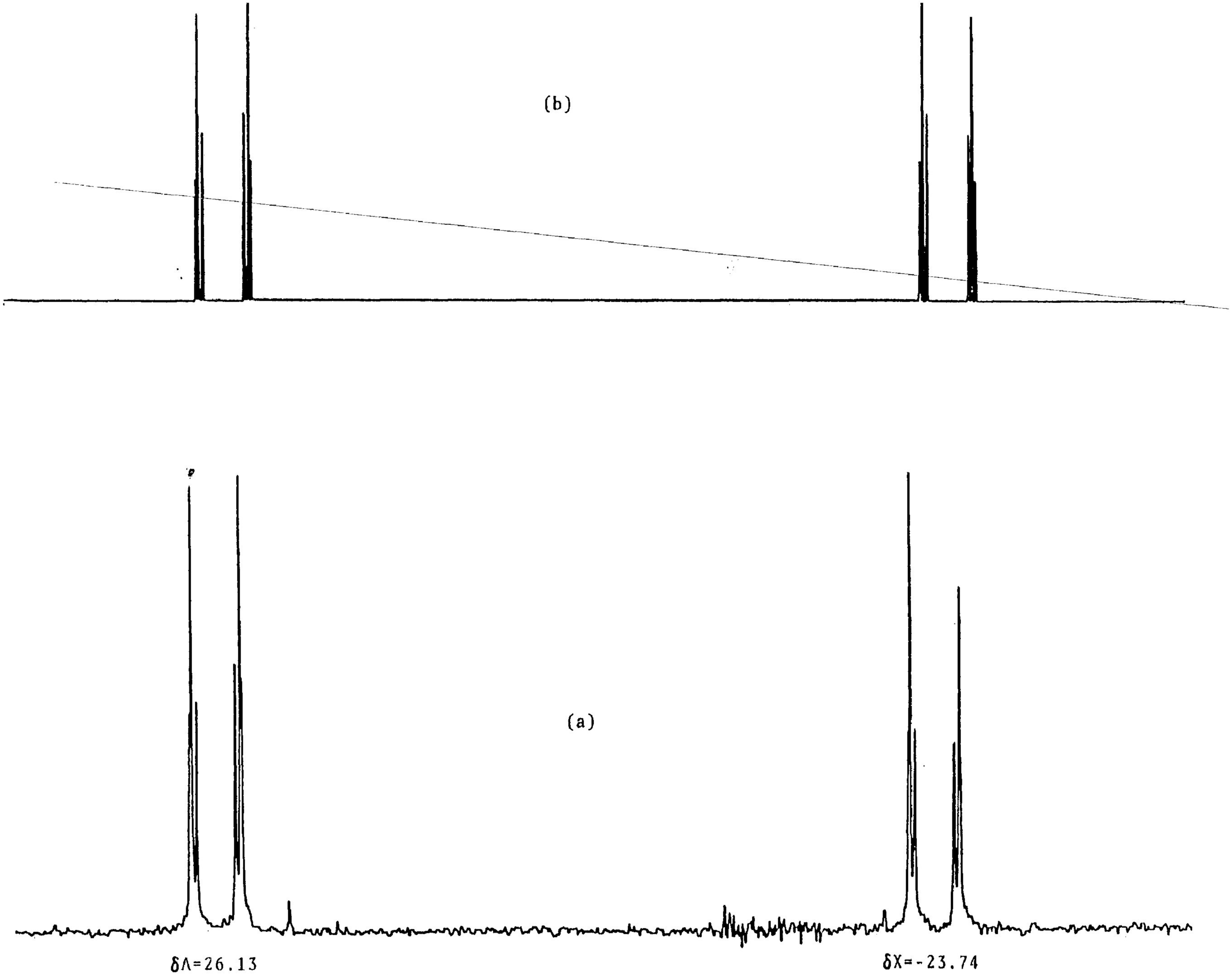


Fig. 120. ^{31}Pn.m.r. Spectrum of Ni(CO)$_2$(η^1-dppm)$_2$.

(a) Experimental (b) Simulated.

dppm)$_2$ should therefore be second order and of the AA'XX' type[520b] which, theoretically, consists of twenty lines. The fact that a centrosymmetric, twelve line pattern is observed clearly means that not all coupling possibilities are being observed. In fact, if $J_{XX'}=0$ Hz, only twelve lines are expected and the spin system can be analyzed with $J_{AX}=108.25$ Hz, $J_{AX'}=2.27$ Hz and $J_{AA'}=16.5$ Hz. Using these parameters, a ^{31}P n.m.r. spectrum was simulated by computer and this is shown in Fig.120(b). Absolute signs of coupling constants were, however, not calculated. The close similarity between the two spectra, confirms that the spectral analysis is correct and verifies that the molecule has the structure shown in Fig.118(a). The complexes $Pt(CH_2CH_2CH_2CH_2)(\eta^1\text{-dppm})_2$ and $Pt(1\text{-naphthyl})_2(\eta^1\text{-dppm})_2$[522] containing two <u>cis</u>-dppm ligands coordinated through only one phosphorus atom have analogous ^{31}P n.m.r. spectra based on an AA'XX' spin system.

A low temperature ^1H n.m.r. spectrum shows a broad unresolved doublet of doublets resonance centered at $\delta=2.5$ p.p.m. due to the PCH_2P protons of the dppm. These resonances occur due to coupling of the non equivalent methylene protons ($\tilde{}J_{H-H}=4$Hz) to the phosphorus atoms ($\tilde{}J_{P-H}=10$Hz). This is similar to the methylene proton resonances of dppm in Pt(1-naphthyl)$_2$(η^1-dppm)$_2$, Pt(C_6H_4Me-o)$_2$(η^1-dppm)$_2$ and Pt($CH_2CH_2CH_2CH_2$)(η^1-dppm)$_2$ which occur at 1.97[522] (complex multiplet), 2.23[522] (complex multiplet) and 2.90[523] p.p.m. respectively. In addition, Ni(CO)$_2$(η^1-dppm)$_2$ exhibits a broad resonance centered at δ=7.1 p.p.m. which is attributed to the phenyl protons of the dppm ligands.

Because of the instability of this complex at room temperature in solution, a molecular weight could not be determined by osmometric methods.

Thus, all the evidence given above is in full agreement with the assigned structure of this complex, which is shown in Fig.118(a).

3.3.2.0. Reactions of Ni(CO)$_2$(η^1-dppm)$_2$.

As expected, Ni(CO)$_2$(η^1-dppm)$_2$ is a very reactive molecule and a wide range of reactions has been studied. For example, when ice cold solutions of Ni(CO)$_2$(η^1-dppm)$_2$ are treated with PPh_3 in a 1:2 molar ratio, ^{31}P n.m.r. spectroscopy shows the formation, over several days, of $Ni(CO)_2(PPh_3)_2$ (discussed earlier) and free dppm, although complete conversion was not achieved even in the presence of an excess of PPh_3. It is interesting to note that a study of the reverse reaction, i.e., the formation of $Ni(CO)_2(\eta^1\text{-dppm})_2$ from $Ni(CO)_2(PPh_3)_2$ and an excess of dppm is also very slow and, again, complete conversion was not achieved even over a period of several days.

It is well known that if the donor atoms of bidentate ligands are of the same element and the ring formed by the coordination of such a ligand does not involve undue strain, then a bidentate ligand will replace monodentate ligands (in this case monocoordinated bidentate ligands). This is known as the chelate effect.[524] Thus, when $Ni(CO)_2(\eta^1\text{-dppm})_2$ is treated with dppe or dppp (in a 1:1 molar ratio) ^{31}P n.m.r. spectra show signals at δ=44.5 and 15.3 consistent with the formation of $Ni(CO)_2(\eta^2\text{-dppe})$ and $Ni(CO)_2(\eta^2\text{-dppp})$, respectively, as well as free dppm. Both of these complexes have also been prepared by different routes and have been fully characterized in this study (see later). However, treatment of $Ni(CO)_2(\eta^1\text{-dppm})_2$ with longer back bone carbon chain bisphosphine ligands, such as dppb gives a mixture of unidentified complexes.

The solution formed when $Ni(CO)_2(\eta^1$-dppm$)_2$, in ice cold toluene solution, is treated with $Ni(CO)_4$, shows a single resonance at δ=15.7 in the ^{31}P n.m.r. at room temperature. Unfortunately, all attempts to isolate a complex from this solution were unsuccessful. From the spectrum it is clear that all the phosphorus atoms are magnetically equivalent and that the dppm ligand is in a bridging mode. We believe that the following reaction occurs.

$$Ni(CO)_2(\eta^1\text{-dppm})_2 + Ni(CO)_4 \dashrightarrow Ni_2(CO)_4(\mu\text{-dppm})_2 + 2CO$$

The resulting complex has been tentatively formulated as shown in Fig.118(b), where two $Ni(CO)_2$ units are bridged by the two <u>trans</u> dppm ligands. A <u>trans</u>- geometry is suggested since the apparently isomeric complex, with <u>cis</u>- geometry has already been prepared from reactions of $Ni_2(\mu$-CO$)(CO)_2(\mu$-dppm$)_2$ with CO and discussed earlier. This shows a chemical shift in the low temperature ^{31}P n.m.r. spectrum at δ=18. As mentioned earlier, the <u>cis</u> isomer is unstable at room temperature forming the starting $Ni_2(\mu$-CO$)(CO)_2(\mu$-dppm$)_2$ complex while the <u>trans</u> isomer is stable at room temperature.

3.3.2.1. Bimetallic complexes synthesized from $Ni(CO)_2(\eta^1\text{-dppm})_2$

Complexes of this type, having bisphosphine ligands coordinated through only one of the phosphorus atoms, have the obvious potential for the coordination of another metal atom, thus forming homo- or heteronuclear bimetallic complexes. This convenient type of reaction has already been explored by several workers (particularly Shaw and his coworkers[31,476]) and a large number of such reports have appeared within the last few years on such systems.

Thus, $Ni(CO)_2(\eta^1\text{-dppm})_2$ reacts with several complexes, particularly those containing weakly bonded ligands such as $Pt(COD)Cl_2$, $Ni(CO)_4$, $Rh_2(CO)_4Cl_2$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ and several others. One of the resulting complexes has been unambiguously characterized by X-ray crystallography as $NiPt(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$, while three other complexes $Ni_2(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$, $NiPd(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$ and $NiRh(CO)_3Cl(dppm)_2$ have been prepared and characterized.

3.3.2.1.1. $NiPt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$.

This is one of the most interesting complexes prepared in this investigation. Details of the synthesis are given in the experimental section. In a typical reaction a 1:1 molar ratio of $Ni(CO)_2(\eta^1\text{-}dppm)_2$ and $Pt(COD)Cl_2$ were mixed in dichloromethane solution, under nitrogen gas. The reaction is very rapid and an intensely coloured purple solution is formed, from which purple crystals were isolated over a period of 3-4 days either by the slow diffusion of ether or by carefully adding a layer of ethanol.

This diamagnetic, purple complex is stable indefinitely in the solid state under nitrogen. Once formed, crystals appear to have very limited solubility in the common organic solvents, and the dilute solutions so formed rapidly decolourize. However, when ground to powder, samples dissolve more readily in dichloromethane and form purple solutions, which decompose within 10-12 hours even under an inert atmosphere.

The chemical analyses are consistent with the formulation of $NiPt(CO)Cl_2(dppm).0.5CH_2Cl_2$. The presence of dichloromethane was supported by both ^1H n.m.r. measurements and mass spectrometry. The mass spectrum shows peaks at 88,86,84 and 51,49,47 due to CH_2Cl_2. The peaks at 88,86 and 51,49 are probably due to the presence of ^{37}Cl and a combination of ^{37}Cl and ^{35}Cl isotopes. The presence of CH_2Cl_2 was confirmed by X-ray crystallographic results,[525] to be discussed shortly.

The i.r. spectrum shows a medium intensity band at 1756 cm^{-1} which suggests that the carbonyl group bridges the two metal atoms. This frequency is in the same region, although higher than the corresponding absorptions in the analogous complexes $PtPd(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ (1680 cm^{-1}),[496] $Pd_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ (1705 cm^{-1})[26] and $Pt_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ (1638 cm^{-1}).[479]

The ^{31}P n.m.r. spectrum in dichloromethane solution is shown in Fig.121. This spectrum consists of two pseudo symmetrical multiplets with a line separation of 299.2 Hz, each resonance containing eight lines resulting from P-P coupling. The down field multiplet centered at $\sim\delta=27.5$, with satellites due to coupling to ^{195}Pt can be assigned to the P atoms bonded to the Pt atom, while the upfield multiplet centered at

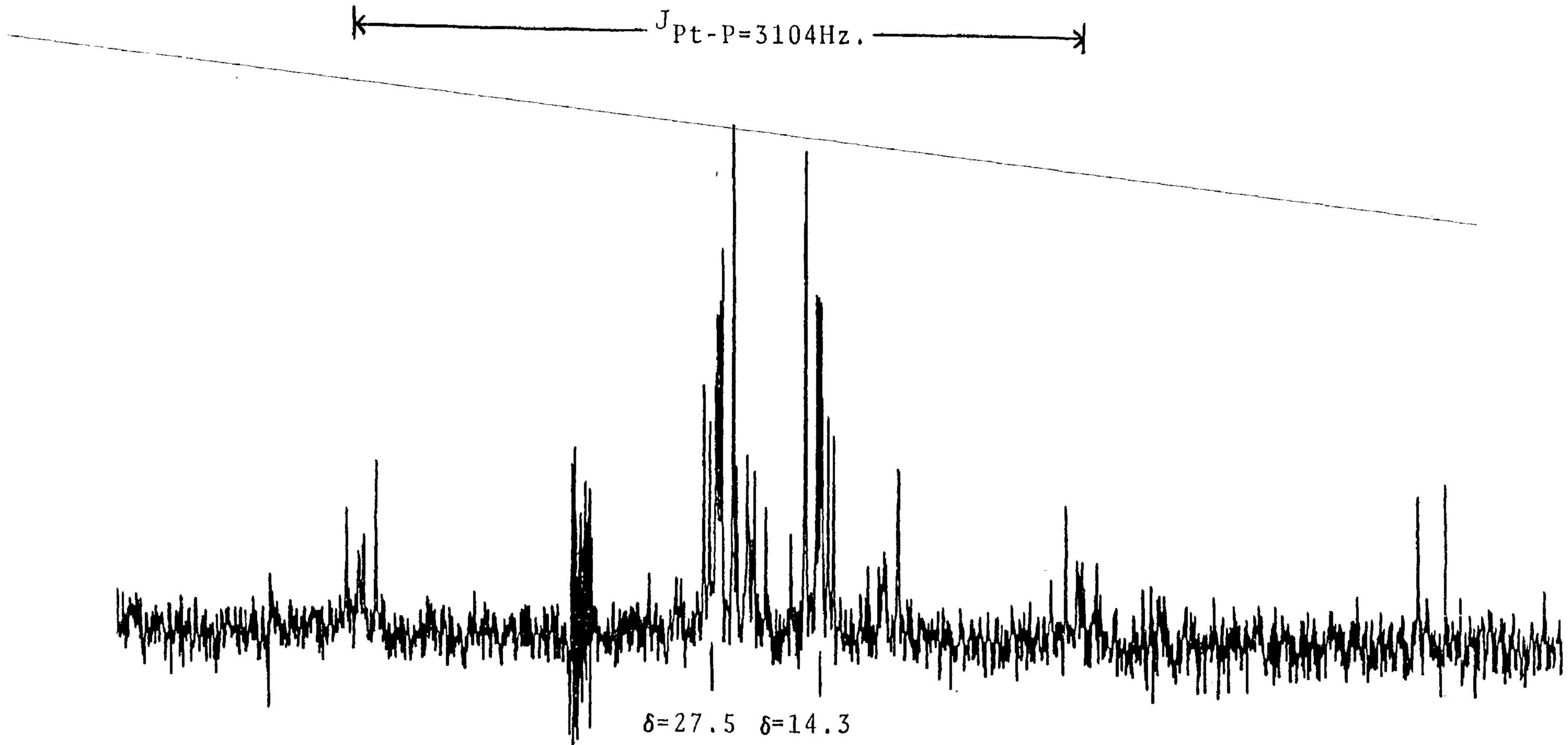


Fig. 121. ^{31}Pn.m.r. Spectrum of NiPt(-CO)CO_2(-dppm)$_2$.

δ=14.3 are attributed to the P atoms bonded to the Ni atom. Detailed analysis of the ^{31}P n.m.r. spectrum could not be done due to decomposition of the complex, but the sixteen line spectrum is typical of an AA'BB'X spin pattern [Fig.118(c)]. Pringle and Shaw have reported[496] a quite similar ^{31}P n.m.r. spectrum for a related complex $PtPd(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$, although they were unable to record the n.m.r. spectrum of the analogous $PtPd(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$, due to its insolubility.

The ^1H n.m.r. spectrum of $NiPt(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$ in $CDCl_3$ solution shows two broad, complex multiplets in the region of 2.6-3.85 p.p.m. with satellites due to coupling to ^{195}Pt, and these are assigned to the non equivalent methylene protons of the bridging dppm ligands. Similar values have been reported for $PtPd(\mu\text{-}SO_2)Cl_2(dppm)_2$[496] and these are recorded in Table[11]. It has been shown[526] recently that the methylene protons of the dppm ligand in the ^1H n.m.r. spectrum shows a characteristic splitting pattern and this is very helpful in characterizing these complexes. These characteristic resonances appear since in the complexes like $Pd_2Cl_2(\mu\text{-dppm})_2$ rapid conformational changes in the CP_2Pd_2 ring render the two methylene protons equivalent while for the molecular A-frames, this is not possible. (no motions of the CP_2M_2 ring can render the two methylene protons of a dppm ligand equivalent). Normally in A-frame type complexes, the two dppm ligands are equivalent by their symmetry. Therefore, the methylene protons of the dppm appears as an AB pattern with $J_{(H,H)}$ in the range of ~12-15 Hz. Often, the chemical shift differences between the two types of protons reach 0.5-1 p.p.m. Superimposed on this AB pattren is the phosphorus-proton coupling which further splits each resonance into a quintet. Thus, these patterns can easily be recognized. Although the ^1H n.m.r. spectrum of the Ni-Pt complex is not very well resolved, it clearly shows a similar pattern to the one exhibited by other related complexes, such as $IrH_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2$[539] and $Rh_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$.[397] In addition, the Ni-Pt complex shows broad, unresolved multiplets between 7.2-7.6 p.p.m. which are attributed to the phenyl protons of dppm . In addition, a resonance at 5.32 p.p.m. is attributed to the CH_2Cl_2 protons, present as solvent of crystallization.

As mentioned earlier, the structure of $NiPt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ has been confirmed unambiguously by X-ray crystallographic studies, from which it is clear (Fig.122) that the Ni and Pt atoms are each bonded to a

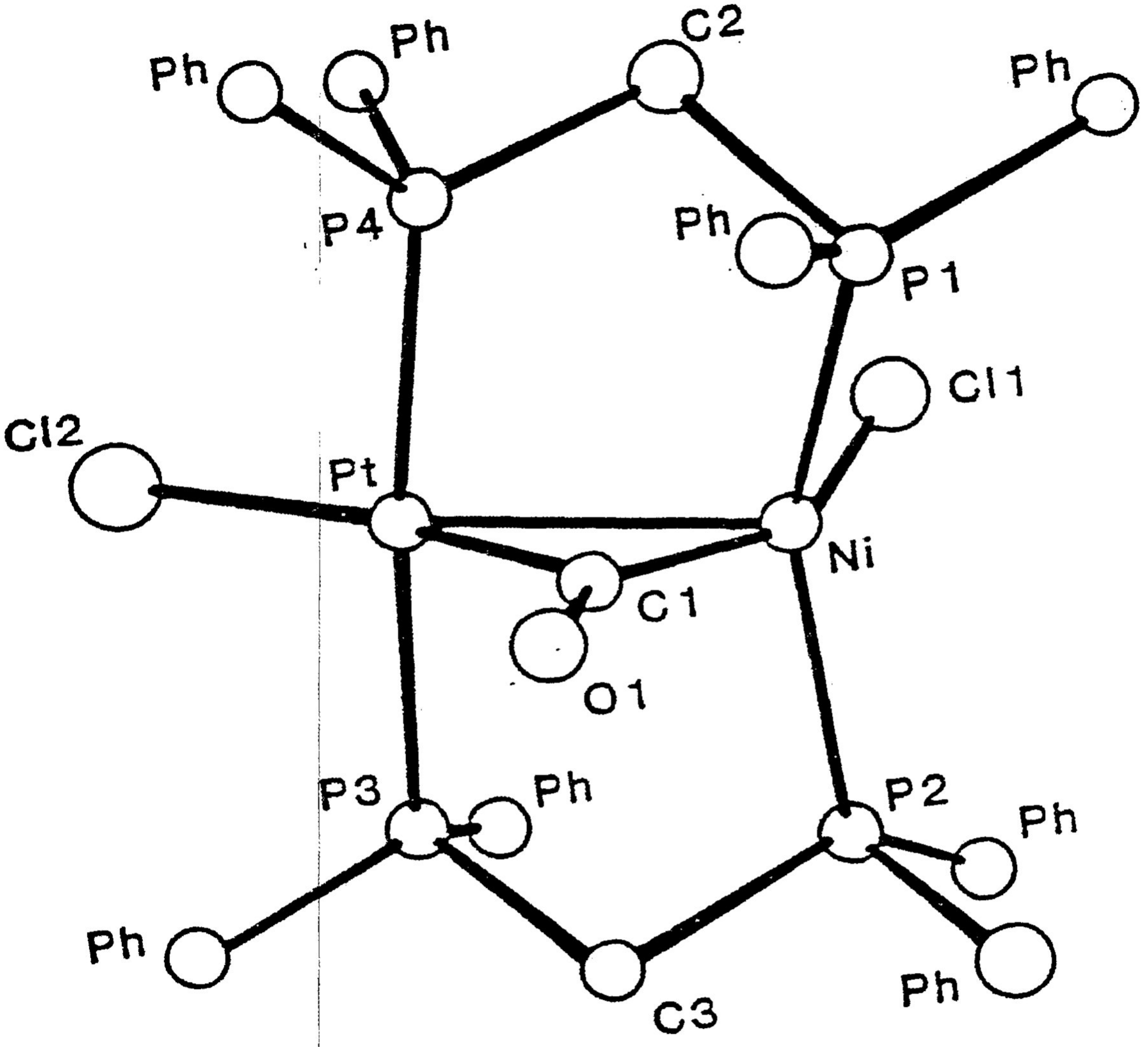


Fig. 122. X-ray Crystal Structure of NiPt(μ-CO)Cl_2(μ-dppm)$_2$.

terminal Cl atom and are bridged by two dppm ligands and one CO group. The metal, Cl and the carbonyl C atoms are essentially coplanar. Furthermore, the phosphorus atoms $P_{(3)}$ and $P_{(4)}$ are perpendicular to this plane, while the bond angles between the atoms $P_{(3)}$-Pt-$P_{(4)}$ and $Cl_{(2)}$-Pt-$C_{(1)}$ are 172.7° and 161.4° respectively, which means that the Pt atom is in an approximately square planar environment. In contrast, the geometry around the Ni atom is considerably removed from square planarity. This can be seen from the bond angles $P_{(1)}$-Ni-$P_{(2)}$ and $Cl_{(1)}$-Ni-$C_{(1)}$ which are 145.7° and 150.1° respectively and this is in fact, is closer to a tetrahedral arrangement. The Ni-Pt bond distance of 2.68Å suggests the presence of a single metal-metal bond, which would be consistent with 18 and 16 electron counts on Ni(0) and Pt(II) respectively. Alternatively, the formulation as Ni(I)-Pt(I) would require either no metal-metal bond, or a double bond for diamagnetism. The former formulation is supported to some extent by the fact that, in solution, the complex decomposes into Ni(0) and Pt(II) (^{31}P n.m.r. δ=22.2 and 64 respectively). Very recently, Jacobsen, Shaw and Pett have reported[527] that in $\mathrm{FePt}(\mu\text{-CO})(\mathrm{CO})_3\mathrm{Br}_2$ (μ-dppm), the Fe-Pt distance is 2.647Å (almost identical to the Ni-Pt distance), and on the basis of this, the presence of a single metal-metal bond has been suggested.

Moreover, X-ray crystallographic studies have shown that the Pt-Pt distances in $Pt_2Cl_2(\mu\text{-dppm})_2$ and $Pt_2(HgCl_2)Cl_2(\mu\text{-dppm})_2$ are 2.651Å and 2.712Å respectively, which further support the postulation of a Ni-Pt single bond in $NiPt(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$.

3.3.2.1.2. $NiPd(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$.

Full details of the synthesis of this complex are given in the experimental section. It is prepared from the reaction of a 1:1 molar mixture of $Ni(CO)_2(\eta^1\text{-dppm})_2$ and $PdCl_2$, in water and acetone under N_2 (The water is necessary to dissolve the $PdCl_2$ which is insoluble in organic solvents). The reaction is rapid and an intensely coloured greenish-purple solution is formed. Deep green microcrystals were formed over a period of two weeks, after carefully setting a layer of hexane over the reaction filtrate.

This diamagnetic complex is stable indefinitely in the solid state if stored under nitrogen. In contrast to $NiPt(\mu\text{-CO})Cl_2(\mu\text{-dppm})_2$, the Ni-Pd complex is highly soluble in dichloromethane although the solutions decompose with in an hour, if exposed to atmospheric oxygen. Decomposition also occurs in solution above room temperature.

Chemical analyses suggest that the complex has an empirical formula of $NiPd(CO)Cl_2(dppm)_2.H_2O$ The presence of water is supported by the i.r. spectrum which shows a broad band at 3460 cm^{-1} which may be attributed due to an O-H stretching frequency. In addition, there is a medium intensity band at 1788 cm^{-1} and a very weak band at 1712 $cm.^{-1}$ The former is attributed to the CO group bridging the two metal atoms. This frequency is 32 cm^{-1} higher in energy than the analogous Ni-Pt complex (discussed earlier). The band at 1712 cm^{-1} probably results from an impurity in the sample.

The ^{31}P n.m.r. spectrum in dichloromethane solution shows (Fig.123) two sets of complex multiplets centered at δ= 26.3 and δ= 20.4 and a singlet at δ= -3.3. Clearly some decomposition occurred during the spectral run making a full analysis difficult, although careful inspection shows that the two multiplets are very similar to each other and appears to be an AA'BB' spin pattern. In fact, the spectrum is very similar to that of $NiPt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ discussed earlier. The multiplet at δ=26.3 is attributed to the P

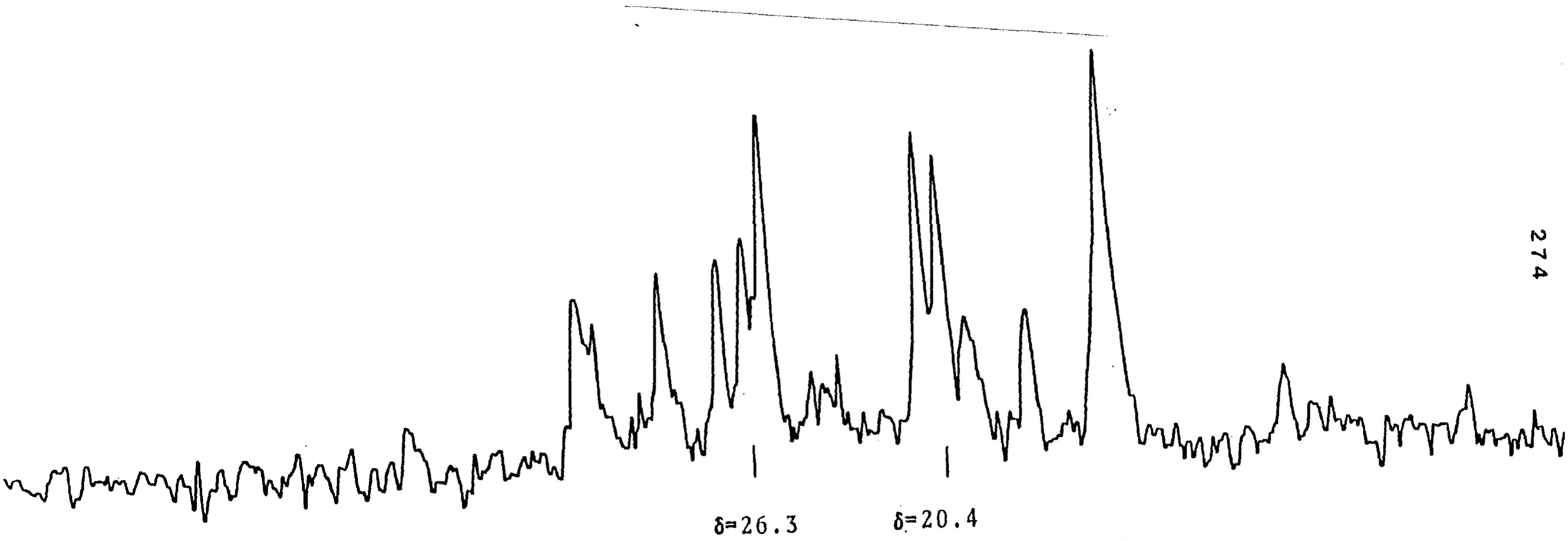


Fig. 123. ^{31}Pn.m.r. Spectrum of NiPd(μ-CO)Cl$_2$(μ-dppm)$_2$.

atoms bonded to the Ni, while the multiplet at δ=20.4 is assigned to the P atoms bonded to the Pd. The latter shows rather broader signals than the multiplet at δ=26.3 indicating that some changes are occurring at the Pd environment. This is probably due to the fact that the Pd is more likely than the Ni atom to lose a CO group in solution. For example, studies on $PdPt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ show that this complex does not lose CO as readily as does $Pd_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ but probably more readily than does $Pt_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$.[476] The signal at δ= -3.3 may be assigned to dppm coordinated in a chelating mode to Pd. This is also supported by the fact that decomposition of $Ni(CO)_2(\eta^1\text{-}dppm)_2$ leads to the cradle complex $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$, $Ni(CO)_4(\mu\text{-}dppm)_2$ and free dppm. Thus, decomposition at the Ni site will be more likely to form the above mentioned complexes preferentially.

The ^1H n.m.r. spectrum in CD_2Cl_2 solution for $NiPd(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ shows two unresolved complex multiplets due to non equivalent methylene protons of the dppm ligand centered at δ=3.69 and 4.25p.p.m. Sample decomposition, once again, precluded any detailed analysis. However, the pattern appears similar to that observed for $NiPt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$. In addition, it shows broad multiplets due to the phenyl protons of dppm in the region 7.25-8.10 p.p.m.

Finally, the X-ray powder diffraction patterns of the Ni-Pt and Ni-Pd complexes are identical, strongly suggesting that the two complexes have very similar geometries. Thus, as with the Ni-Pt compound, the most reasonable electronic arrangement would be Ni(0) and Pd(II) atoms [Fig.118(d)].

3.3.2.1.3. $Ni_2(\mu-CO)Cl_2(\mu-dppm)_2$.

This complex is prepared (see experimental) from 1:1 mixtures of $Ni(CO)_2(\eta^1-dppm)_2$ and $NiCl_2.6H_2O$ in a mixed solvent system under nitrogen. This reaction is also very rapid and the deep green solution which forms produced deep green microcrystals over a two day period after a layer of hexane was carefully added to the solution.

The green diamagnetic complex is stable indefinitely in the solid state under nitrogen and, like the Ni-Pd complex discussed earlier, is highly soluble in dichloromethane. However, these solutions decompose within one hour, even under an inert atmosphere, to

$Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$. Chemical analyses are consistent with the empirical formula $Ni_2(CO)Cl_2(dppm)_2$.

The infrared spectrum shows a medium intensity absorption band at 1769 cm^{-1}, consistent with a CO group bridging the two nickel atoms. The analogous palladium[476] and platinum[479] complexes exhibit νCO bands at 1705 and 1638 cm^{-1} respectively as has been mentioned earlier. These i.r. frequencies clearly decrease in the order Ni-Ni>Ni-Pd>Ni-Pt with the Ni-Pd value being very close to the average of the other two. It is interesting to note that a very similar situation arises in the i.r. frequencies of $M_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ (M=Ni,Pd and Pt).[479,476]

The ^{31}P n.m.r. spectrum of $Ni_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ in dichloromethane shows a single resonance at δ=22.2. This indicates that in solution all P atoms are in a magnetically equivalent environment, at least on the n.m.r. time scale. Similar observations have been reported earlier for the analogous Pt complex,[479] where both metals have been suggested to be in the +1 oxidation state, which is supported by the fact that the neutral CO group is inserted into the Pt-Pt bond of the $Pt_2Cl_2(\mu\text{-}dppm)_2$. However, $Ni_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ is prepared by a different route, where Ni(0) and Ni(II) were reacted together in a manner similar to that used for the synthesis of the Ni(0)-Pt(II) complex dicussed earlier. On the basis of this reasoning, it is suggested that it may have produced a mixed oxidation state Ni(0)-Ni(II) complex [Fig.118(e)], analogous to that of the Ni(0)-Pt(II) complex and, in the solid state, it may have a tetrahedral geometry around Ni(0) and probably square planar around Ni(II). However, in solution only an averge of these two geometries is observed, making the P atoms magnetically equivalent. Alternatively, it may have produced a Ni(I) dimeric species with no metal-metal bond which would be analogous to $Pd_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$[24] and $Pt_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$[479] reported earlier. A single crystal X-ray diffraction study would be highly desirable.

The ^1H n.m.r. spectrum of $Ni_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ in $CDCl_3$ solution shows two broad, unresolved multiplets for the methylene protons of the dppm centered at $\delta=3.0$ and 3.6p.p.m. respectively. Although this spectrum is not very well resolved, the pattern is quite similar to that observed earlier for $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ and $NiPt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$. These characteristic multiplets occur as a result of the non equivalent methylene protons of the bridging dppm ligands in 'A frame' type complexes. In addition, this complex also shows a broad and unresolved multiplet centered at δ=7.20 p.p.m. which may be attributed to the phenyl protons of the dppm ligands.

Results from several X-ray Powder diffraction patterns were not definitive. The complex clearly diffracts poorly and the patterns are extremely weak even after long exposure times. There appears to be close similarities between the patterns of the Ni-Pd and Ni-Pt compounds but, on the basis of these results, it is not clear whether all three complexes are isostructural.

3.3.2.1.4. $NiRh(\mu-CO)(CO)_2(\mu-Cl)(\mu-dppm)_2$.

This bimetallic complex is obtained when $Ni(CO)_2(\eta^1-dppm)_2$ is treated with $Rh_2(CO)_4Cl_2$ in a 1:0.5 molar ratio in toluene/dichloromethane under CO (see experimental for details) forming a yellow microcrystalline complex of analytical purity. The presence of Ni,Rh and Cl was confirmed from the X-ray fluorescence spectrum. This diamagnetic complex is stable indefinitely under dry nitrogen, but solutions decompose when exposed to atmospheric oxygen.

Chemical analyses are consistent with the emperical formula $NiRh(CO)_3Cl(dppm)_2.1.25CH_2Cl_2$. The presence of CH_2Cl_2 is supported by a ^1H n.m.r. spectrum which shows a resonance at δ=5.32 p.p.m. for the CH_2Cl_2 protons.

The i.r. spectrum shows (Fig.124) absorptions at 2010(s),1975(vs),1965(vs) and 1878(m) cm.$^{-1}$ The lowest energy band, which is well separated from the other three, is attributed to a bridging carbonyl group. A similar value (1873 cm^{-1}) for the μ-CO of $[FePt(\mu-CO)(CO)_3(acac)(dppm)][BF_4]$ has recently been observed.[527] The remaining three absorptions are assigned to the terminal carbonyl groups.

The ^{31}P n.m.r. spectrum is shown in Fig.125 and shows two sets of three line resonances (at 32.3 MHz) centered at δ=21.5 and 18.0 respectively showing P-P coupling and, possibly, P-Rh coupling. There are apparently too few lines for a bimetallic system such as this [Fig.118(e)] where an AA'BB'X type of spectrum would be expected. It is not clear, at this stage, why such an unusual spectrum is observed, although if some of the coupling constants are nearly zero, fewer lines would

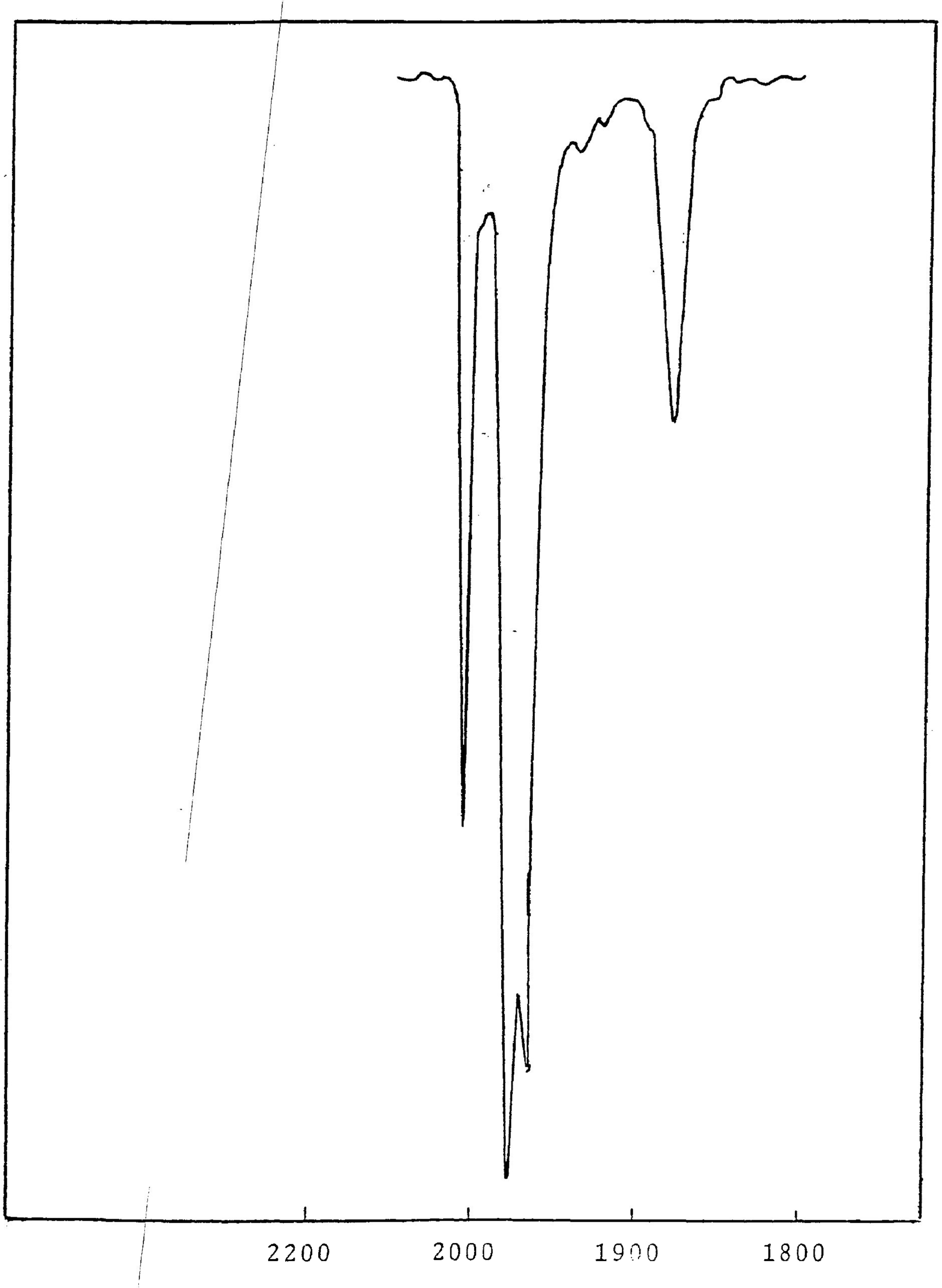


Fig. 124. Selected Features of the Infrared Spectra of NiRh(μ-CO)(CO)$_2$(μ-Cl)(μ-dppm)$_2$.

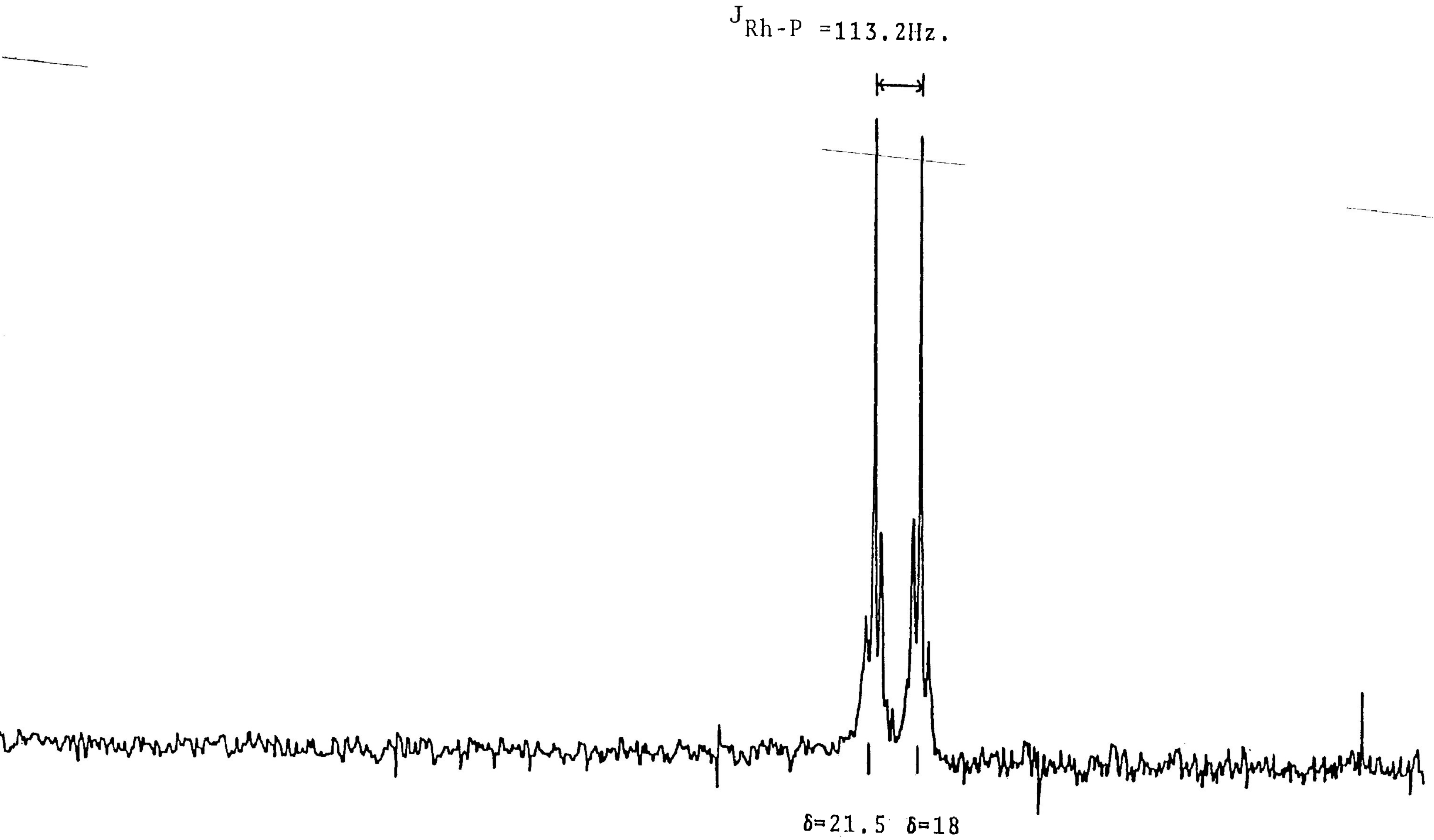


Fig. 125. ^{31}Pn.m.r. Spectrum of NiRh(μ-CO)(μ-Cl)(CO)$_2$(μ-dppm)$_2$.

result and these might not be well resolved at 32.3 MHz. A similar type of spectrum has recently been reported[528] for the related complex [PtRh(CO)(μ-MeC≡C)(MeC≡C)(μ-dppm)$_2$][Cl]. This also shows two sets of three line resonances, one centered at δ=21.1 with ^{J}Rh-P$_B$=115. and the other for the Pt bonded P atoms, centered at δ=0.3 with Pt satellites. At present, the spectrum of the Ni-Rh complex could not be analyzed further. X-ray crystallography would be highly desirable to characterize unambiguously this complex and higher field ^{31}P n.m.r. studies might also be helpful.

In addition to these reactions several others were studied in attempts to prepare more bimetallic complexes. Thus, 1:1 molar reactions between Ni(CO)$_2$(η^1-dppm)$_2$ and CoCl$_2$.6H$_2$O in benzene/ethanol produced dark brown crystals, which show CO absorptions in the i.r. spectrum at 1955(w), 1940(s) 1780(v.w) cm.$^{-1}$ and two very broad resonances probably due to paramagnetism in the ^{31}P n.m.r. spectrum because of a low yield and time limitations, further work could not be done on this species. Similar reactions were also carried out with HgCl$_2$, ZnCl$_2$ and Fe(CO)$_5$. However no complexes have yet been isolated.

3.3.3. Other reactions:

In addition to the already discussed complexes with dppm it has been observed that, when the sequence of the reaction is changed some very unusual complexes are formed. For example, when $NaBH_4$ is added quickly to a mixture of $NiCl_2.6H_2O$ and dppm (1:2.5) a green solution is formed which on treatment with CO gas produces a purple solution (see experimental)..The ^{31}P n.m.r. spectrum of the purple solution shows, in addition to other signals a triplet (~J=58Hz.) centered at δ= 239.4 and two sets of doublet resonances centered at δ= 15.3 (~J=58.4Hz) and -26.7 (~J=67.1). The chemical shift of triplet clearly indicate the formation of a species containing phosphido ligand,[529] produced from dppm by the cleavage of a P-C bond. This species may also have bridging dppm (δ=15.3). All attempts to isolate this complex by adding hexane or ethanol or by removing solvent under reduced pressure were unfortunately unsuccessful. It is not clear at this stage how or why cleavage of P-C bond occur under such mild conditions. It is interesting to note here that similar reactions with Co produced a known phosphido complex $Co_2(CO)_4(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)$.[398,530]

3.4. Reactions of Ni(II), dppe, $NaBH_4$ or $NaBH_3CN$ and CO.

It was mentioned earlier that the vast majority of dppe containing complexes involve the ligand in the chelating mode, while dppm is much more versatile in its coordination. This is mainly due to the ring strain imposed on the four-membered ring formed by chelating dppm whereas the five-membered ring formed by chelation of dppe is strain free. As a consequence of this, these two bisphosphine ligands behave in very different ways, and produce quite different products from reactions carried out under very similar conditions. In some cases there are even differences in the oxidation states of the metal ions in the complexes formed.[1]

An extensive investigation has been carried out in this study on the reactions between $NiCl_2.6H_2O$, dppe and $NaBH_4$ or $NaBH_3CN$ under a CO atmosphere. Of the several products which have been obtained, four are reasonably well characterized, although, as will be seen later, unusual features of at least one of them make confirmation of the proposed structure by X-ray methods highly desirable. The syntheses of these Ni-dppe complexes are very sensitive to such factors as the ratio of the metal to phosphine, the nature of the reducing agent ($NaBH_4$ or $NaBH_3CN$) and the time of the reactions.

3.4.1. $Ni_2(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$.

This complex can be made under a wide range of conditions, using either $NaBH_4$ or $NaBH_3CN$. Full details of the syntheses are described in the experimental section. Briefly, $NiCl_26H_2O$, dppe and $NaBH_4$ were reacted in a ratio of 1:2:2 under a slow stream of CO gas. The original dark brown solution slowly produced a yellow solid on addition of reducing agent and bright yellow crystals were obtained after recrystallization from dichloromethane and ethanol. The same complex is formed when the reaction is carried out under refluxing conditions, or when the amount of reducing agent is increased. Moreover, the reaction time can be reduced if the rate of stirring is increased, although this factor was not systematically studied. However, when the amount of dppe is increased, an orange complex, which will be discussed shortly, is obtained from the mother liquor with a smaller yield of the yellow complex in the residue.

The yellow complex is stable indefinitely in the solid state under dry nitrogen. In solution, it is stable for several days but decomposes within a few minutes if exposed to air. Moreover, above 70°C, decomposition is even faster. Analytical results are in excellent agreement with the empirical formula $Ni_2(CO)_2(dppe)_3.CH_2Cl_2$.

The i.r. spectrum is depicted in Fig.126 and shows a single very strong absorption at 1920 cm.$^{-1}$ which suggests that the CO groups are coordinated in a terminal fashion. The related Co complex $[Co(CO)_4(dppe)_3]^{2+}$ shows[401] CO absorptions at 1964 and 2012 cm^{-1}. In this, each unit of the dimer is coordinated by a chelating dppe ligand and two terminal CO groups, and the third dppe ligand bridges the two units, resulting in a trigonal bipyramidal geometry around each Co atom. Similar dppe complexes have also been reported for Mo and W.[153] A similar dimeric structure, with each Ni coordinated by a chelating phosphine and a terminal CO and linked by a single bridging dppe, is certainly a possibility for $Ni_2(CO)_2(dppe)_3$ shown in Fig.127(a) (and its analogue $Ni_2(CO)_2(dppp)_3$, see later).

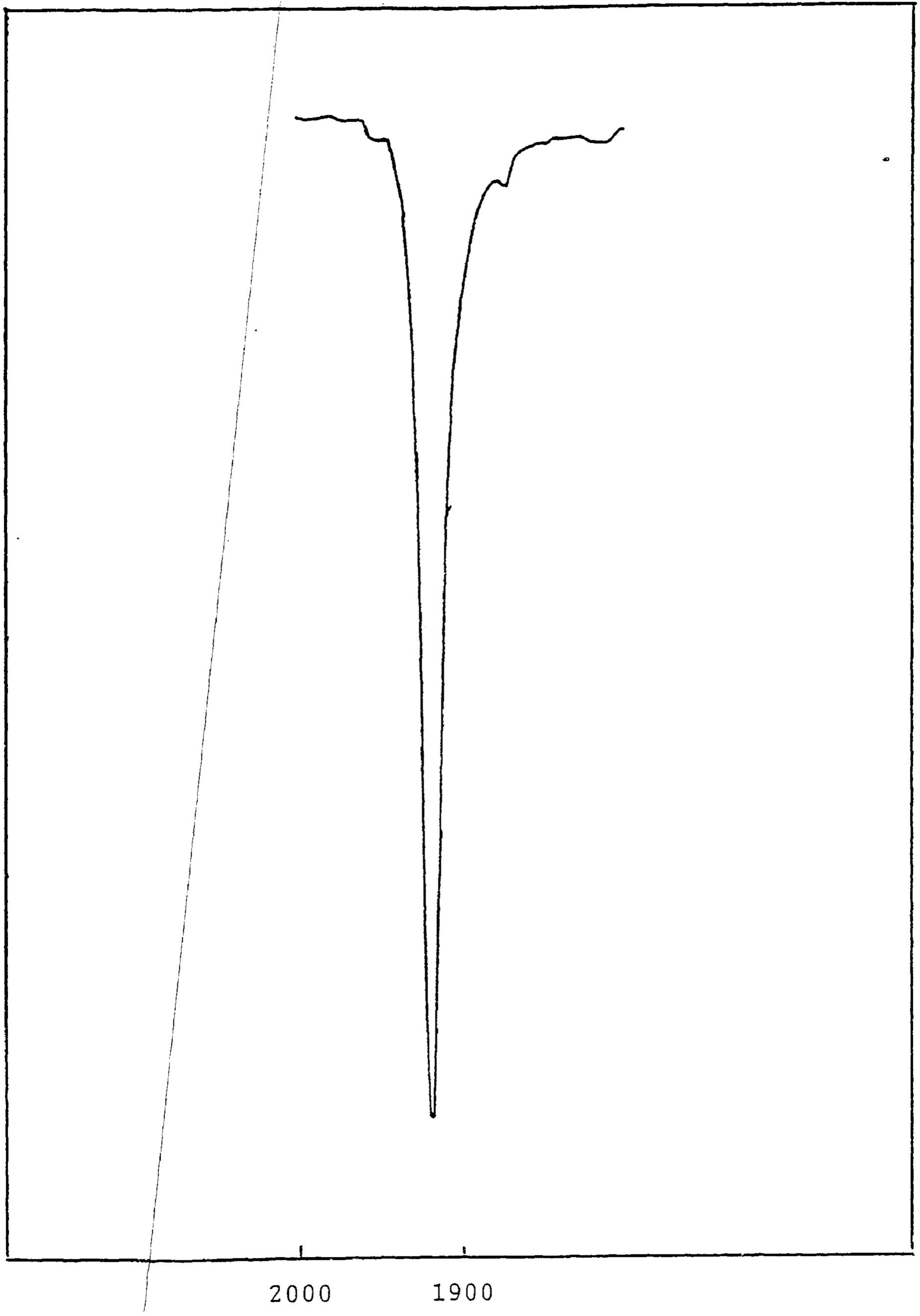
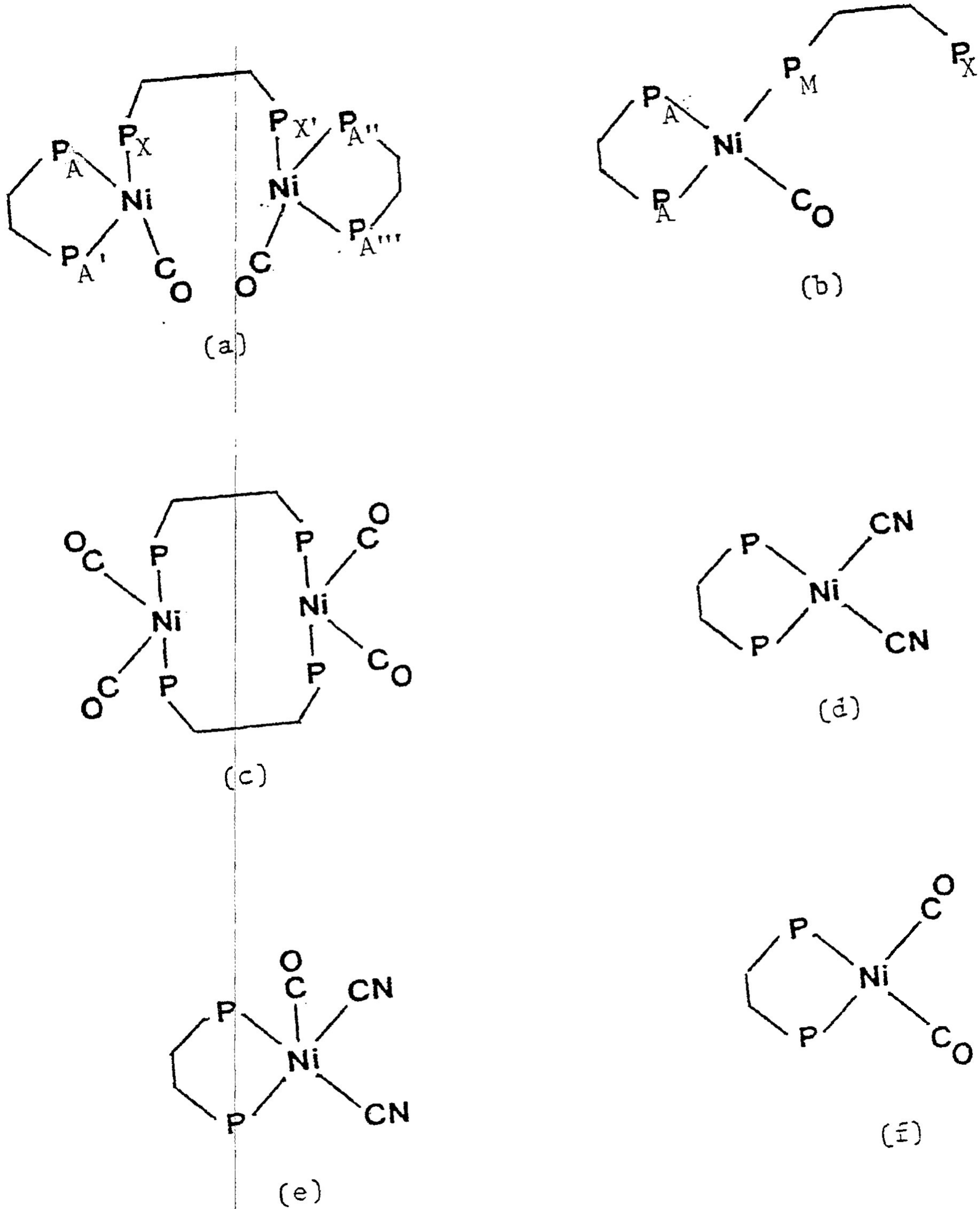


Fig. 126. Selected Features of the Infrared Spectra of $Ni_2(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$.

The ^{31}P n.m.r. spectrum of this complex is shown in Fig.128. This shows two complex multiplets, with P-P coupling, centered at δ=44.0 and 31.3. The downfield signals are attributed to the chelating P atoms, while the upfield signals are assigned to the bridging P atoms (2:1 by integration).

However, in the tetrahedrally coordinated Ni atoms of Fig.127(a), the chelating P atoms should be equivalent and therefore one would expect a highfield triplet and a doublet at lowfield, (which is indeed the case, for the related $Ni_2(CO)_2(dppp)_3$ discussed in a later section).

At first it was thought that the complex ^{31}P n.m.r. spectrum results from the couplings between P atoms rendered non equivalent due to conformational reasons[531] as shown in Fig.129. However, a variable temperature ^{31}P n.m.r. study from -70°C to +70°C (above this temperature irreversible decomposition of the complex occurs) showed no spectral changes, and therefore, this conformational cause can probably be ruled out. Furthermore, a careful inspection of the spectrum and the line separations, suggests that the



(a) (b) (c) (d) (e) (f)

Fig. 127.

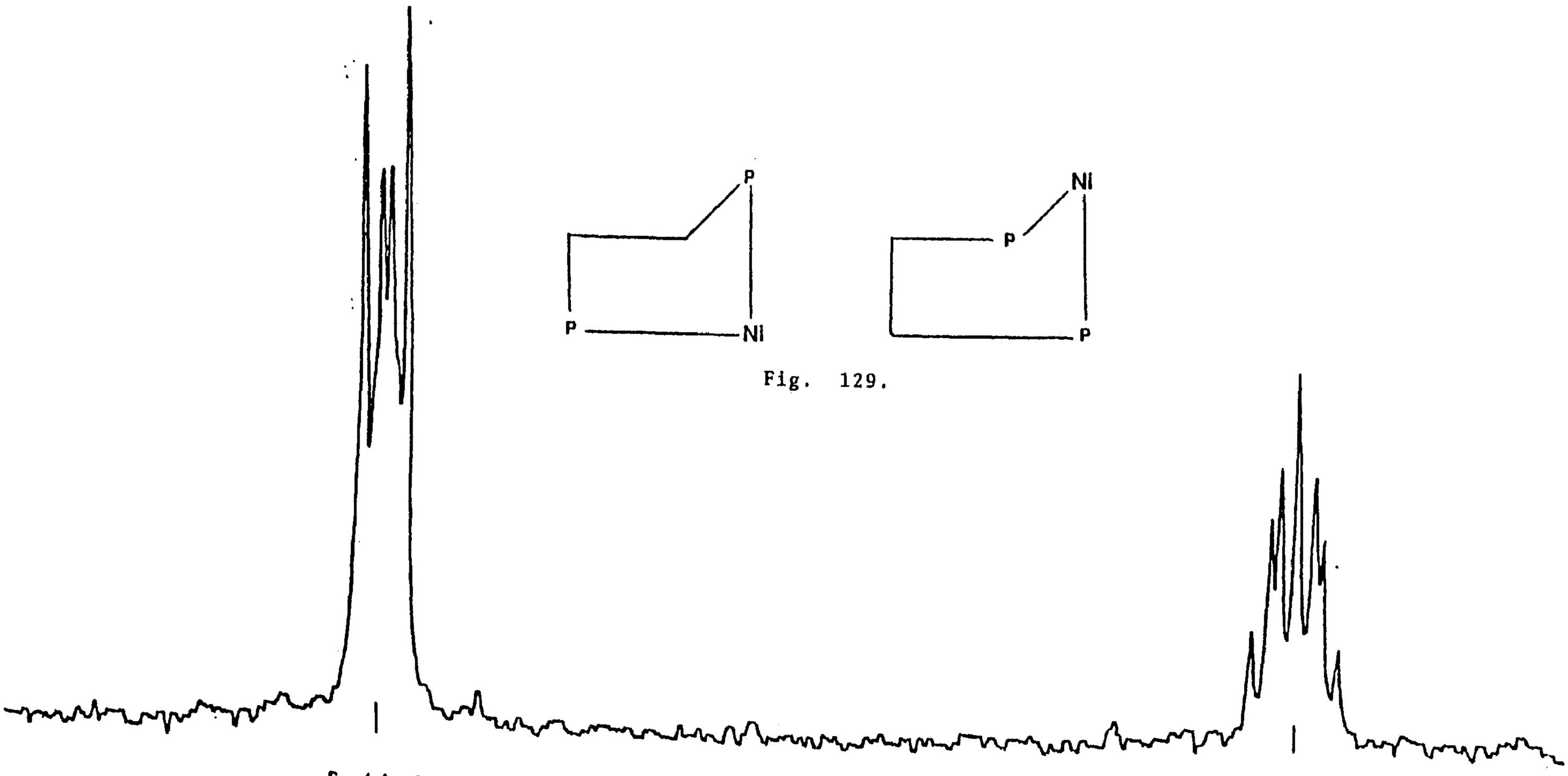


Fig. 129.

Fig. 128. ^{31}P n.m.r. Spectrum of $Ni_2(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$.

spectrum is not first order. The spectrum is more probably of the AA'A"A"'XX' type, where some of the coupling constants are close to zero, thereby reducing the number of lines normally expected for such spin systems. The complexity of this ^{31}P n.m.r. spectrum, precluded a detailed analysis and caused considerable difficulty in characterizing this complex. The presence of five-bond P-P couplings, which would be necessary for a structure like that shown in Fig.127(a) to give the spectrum observed, is unexpected.

The ^{1}H n.m.r. spectrum shows a broad unresolved multiplet and a broad doublet at 1.28 and 2.45 p.p.m., which may be attributed to the $-CH_2-$ protons of the bridging and chelating dppe ligands respectively. For the bridging dppe ligands in the complex $Cr_2(CO)_4(C_6H_6)_2(\mu\text{-dppe})$, the $-CH_2-$ protons have been reported[165] to appear at 2.20 p.p.m. Similarly the $-CH_2-$ protons for chelating dppe ligands in, for example, the complex $[Rh(\eta^2\text{-dppe})_2]^+$ have been reported[532] in the region of 2.5-3.3 p.p.m. as a multiplet. In addition, $Ni_2(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$ also shows three resonances as broad unresolved multiplets at 6.88, 7.30 and 7.65 p.p.m. due to the protons of the phenyl rings of the dppe ligands. Furthermore, it shows a resonance at 5.32 p.p.m.

for the Ch_2Cl_2 protons, which is present as solvent of crystallization even after 16-18 hours of high vacuum drying conditions.

Thus, on the basis of the above evidence, the structure shown in Fig.127(a) seems to be the most reasonable one. Each Ni atom is coordinated to a chelating dppe and a terminal CO ligand, and two such units are bridged by a third dppe ligand. The geometry around each nickel atom is expected to be distorted tetrahedral.

3.4.2. Ni(CO)(η^2-dppe)(η^1-dppe).

Reaction conditions must be carefully adjusted for the preparation of this complex. It is best prepared (see experimental) from the reaction of $NiCl_2.6H_2O$, dppe and $NaBH_3CN$ under a slow stream of carbon monoxide gas in a mixed benzene and ethanol solvent system. The course of the reaction is mainly dependent upon whether $NaBH_4$ or $NaBH_3CN$ is used and the Ni:dppe ratio. A very high yield (89 %) is obtained when $NiCl_2.6H_2O$, dppe and $NaBH_3CN$ are reacted in a ratio of 1:3:3.5. If the amount of dppe is decreased, the formation of $Ni_2(CO)_2(\eta^2\text{-dppe})_2(\mu\text{-dppe})$ occurs exclusively. If $NaBH_4$ is used, then a low yield of $Ni(CO)(\eta^2\text{-dppe})(\eta^1\text{-dppe})$ is obtained. This complex is obtained from the mother liquor by evaporating most of the solvent under reduced pressure, thus forming an orange oily substance, which is then filtered off and washed with small portions of ethanol and hexane. It is very important to dry the complex completely under reduced pressure, forming a cake like-orange substance, otherwise decomposition occurs within a few hours forming a greasy dark orange substance. Surprisingly, the product obtained after drying is in an analytically pure form. All attempts to recrystallize this compound gave crystals of $Ni_2(CO)_2(\eta^2\text{-dppe})_2(\mu\text{-dppe})$, discussed earlier.

The complex is stable indefinitely in the solid state under a dry nitrogen atmosphere, but decomposes within a few hours when exposed to air. In solution, decomposition is very rapid, if it is exposed to atmospheric oxygen. It is soluble in most organic solvents, such as ethanol, ether, benzene, toluene, dichloromethane, THF and 1,4-dioxane, etc.

Elemental analyses are in excellent agreement with the formulation of $Ni(CO)(dppe)_2$. In fact, a complex of this proposed stoichiometry was very briefly reported by Corain et.al.[446b] who treated Ni(η^2-dppe) in benzene solution with CO for about an hour. The complex was not isolated in the pure state, and its formulation was suggested only on the basis of an i.r. spectrum.

The i.r. spectrum shows a very strong band at 1918 cm^{-1} as shown in Fig.130. This suggests that the CO group is coordinated terminally to the Ni atom. This value is quite close to the value reported by Corain et.al.[446b] at 1920 $cm.^{-1}$ although they observed also a small band at 2000 cm^{-1} which they attributed to $Ni(CO)_2(\eta^2$-dppe), present as an impurity.

The ^{31}P n.m.r. spectrum of this complex in benzene solution shows three sets of resonances, each with P-P coupling, centered at $\delta=43.46$, 30.92 and -12.0 with an intensity ratio of 2:1:1 as shown in Fig.131(a). The positions of the signals at $\delta=43.96$ and -12.0 are consistent with the presence of chelating dppe and an uncoordinated P atom respectively. Given, therefore, the empirical formula of the complex and the electronic and structural requirements of Ni(0), i.e. 18 electron and a tetrahedral geometry, the structure shown in Fig.127(b) seems possible.

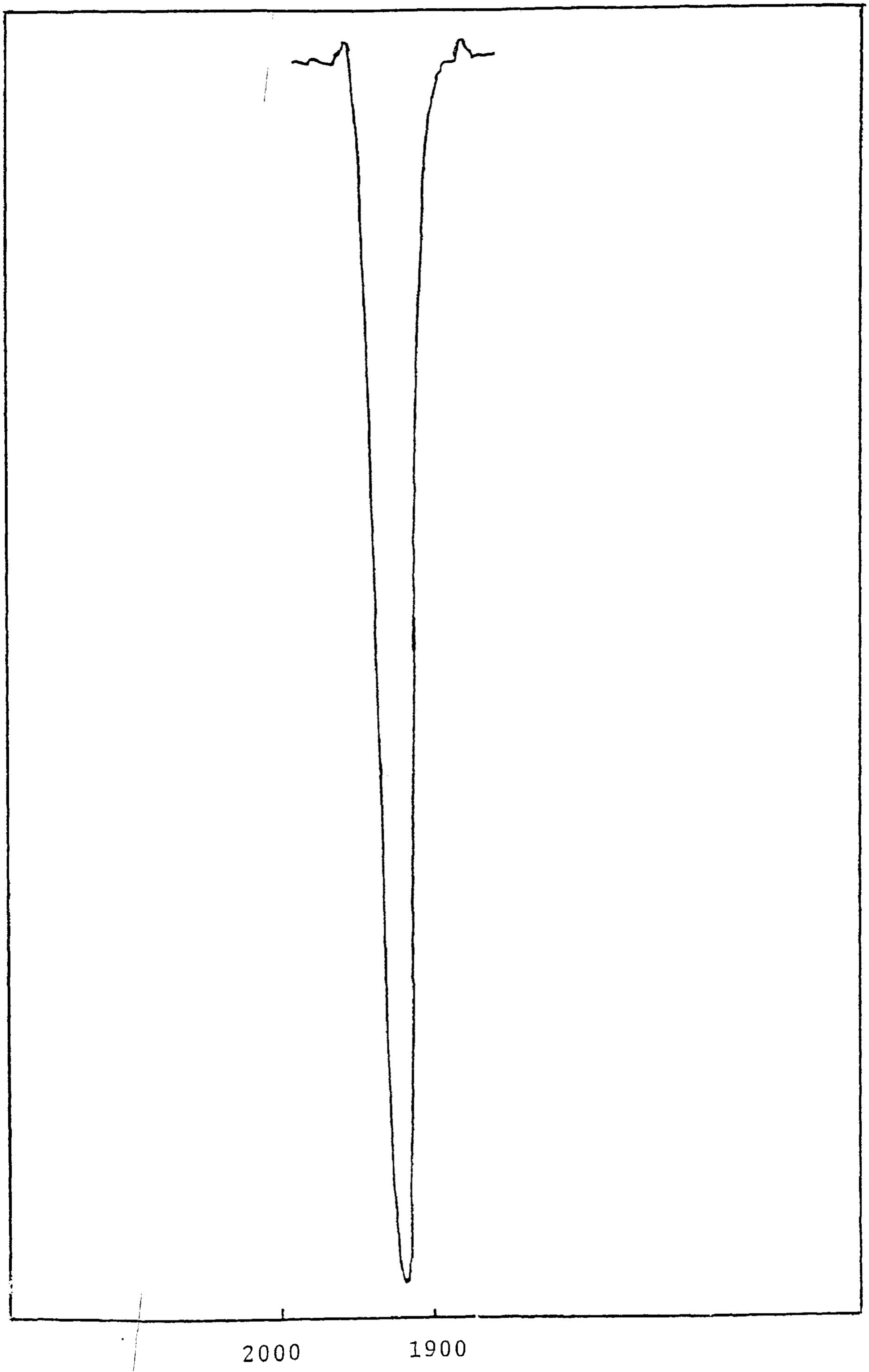


Fig. 130. Selected Features of the Infrared Spectra of Ni(CO)(η^1-dppe)(η^2-dppe).

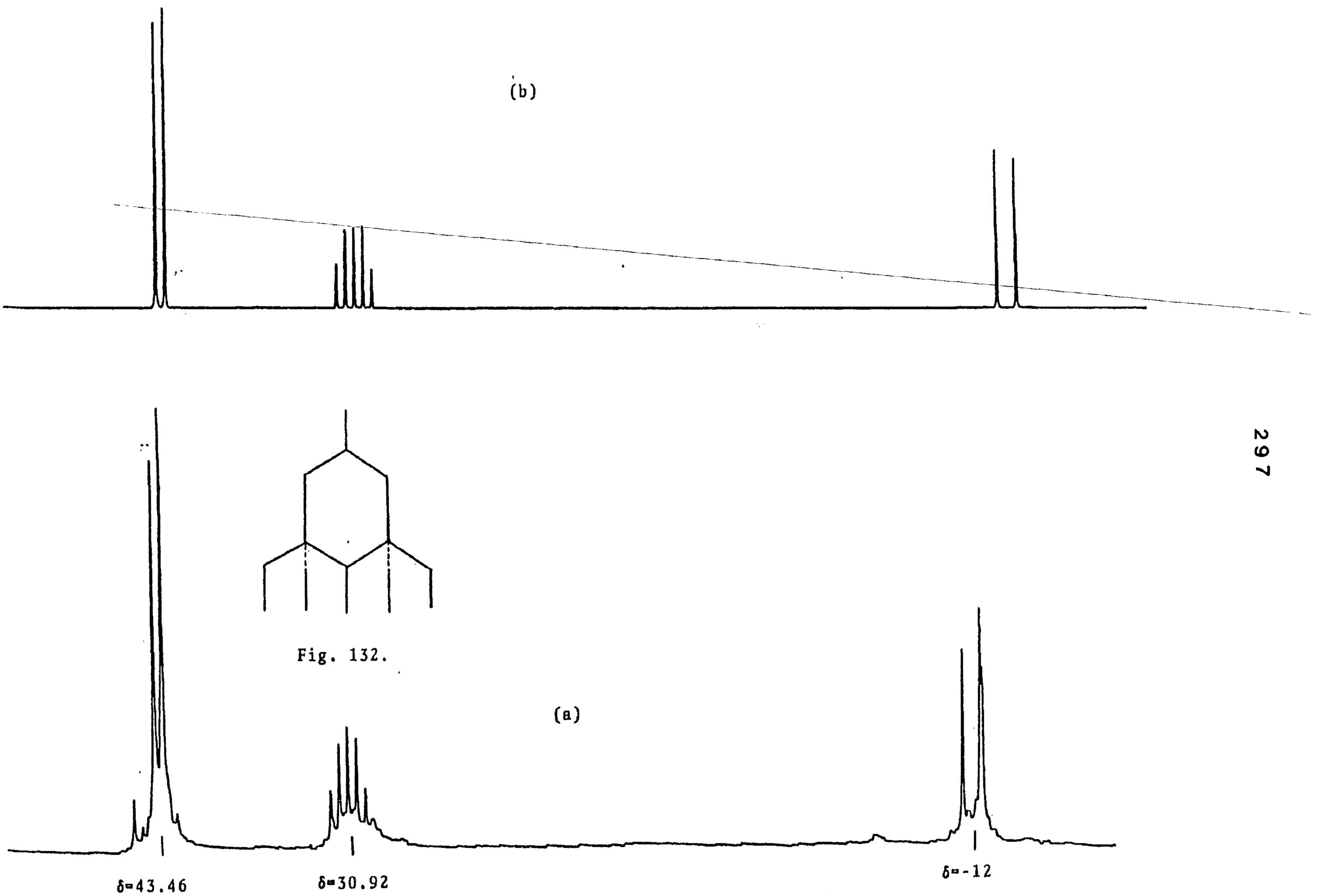


Fig. 132.

Fig. 131. ^{31}Pn.m.r. Spectrum of Ni(CO)(η^1-dppe)(η^2-dppe).

(a) Experimental (b) Simulated.

In fact, the spectrum can be analyzed as an A_2MX spin system, in which J_{MX} is almost exactly twice $^2J_{AM}$. The resonance at δ=43.96 (due to chelating P atoms) occurs as a doublet, because of coupling with the coordinated P atom P_M of the monocoordinated dppe ligand (J_{AM}= 19.0 Hz). The farthest upfield resonance (due to the uncoordinated P atom P_X of the monocoordinated dppe ligand) also occurs as a doublet, due to coupling with the coordinated P atom P_M of the monocoordinated dppe ligand (J_{MX}= 39.2 Hz). Finally, the pseudo quintet centered at δ= 30.92 with a line separation of 19Hz is assigned to P_M, the coordinated P atom of the monocoordinated dppe ligand. Coupling of P_M with P_X (to give a doublet) and with P_A (to give a doublet of triplets) is shown in Fig.132, and the resulting pattern appears as an apparent quintet because of the chance relationship between J_{MX} and J_{AM}. On this basis, the spectrum was simulated by the computer and the simulated spectrum is shown in Fig.**b**. A similar spectral pattern has been reported for <u>fac</u>-Mo(CO)$_3$(η^2-dppm)(η^1-dppm) by Isaacs and Graham.[176] However for this complex, the signals of the chelating P atoms are upfield of the monocoordinated P signals, consistent with the ring size effect[229] for the four membered ring.

The ^{1}H n.m.r. spectrum of Ni(CO)(η^2-

dppe)(η^1-dppe) shows resonances due to the $-CH_2-$ protons of dppe at δ=2.1 (broad) and δ=2.42 (broad doublet) p.p.m. The former is attributed to the $-CH_2-$ protons of monocoordinated dppe, while the latter are due to the $-CH_2-$ protons of the chelating dppe ligand. Similar δ values of $-CH_2-$ protons have been reported for $Cr(CO)_2(C_6H_6)(\eta^1$-dppe) [2.22-2.44 p.p.m. (multiplet)][168] and $[Rh(\eta^2$-dppe$)_2]^+$ [2.5-3.3 p.p.m. (broad)][532]. Moreover, Ni(CO)(η^2-dppe)(η^1-dppe) also exhibits three broad unresolved multiplets in the region 7-7.7 p.p.m. due to the phenyl protons of the dppe ligands.

Molecular weight determination by the osmometric method, in benzene solution, gave a value of 688 for Ni(CO)(η^2-dppe)(η^1-dppe). The expected value is 882.7.

Thus, all the evidence supports the structure depicted in Fig.127(b) in which the Ni atom has a basic tetrahedral geometry. Clearly, one of the dppe ligands is chelating while the other is bonded through only one of the P atoms leaving the other atom uncoordinated.

3.4.2.1. Reactions of Ni(CO)(η^1-dppe)(η^2-dppe).

As mentioned earlier, complexes with bisphosphine ligands coordinated through only one of the P atoms are very reactive (see section 3.2.). The interesting complex, Ni(CO)(η^1-dppe)(η^2-dppe) is expected to show a similar behaviour, and indeed it reacts with $Ni(CO)_4$, $Pt(COD)Cl_2$, $Mo(CO)_6$ and $Fe(CO)_5$. Unfortunately none of the products of these reactions could be isolated, although evidence for the presence of bimetallic complexes was seen in the ^{31}P n.m.r. spectra of reactions involving $Ni(CO)_4$ and $Mo(CO)_6$.

Thus, when $Ni(CO)_4$ is bubbled through a dichloromethane solution of Ni(CO)(η^1-dppe)(η^2-dppe) for about ten minutes, an orange-yellow solution is formed. The ^{31}P n.m.r. spectrum of this shows, in addition to some weak resonances, a strong signal at δ=37. This is consistent with dppe being coordinated in a bridging fashion with magnetically equivalent P atoms. Similar chemical shift valus for the bridging dppe ligand were observed for the $Ni(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$ complex discussed earlier. All attempts to isolate the complex by adding ethanol or hexane were unsuccessful, and on removing the solvent under reduced pressure, a mixture is obtained which decomposes on recrystallization making it very difficult to obtain a pure product. The infrared spectrum on the solid shows absorptions at 2088(s) and 2000(vs,br) cm^{-1} which is consistent with CO groups coordinated terminally to the Ni atoms. It is likely that the same complex was obtained in solution by irradiating $Mo(CO)_6$ in THF with UV light under N_2 [$Mo(CO)_6$ is irradiated with UV light to cleave CO group(s)] and then treating it with Ni(CO)(η^1-dppe(η^2-dppe). The resulting yellow solution shows a single resonance in the ^{31}P n.m.r. spectrum at δ=35 (THF) compared to δ=37 (CH_2Cl_2 see above). The difference in the chemical shifts is probably due to solvent effects and $Mo(CO)_6$ does not appear to be involved. All attempts to isolate this complex, which seems to be a dppe bridged Ni-CO dimer [Fig.127(c)], were unsuccessful.

Similar reactions of Ni(CO)(η^1-dppe)(η^2-dppe) with $Pt(COD)Cl_2$ in a 1:1 molar ratio resulted in the formation of an orange-purple solution. The ^{31}P n.m.r. spectrum shows the formation of a mixture of complexes. The resonance at δ=42.1, with Pt satellites (^{J}Pt-P=1810Hz), may be assigned to the known[529] species $PtCl_2$(η^2-dppe), while the other complexes present in the solution could not be identified. Also, reactions between

$Fe(CO)_5$ and $Ni(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ resulted in the formation of a mixture of complexes, although there is some indication of the formation of a heterobimetallic complex. The ^{31}P n.m.r. shows three sets of complex multiplets centered at δ=68.9, 44.0 and 27.2. A pure complex has not yet been isolated, and clearly more work is needed before any further comments can be made.

3.4.3. $Ni(CN)_2(\eta^2\text{-dppe})$.

This dppe complex is obtained when reactions between $NiCl_2.6H_2O$, dppe and $NaBH_3CN$ were carried out (see experimental) in a molar ratio of 1:3:5 under a slow stream of CO gas at 0°C. The brown suspension so formed was filtered off and the residue was redissolved in dichloromethane. Addition of ethanol produced two crops of yellow crystals (discussed earlier) which were removed and finally, after two weeks at room temperature red crystals were produced.

The red crystals are diamagnetic and, in the solid state, are stable indefinitely under nitrogen. Solutions very slowly decompose on exposure to atmospheric oxygen.

The chemical analyses are consistent with the formulation of $Ni(CN)_2(dppe).EtOH$. The presence of ethanol is supported by the i.r. spectrum which shows a broad absorption at 3420 cm^{-1} which is attributed to the O-H stretching frequency. In addition the i.r. spectrum shows a strong absorption at 2121 cm^{-1} (Fig.133(a) assigned to the νCN stretching frequency[533] which is similar to that reported[534] for the $PtH(CN)(PPh_3)_2$ at 2146 $cm.^{-1}$.

The ^{31}P n.m.r. spectrum shows a strong single resonance at δ=59.6, confirming that both P atoms are magnetically equivalent. This large chemical shift represents a rather large coordination shift of about 72.8 p.p.m. downfield from the resonance due to the free dppe ligand which appears at 13.2. This is consistent with a chelating dppe, since the resulting five membered ring causes strong deshielding.[529]

The ^{1}H n.m.r. spectrum shows a broad resonance at δ=3.62 p.p.m., assigned to the $-CH_2-$ protons of dppe. A similar shift in the region of 2.5-3.3 p.p.m. was observed[532] for the $-CH_2-$ protons in $[Rh(\eta^2\text{-dppe})]^{2+}$. In addition, the ^{1}H n.m.r. spectrum shows an unresolved

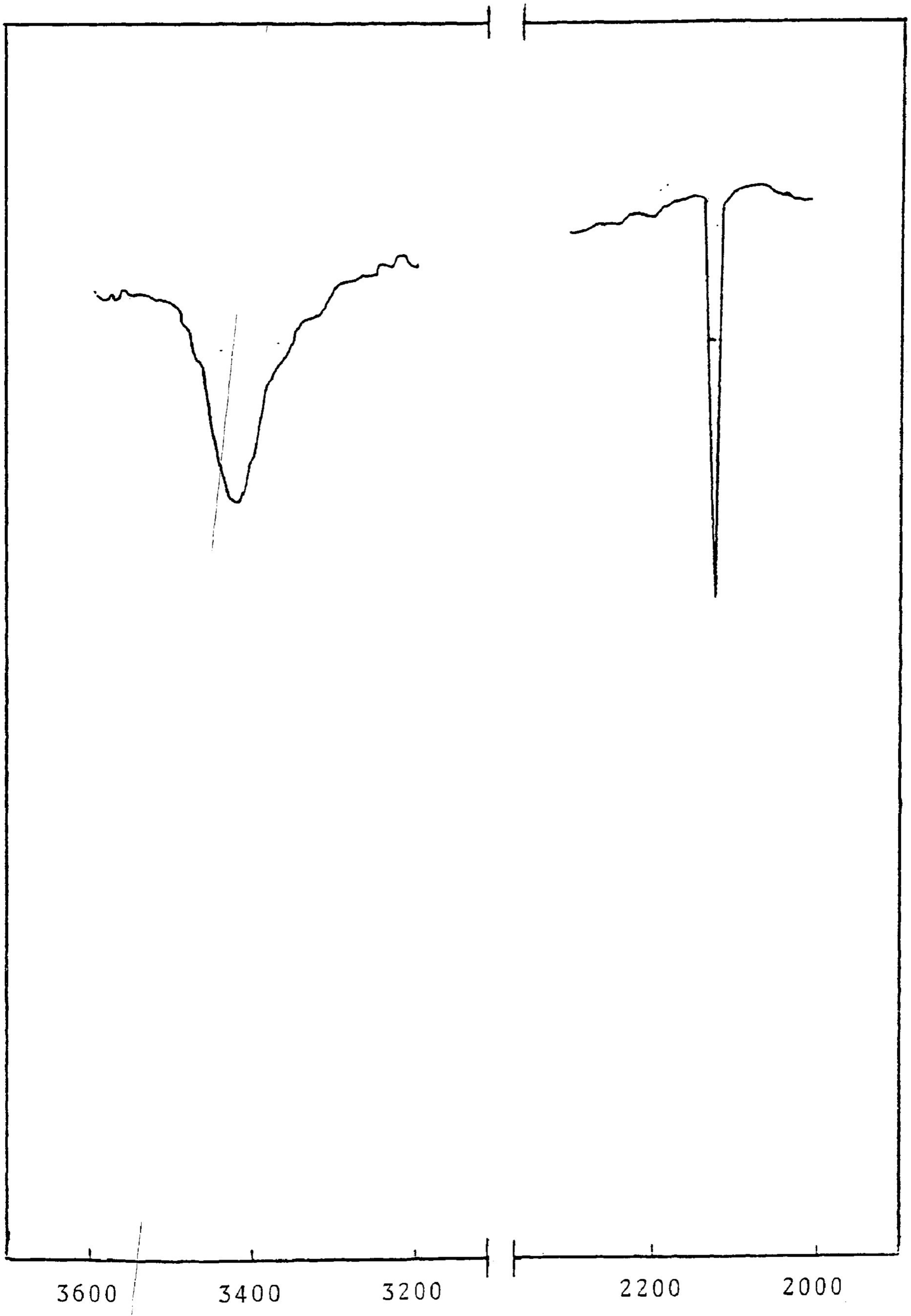


Fig.133 (a). Selected Features of the Infrared Spectra of $Ni(CN)_2(\eta^2\text{-dppe})$.

broad multiplet resonance centered at δ=7.0 p.p.m. attributed to the phenyl protons of the dppe ligand.

On the basis of the above evidence, it is reasonable to assign this complex the structure shown in Fig.127 where nickel(II) is coordinated to two CN groups and a chelating dppe ligand. Ready cleavage of the B-C bond of BH_3CN^- has been seen before.[505,535]

$Ni(CO)(CN)_2(\eta^2$-dppe).

Details of the synthesis of this complex are given in section 2. However, briefly, it was prepared when $NiCl_2.6H_2O$, dppe and $NaBH_3CN$ were reacted in a molar ratio of 1:2:2 in a mixed solvent (toluene/ethanol) system. The mother liquor (i.e. reaction filtrate) was allowed to stand for about one week at room temprature. It was then concentrated under a dry nitrogen flow and the first crop of orange solid was filtered off. The solution was further concentrated to minimum volume, forming red microcrystals.

The red diamagnetic solid is insoluble in most organic solvents except DMF. In the solid state, it is stable indefinitely under dry nitrogen, but solutions decompose on exposure to atmospheric oxygen.

Chemical analyses suggest the formulation of $Ni(CO)(CN)_2(dppe).0.25EtOH$. The presence of ethanol is supported by an i.r. absorption at 3420 $cm.^{-1}$ In addition, the i.r. spectrum shows absorptions at 2121(m) and 1912(s) $cm.^{-1}$ [Fig.133(b)]. The former band is attributed to the CN stretching frequency[533,534] which is at almost the same frequency as for the CN in $Ni(CN)_2(dppe)$ discussed earlier. The latter band is attributed to the stretching frequency of a terminally coordinated CO group.

The ^{31}P n.m.r. spectrum shows a single strong resonance at δ=59.7 due to chelating dppe.

Thus, from the available evidence, it is reasonable to assign to this complex the structure shown in Fig.127(e), where five coordinated nickel(II) is in a square pyramidal geometry, basal positions are occupied with two terminally bonded CN groups and a chelating dppe ligand, while CO occupies an apical position, thus making both phosphorus atoms equivalent.

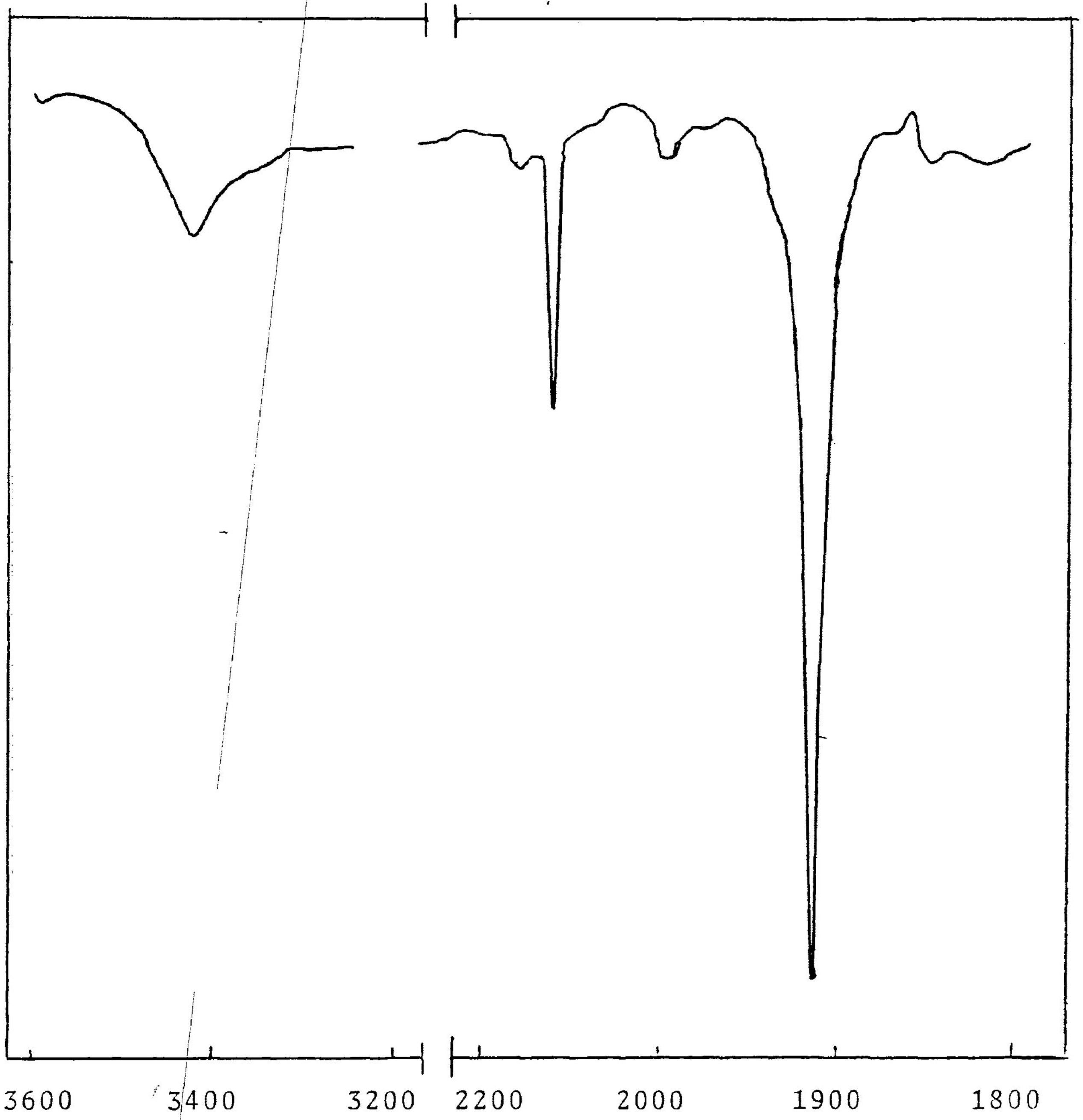


Fig. 133(b). Selected Features of the Infrared Spectra of $Ni(CO)(CN)_2(\eta^2\text{-dppe})$.

3.4.5. $Ni(CO)_2(\eta^2\text{-dppe})$.

Evidence of this complex has been observed in solutions from two different reactions, and although it was not isolated in the solid state, it is tentatively formulated on the basis of ^{31}P n.m.r. data as the known species[446] $Ni(CO)_2(\eta^2\text{-dppe})$. The complex can be prepared by reacting, in a 1:1 molar ratio, either $Ni(CO)_2(PPh_3)_2$ or $Ni(CO)_2(\eta^1\text{-dppm})_2$ with dppe, forming a yellow air sensitive solution. All attempts to precipitate a solid by adding hexane or ethanol to the reaction solution were unsuccessful.

The ^{31}P n.m.r. spectrum of the reaction solutions show, in addition to weak resonances due to starting materials, free dppe and either free PPh_3 or dppm depending on the starting complex, a very strong signal at $\delta=44.5$, which is attributed to the coordinated dppe. Such a large shift is consistent with the ligand being chelated to the Ni atom [Fig.127(f)]. The analogous $Ni(CO)_2(\eta^2\text{-depe})$ complex, which also has a chelating ligand, shows[529] a single resonance in the ^{31}P n.m.r. spectrum at $\delta=48.6$.

3.5. Reactions involving other phosphines.

Although most of the work described in this thesis involves complexes of dppm and dppe, some exploratory reactions were carried out with cis-dppe and longer carbon chain phosphine ligands such as dppp, dppb and dpppe. With the exception of dppp, most of the complexes formed in these reactions have not yet been fully characterized and the following results and formulations are tentative.

3.5.0. Reactions of $NiCl_2.6H_2O$,dppp,$NaBH_4$ or $NaBH_3CN$ and CO.

The clean, very reproducible, reactions between Ni(II), dppp and $NaBH_4$ or $NaBH_3CN$ have produced only nickel(0) species, $Ni_2(CO)_2(dppp)_3$ and $Ni(CO)_2(dppp)$.

3.5.0.1. $Ni_2(CO)_2(\mu\text{-dppp})(\eta^2\text{-dppp})_2$.

Full details of the synthesis of the complex are given in the experimental section. Very briefly, $NiCl_2.6H_2O$, dppp and $NaBH_4$ were reacted in a 1:2:2 molar ratio under a slow stream of CO. Reactions go smoothly to completion within 40 minutes of the addition of $NaBH_4$, and the yellow precipitate which forms was recrystallized from benzene and ethanol to yield a yellow microcrystalline product.

The diamagnetic complex is stable in the solid state for several months under nitrogen, but in solution, decomposition is faster when it is exposed to oxygen.

Elemental analyses are consistent with the formulation of $Ni_2(CO)_2(dppp)_3.2EtOH$. The presence of ethanol is supported by the i.r. spectrum, which shows a broad absorption in the region of 3300-3500 $cm.^{-1}$ and absorptions at 1275 and 1030 $cm.^{-1}$ due to the O-H stretching, O-H bending and C-O stretching modes respectively. In addition, νCO bands (Fig.134) at 1970(sh),1930(v.s.),1915(v.s.),1875(w) and 1817(v.w.)cm^{-1} suggest that both CO groups are coordinated to the Ni atom in a terminal fashion. The compound [Fig.135(a)] appears therefore to be similar to $Ni(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$ with one bridging phosphine (discussed earlier) although this shows, as expected, one very strong and

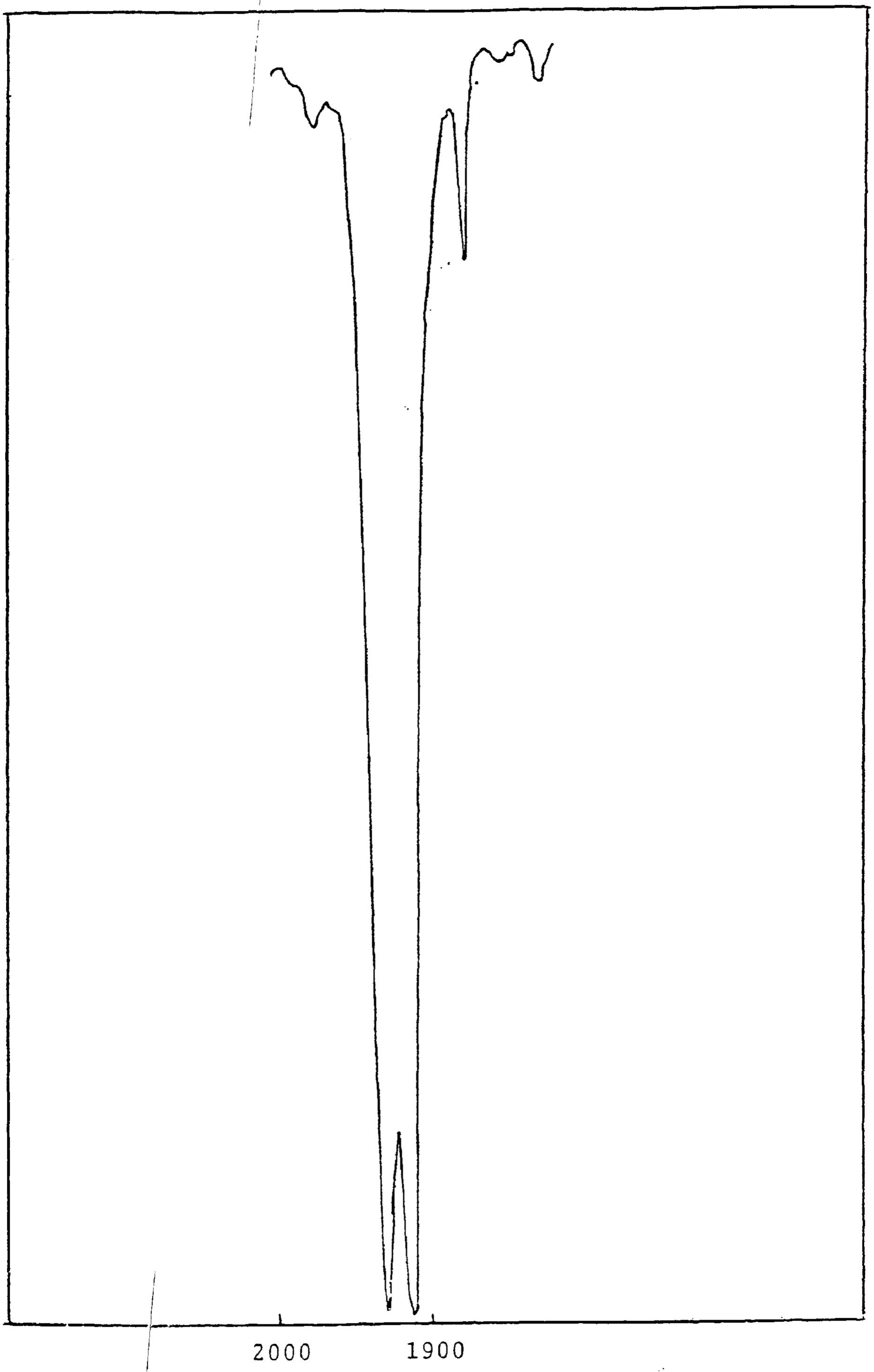
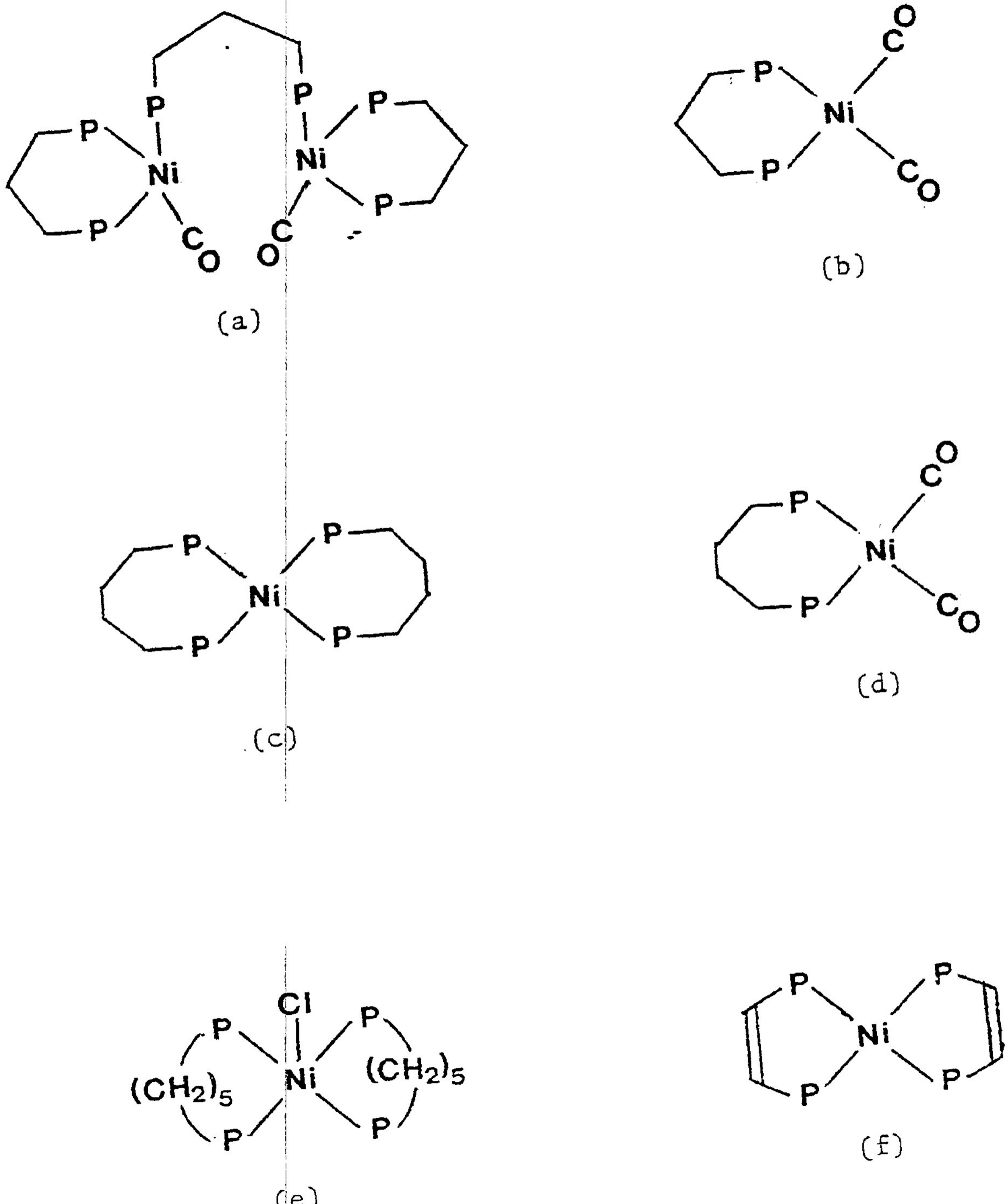


Fig. 134. Selected Features of the Infrared Spectra of $Ni_2(CO)_2(\mu\text{-dppp})(\eta^2\text{-dppp})_2$.



(a)

(b)

(c)

(d)

(e)

(f)

Fig. 135.

broad absorption at 1918 $cm.^{-1}$ in the terminal CO region. However, if each Ni atom has local C_{3V} symmetry, only one CO band (A_1) is expected, and indeed one band has been observed in the related complexes $Ni(CO)(PF_3)_3$ and $Ni(CO)(PMe_3)_3$ (2073 and 1917 $cm.^{-1}$ respectively).[536] Moreover, the complex $Ni(CO)(\eta^1\text{-dppp})(\eta^2\text{-dppp})$[446] also shows a single absorption at 1910 $cm.^{-1}$

The ^{31}P n.m.r. spectrum in benzene solution is illustrated in Fig.136(a) and shows two sets of resonances, each with P-P coupling, centered at δ=13.16 and 26.1 with an intensity ratio of 2:1. In fact, the spectrum can be analyzed as a typical A_2X spin system (J=17.7 Hz). The resonance at δ=13.16 is assigned to the two magnetically equivalent chelating P atoms, P_A, [Fig.135(a)] which splits into a doublet due to coupling with the P atom, P_X, of the bridging dppp ligand while the resonance centered at δ=26.1 is assigned to P_X , the bridging P atoms of the dppp ligand which splits into a triplet because of coupling with the two magnetically equivalent chelating P atoms, P_A. This ^{31}P n.m.r. spectrum was simulated on the basis of the above parameters by computer and this simulation is shown in Fig.136(b). This further confirms the structural assignment made above. The assigned chemical shift values for the bridging and chelating dppp ligands are similar to literature values for related complexes. Thus,

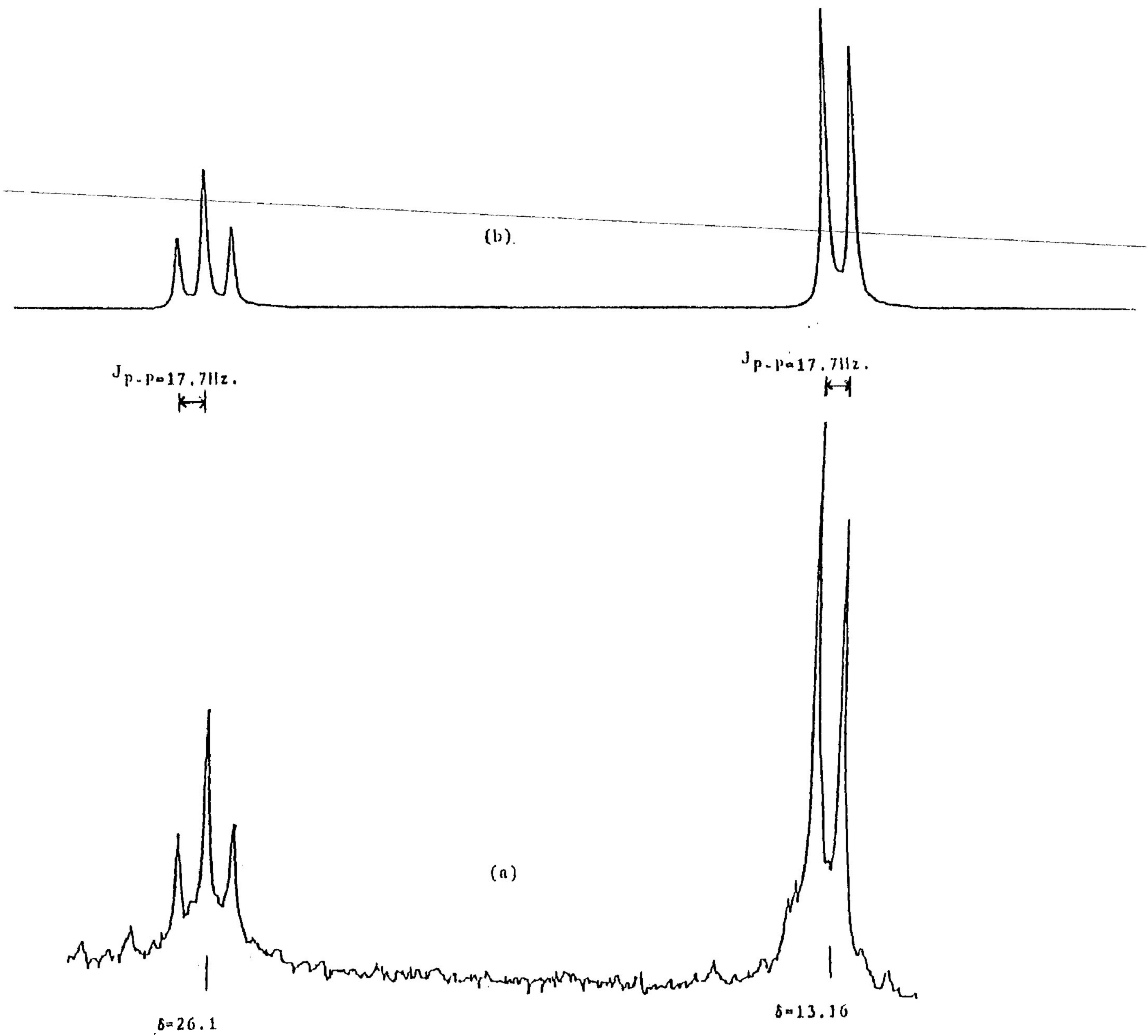


Fig. 136. ^{31}P n.m.r. Spectrum of $Ni_2(CO)_2(\mu\text{-dppp})(\eta^2\text{-dppp})_2$.

(a) Experimental (b) Simulated.

$Mo_2(CO)_{10}(\mu\text{-dppp})$ exhibits a single resonance in the ^{31}P n.m.r. at δ=27.59 (bridging dppp)[164] while $PdCl_2(\eta^2\text{-dppp})$ also shows a single resonance at δ=12.9 (chelating dppp).[15] Morever, it was shown earlier that the ^{31}P chemical shift for a six membered ring appears upfield of that for a five membered ring[527] and, indeed, a comparison of the spectrum of $Ni_2(CO)_2(\mu\text{-dppe})(\eta^2\text{-dppe})_2$ with the above complex illustrates this trend.

Thus, in solution, it is clear that the compound has the dimeric structure depicted in Fig.135(a), although there are apparently some distortions in the solid state.

3.5.0.2. $Ni(CO)_2(\eta^2\text{-dppp})$.

This complex is best made when $NiCl_2.6H_2O$, dppp and $NaBH_3CN$ are reacted in a 1:2:1 molar ratio under a slow stream of CO gas (see experimental). The red solution so formed was concentrated under reduced pressure after ten days of room temperature standing. Pink microcrystals were obtained.

The diamagnetic complex is stable

indefinitely in the solid state under dry nitrogen. However, solutions slowly decomposes on exposure to atmospheric oxygen. Elemental analyses are in excellent agreement with the empirical formula $Ni(CO)_2(dppp)$.

The i.r. spectrum is shown in Fig.137 and it shows νCO absorptions at 1992(v.s),1975(sh),1930(v.s) and 1878(w) cm^{-1} consistent with both CO groups being coordinated terminally to the Ni atom. With C_{2V} symmetry, two bands (A_1 and B_1) are expected and, indeed, in the related $Ni(CO)_2(\eta^2\text{-dppe})$ complex two absorptions have been reported[536] at 2000. and 1937 cm^{-1}. It is possible that the other two bands at 1975 and 1898 cm^{-1} in $Ni(CO)_2(\eta^2\text{-dppp})$ are due to distortions in the solid state. Further more, this i.r. spectrum shows a very close similarity to that of $Ni(CO)_2(PPh_3)_2$ and $Ni(CO)_2(\eta^1\text{-dppm})_2$ discussed earlier, where the basically tetrahedral Ni(0) atoms also have C_{2V} symmetry.

The ^{31}P n.m.r. spectrum in benzene solution shows a single resonance at δ=15.3 consistent with the phosphine coordinated in a chelating fashion. Both the P atoms are in magnetically equivalent environments. A similar chemical shift has been

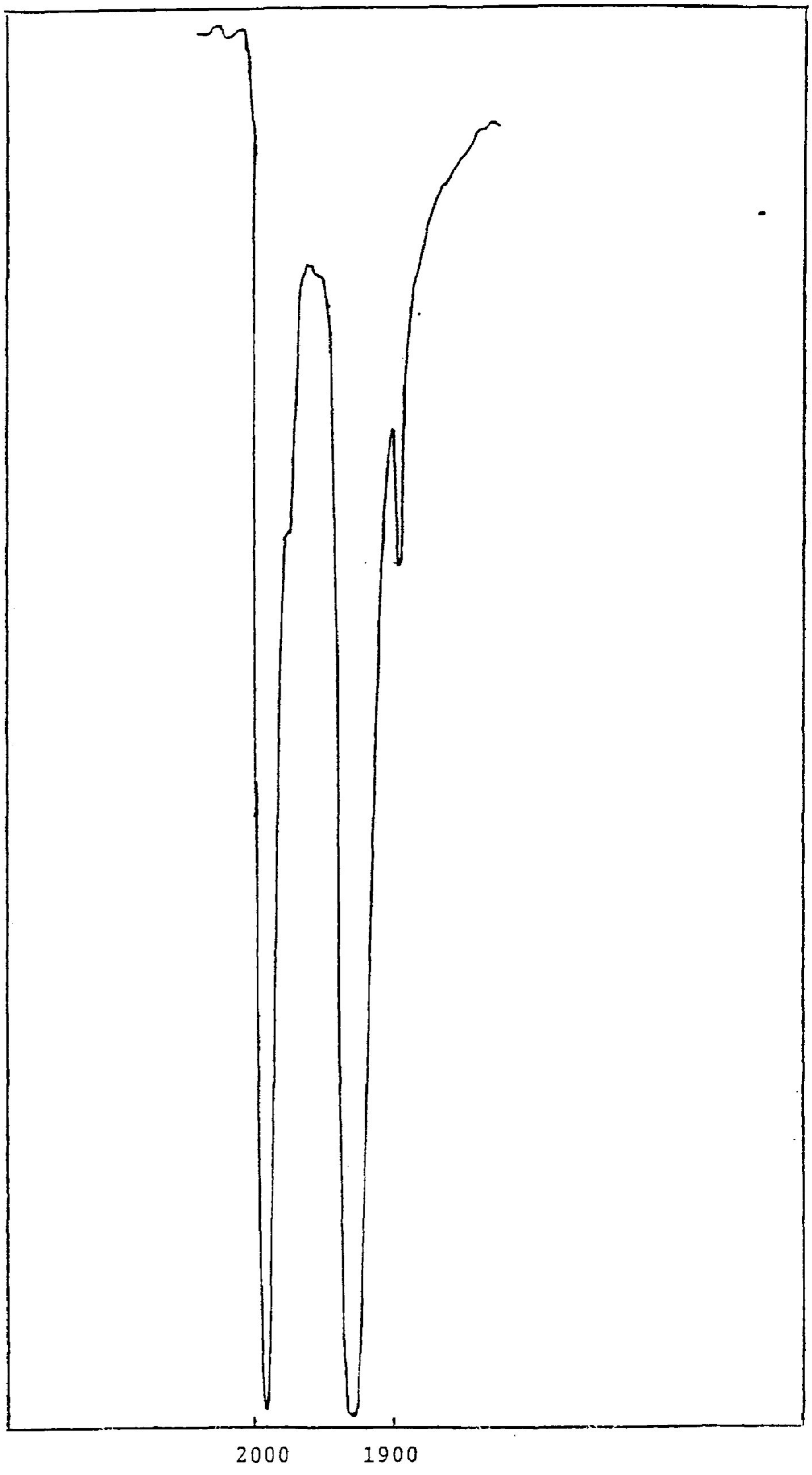


Fig. 137. Selected features of the Infrared Spectra of $Ni(CO)_2(\eta^2\text{-dppp})$.

reported[15] for the related $PdCl_2(\eta^2$-dppp) complex, which shows a single resonance at δ=12.9 attributed to chelating dppp. Furthermore, the chelating phosphorus atoms in $Ni_2(CO)_2(\mu$-dppp)(η^2-dppp) discussed earlier give a resonance at δ= 13.16.

The ^1H n.m.r. spectrum of $Ni(CO)_2(\eta^2$-dppp) did not give any information for the $P-CH_2-CH_2-CH_2-P$ protons. However, it shows a complex multiplet centered at δ=7.55 p.p.m. which may be assigned to the phenyl protons of the dppp ligand.

A molecular weight determination by the osmometric method in benzene shows a molecular weight of 497 as compared to the expected value of 526.7 for the monomeric species. Thus, all the available evidence is consistent with the structure shown in Fig.135(b), in which the Ni atom has a basic tetrahedral geometry.

3.5.1. Reactions of $NiCl_2.6H_2O$,dppb,$NaBH_4$ or $NaBH_3CN$ and CO.

When a still longer backbone carbon chain length phosphine ligand such as dppb is used it was possible to isolate two products, as reported below.

3.5.1.1. Ni(η^2-dppb)$_2$.

In a typical reaction(see experimental) $NiCl_2.6H_2O$, dppb and $NaBH_4$ were reacted in a molar ratio of 1:2:14.5 in a mixed solvent (toluene/ethanol) system under a slow stream of CO, forming an orange-red suspension. This was filtered off and a red crystalline complex was isolated from the filtrate over a period of two days after adding ethanol (smaller quantities of $NaBH_4$ leads to the formation of mixture of complexes which could not be isolated).

The red diamagnetic crystals are stable indefinitely in the solid state under nitrogen. However, solutions are extremely air sensitive and the slightest exposure to atmospheric oxygen results in decomposition. Decomposition is very rapid above room temperature.

Elemental analyses suggest an empirical formula of Ni(dppb)$_2$.0.5EtOH. The presence of ethanol is supported by the i.r. spectrum which shows a weak broad absorption in the region of 3500-3300 cm^{-1} for νO-H of EtOH. Bands at 1275 and 1030 cm^{-1} occur due to the O-H bending and C-O stretching modes of ethanol respectively.[537] No other significant absorptions were observed in the i.r. spectrum.

The ^{31}P n.m.r. spectrum in dichloromethane shows a resonance at δ=30.7. Because of the sensitivity of the compound, it is difficult to obtain a clean spectrum, and usually a second peak at δ=31.2 due to a decomposition product is visible. The chemical shift at δ=30.7 is consistent with dppb being coordinated in a chelating mode[529] with the P atoms in a magnetically equivalent environment. A similar chemical shift value of δ=31.4 has been reported[122] for the chelating dppb ligand in $Nb(CO)_4(dppb)$.

Thus, the available evidence supports the suggestion that this complex is a simple tetrahedral Ni(0) complex as shown in Fig.135(c).

3.5.1.2. $Ni(CO)_2(\eta^2\text{-dppb})$.

This complex is isolated when $NiCl_2.6H_2O$, dppb and $NaBH_3CN$ are reacted in a 1:2:4 molar ratio under a slow stream of CO (see experimental for details), forming a dirty-gray suspension which was filtered off. A pale-yellow complex was obtained from the filtrate when ethanol was added and the solution allowed to stand for a period of four weeks.

The pale-yellow complex is virtually insoluble in most organic solvents. It appears to be the most soluble in dichloromethane but only dilute solutions could be obtained. In the solid state, it is stable indefinitely under nitrogen, but decomposition occurs in solution within a few minutes when it is exposed to atmospheric oxygen. Solutions are also unstable above room temperature.

Elemental analyses are in excellent agreement with the empirical formula $Ni(CO)_2(dppb).0.75C_6H_6$. The presence of benzene is further supported by the mass spectrum which shows peaks at 78,77,76 and 75.

This i.r. spectrum shows absorptions at 3065 and 3042 cm^{-1} for the C-H stretching frequency of the aromatic group[537] (benzene solvent) and an additional pair of absorptions at 1588 and 1572 cm^{-1} due to ring breathing vibrations of the benzene.[537] In addition it shows νCO bands at 1998(v.s), 1935(v.s) and 1912(s) cm^{-1} suggesting that the CO groups are coordinated in a terminal fashion. The characteristic features of the i.r. spectrum are shown in Fig.138. The band at 1935 cm^{-1} seems to be split into two bands (1935 and 1912 cm^{-1}) probably due to stronger distortions in the solid state caused by the larger ring size. Furthermore, when the carbonyl region in the i.r. spectrum of $Ni(CO)_2(\eta^2\text{-dppb})$ [if the peak at 1912 cm^{-1} is ignored] is compared with $Ni(CO)_2(PPh_3)_2$, $Ni(CO)_2(\eta^1\text{-dppm})_2$ and $Ni(CO)_2(\eta^2\text{-dppp})$ complexes discussed earlier, a similar pattern could easily be established. The line separation between the two most strong bands in all cases is found to be ~60 $cm.^{-1}$ In fact, the spectrum of $Ni(CO)_2(PPh_3)_2$ very closely resembles this spectrum [see Fig.110 for the $Ni(CO)_2(PPh_3)_2$ complex].

The ^{31}P n.m.r. spectrum in dichloromethane solution shows a strong singlet resonance at δ=24.4 and additional signals probably due to decomposition products at δ=24.9 and 30.6. The resonance at δ=24.4 is consistent with the dppb being coordinated in a chelating fashion[122,529] with magnetically equivalent P atoms.

Thus, on the basis of the above evidence, it is very reasonable to assign the structure of this complex as shown in Fig.135(d) where tetrahedral

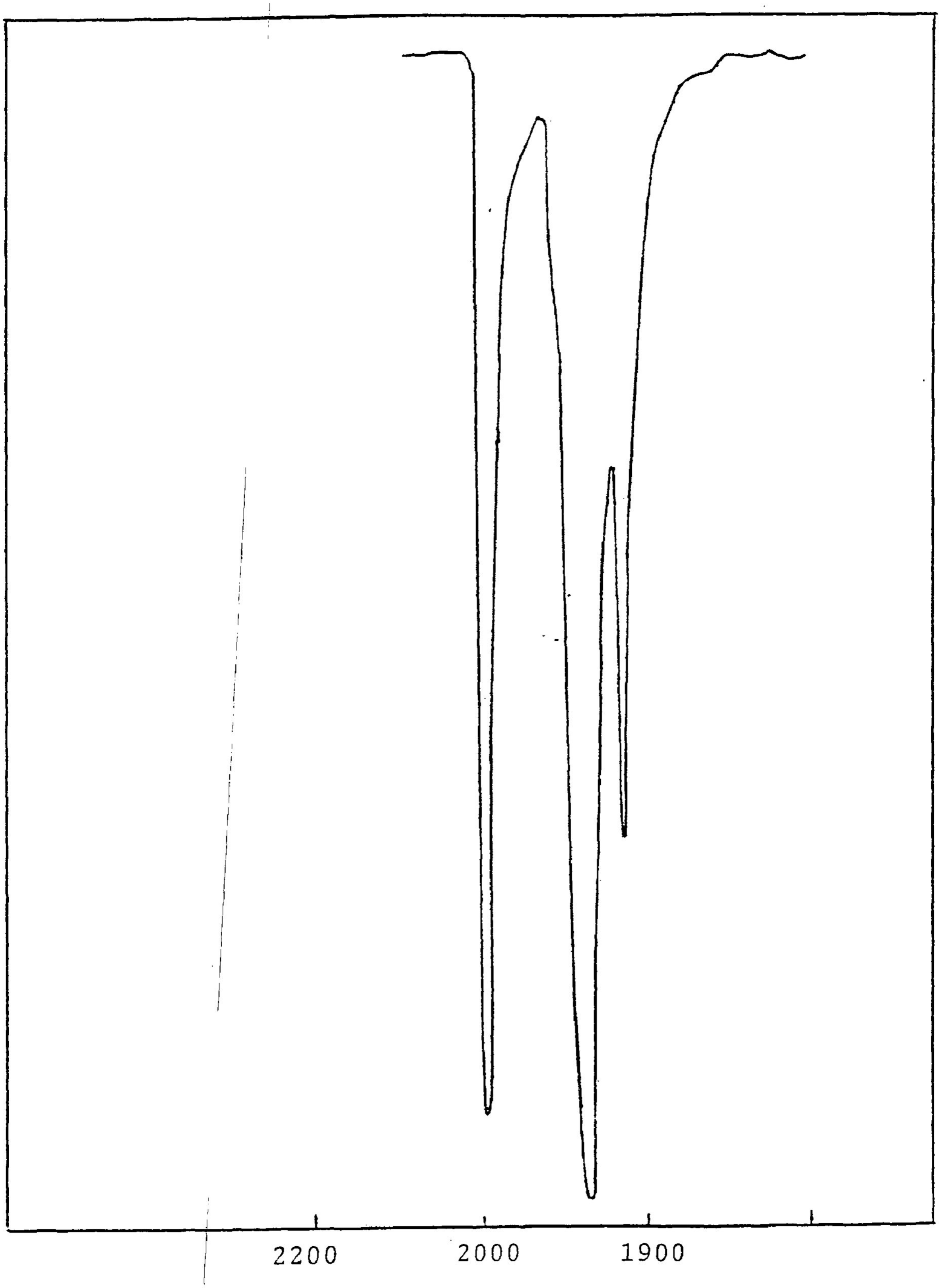


Fig. 138. Selected Features of the Infrared Spectra of $Ni(CO)_2(\eta^2\text{-dppb})$.

nickel(0) is bonded with two terminal CO groups and a chelating dppb ligand.

3.5.2. NiCl(η^2-dpppe).

From several reactions carried out with this ligand only one complex could be isolated. Thus, $NiCl_2.6H_2O$, dpppe and $NaBH_4$ were reacted in a molar ratio of 1:2:2 in toluene/ethanol under a slow stream of CO. The greenish-gray solid so formed was redissolved in DMF and ether was added, some pink crystals were formed over a period of four months.

The pink paramagnetic crystals are stable indefinitely under nitrogen, but solutions decompose on contact with atmospheric oxygen.

Chemical analyses are consistent with the formulation $NiCl(dpppe)_2.1.75DMF0.25EtOH$. The presence of DMF is supported by the i.r. spectrum which shows and a broad absorption at $3370cm^{-1}$ a medium intensity at 1680 cm^{-1}(Fig.139), attributed to the (O-H) and $\nu C=O$ frequencies of EtOH and DMF.[537] No signal in the ^{31}P n.m.r. spectrum could be observed due to paramagnetism.

Thus, on the basis of the above (somewhat limited) evidence, a tentative structure is assigned to this species which is shown in Fig.135(e), where five coordinated Ni(I) is in a square pyramidal geometry with two chelating dpppe ligands and an apical chloride group.

3.5.3. Ni(η^2-cis-dppee)$_2$.

As mentioned earlier only exploratory reactions were carried out with this ligand. In a typical synthesis $NiCl_2.6H_2O$, *cis*-dppee and $NaBH_3CN$ were reacted in a molar ratio of 1:2:3 in a mixed solvent (benzene/ethanol) system, under a slow stream of CO. This forms a red solution, from which red crystals were isolated over a period of four days after adding hexane.

The diamagnetic, red crystalline species is stable indefinitely under nitrogen, but solutions decomposes when exposed to atmospheric oxygen. Chemical analyses are consistent with the empirical formula Ni(*cis*-dppe)$_2$, which is a known complex.[505]

The infrared spectrum shows no significant absorptions in the region of 2400-1600 cm^{-1}. The ^{31}P n.m.r. spectrum in dichloromethane solutions show a sharp singlet at δ=50, suggesting that P atoms of cis-dppee are magnetically equivalent. The large chemical shift is consistent with a five membered ring system[329] and chelating phosphines.

Thus, the compound most likely contains a Ni(0) atom tetrahedrally coordinated by two chelating cis-dppee ligands as shown in Fig.135(f).

3.6. Conclusions.

It is clear from the discussion that reduction of Ni(II) salts by a combination of either $NaBH_4$ or $NaBH_3CN$ and CO is one of the most convenient routes to low valent phosphine-substituted Ni-carbonyl complexes. Other work in this laboratory has established that this is also true for cobalt. This route not only avoids the direct use of metal carbonyls (which is sometimes inconvenient, expensive or time consuming) but also gives some unusual and novel products.

It is also evident, that the reactions involving dppm are fundamentally different from reactions with the other bis phosphines studied. For example, in most cases, dppm is coordinated in a bridging mode, although, monodentate coordination has been observed in this and in related work.[532] The other bisphosphines generally adopt the chelating mode.

Reactions with $NaBH_3CN$ are easier to control, more versatile and produce novel monocoordinated bisphosphine complexes (dppm,dppe), whereas reactions with $NaBH_4$ are generally faster and more difficult to control. Higher metal to ligand ratios play an important role in the production of the intermediate, monocoordinated bisphosphine complexes. These intermediates are very reactive and are excellent precursors of a variety of hetero and homobimetallic complexes. In most cases, reactions are rapid under normal conditions, and constitute a very convenient route for the syntheses of such complexes.

In addition, $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ is also very reactive towards a variety of molecules. In some cases, the metal-metal bond is retained but in others, oxidative addition occurs which may have implications in catalytic processes.

There are also indications of the formation of phosphido complexes, formed by cleavage of dppm, under the mildest conditions yet observed. More work is necessary, but preliminary observations suggest that this may result in an entirely new synthetic route towards phosphido compounds.

Finally, from a synthetic point of view, it has to be emphasised that reaction conditions, such as ratios of metal to ligand to reducing agent, duration of the reaction, nature of both the phosphine and the reducing agent and the temperature all play an important role in the reactions and can have major influences not only on the nature of the product(s) which result(s) but also on the reproducibility of the reactions.

A combination of infrared and ^{31}P n.m.r. spectroscopy has been shown to be powerful tools in characterizing these complexes. Extensive use has been made of i.r. criteria already in the literature to distinguish between bridging and terminal carbonyl groups. Furthermore, ^{31}P chemical shifts and splitting patterns have proved to be extremely useful in assesing whether phosphines are chelating, bridging or monocoordinated. Computer simulations and integration of signals in ^{31}P n.m.r. spectra were also helpful in establishing structures.

Finally, X-ray crystallography has proved to be vital for the absolute characterization of complexes like $NiPt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$.

3.7. Suggestions:

Some very interesting substituted carbonyl complexes have been obtained in this study of the reduction of Ni(II) salts by $NaBH_4$ or $NaBH_3CN$ in the presence of phosphines under a CO atmosphere. Some of these reactions have proved to be far more complex than had been expected.

The work described in this thesis clearly shows that these reactions are a most convenient route to make phosphine-substituted carbonyl complexes. Although extensive work has been done on dppm and dppe, there is still room for further work with these ligands under different conditions such as (i) increasing the reaction times (ii) increasing the temperatures over longer periods of time (iii) varing metal:ligand: reducing agent ratios beyond those investigated and (iv) changing the sequence of mixing the reactions by, for example adding the reducing agent before introducing the CO etc.

As mentioned in the discussion section, the presence of a phosphido complex was confirmed by ^{31}P n.m.r. spectroscopy but a solid complex was not isolated. This is one very interesting area where more work is required in an attempt to isolate and investigate the nature of the phosphido complex and how P-C bond cleavage occurs under such mild conditions. In fact there is no report of the formation of a phosphido complex from dppm under such mild conditions.

The reactivities of the metal-metal bonded species $Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ has been studied. Some of the products from these reactions have been fully characterized, while more work is required to charecterize products from reactions with NO, HCl, C_2H_4 and S_8. As mentioned in the disscussion, the reaction with S_8 produced a highly crystalline black complex on which further work should be productive and which may reveal some very interesting features of sulfur coordination. X-ray crystallography may be required to fully characterize this product. In addition, similar reactions with other metal-metal bonded complexes such as $Ni_2Pt(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$, $NiPd(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ and $Ni_2(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2$ will almost certainly produce more interesting complexes.

The few bimetallic complexes which have already been made in this study were prepared from $Ni(CO)_2(\mu\text{-}dppm)_2$. This system can be further explored by carring out analogous reactions with other metal ions. while most of the work described in this thesis involves dppm complexes, there is potential to expolre reactions with the mono coordinated dppe complex.

Attempts to isolate solid trimetallic systems were largely unsuccessful although indications that reactions aimed at making such complexes have indeed occured. This is therefore, another area which requires more work and may well lead to some new and exciting results.

Finally, work with higher phosphines such as dppp, dppb and dpppe require some systematic study. It will be interesting to compare these results with those already obtained with dppm and dppe and it is hoped that this type of study will provide more information about the coordination and reaction chemistry of these phosphine ligands.

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