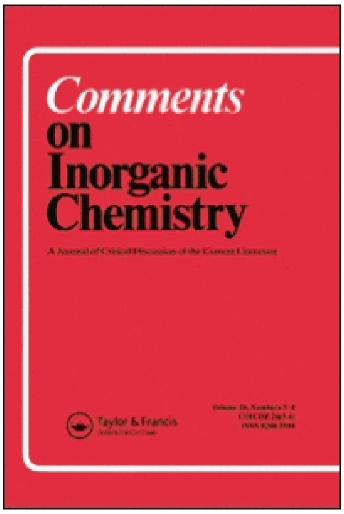


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Reactions Involving Transition-Metal Ions and Tripodal Phosphines and Arsines

F. Mani[a]; L. Sacconi[a]
[a] Institute of General and Inorganic Chemistry, University of Florence, Florence, Italy

To cite this Article Mani, F. and Sacconi, L.(1983) 'Reactions Involving Transition-Metal Ions and Tripodal Phosphines and Arsines', Comments on Inorganic Chemistry, 2: 3, 157 — 186
To link to this Article: DOI: 10.1080/02603598308078115
URL: http://dx.doi.org/10.1080/02603598308078115

Reactions Involving Transition-Metal Ions and Tripodal Phosphines and Arsines

I. INTRODUCTION

A. General

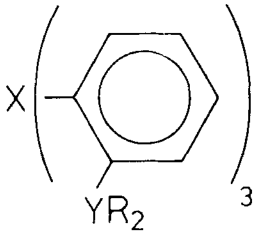
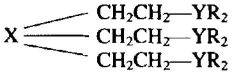
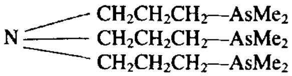
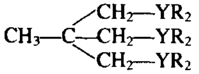
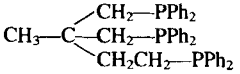
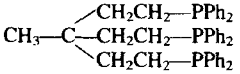
This comment will review reactions involving transition metal ions and tripodal ligands whose donor centers are tertiary phosphine or arsine groups, and will describe typical products that are formed in these reactions. The reactions involving tripodal ligands often have no counterpart in reactions involving ligands with similar donor centers but having shapes other than tripodal. Also, complexes with tripodal ligands often have unique structural properties. Both of these characteristics derive from the particular geometric requirements of tripodal ligands, so we will begin by considering the ways in which these ligands bind to transition metal ions. An exhaustive review covering the whole known range of tripodal ligands will appear elsewhere.[1]

B. Some Aspects of the Stereochemistry of Complexes of Tripodal Ligands

In this review we shall consider only those tripodal ligands with $-PR_2$ or $-AsR_2$ groups (R = alkyl, aryl) at the triangular base of the tripod. The basal donor groups are linked through three legs consisting of CH_2, $(CH_2)_2$, $(CH_2)_3$ or *o*-phenylene groups to an apical atom of carbon, nitrogen, phosphorous or arsenic; a list of these ligands is given in Table

Comments Inorg. Chem.
1983, Vol. 2, Nos. 3–4, pp. 157–186
0260-3594/83/0204-0157/$18.50/0

TABLE I
Summary of the tripod ligands

Structure	Legend	Reference
	X = Y = P; R = Ph; QP	2
	X = Y = As; R = Ph; QAS	3
	X = Y = As; R = Me; Qas	4
 $X\begin{matrix}CH_2CH_2-YR_2\\CH_2CH_2-YR_2\\CH_2CH_2-YR_2\end{matrix}$	X = N; Y = P; R = Ph; np_3	5
	X = N; Y = P; R = Me; Me_6np_3	6
	X = N; Y = P; R = Et; Et_6np_3	7
	X = N; Y = As; R = Ph, nas_3	8
	X = N; Y = As; R = Me; Me_6nas_3	9
	X = Y = P; R = Ph;pp_3	10
 $N\begin{matrix}CH_2CH_2CH_2-AsMe_2\\CH_2CH_2CH_2-AsMe_2\\CH_2CH_2CH_2-AsMe_2\end{matrix}$	qas	11
 $CH_3-C\begin{matrix}CH_2-YR_2\\CH_2-YR_2\\CH_2-YR_2\end{matrix}$	Y = P; R = Ph; p_3 (triphos)	12
	Y = P; R = Et; Et_6p_3 (etriphos)	13
	Y = As; R = Ph; as_3	14
	Y = As; R = Me; Me_6as_3	15
 $CH_3-C\begin{matrix}CH_2-PPh_2\\CH_2-PPh_2\\CH_2CH_2-PPh_2\end{matrix}$	ap_3 (atriphos)	16
 $CH_3-C\begin{matrix}CH_2CH_2-PPh_2\\CH_2CH_2-PPh_2\\CH_2CH_2-PPh_2\end{matrix}$	etp_3	17

I. They divide into two groups: those with four donor atoms (4-D) which are potentially tetradentate and the potentially tridentate ligands that have only three basal donor atoms (3-D).

The ligands QP, QAS, np_3, nas_3 and pp_3 are 4-D ligands in which each leg of the tripod contains an ethylene or a *o*-phenylene chain and each basal atom is attached to two phenyl groups. These ligands usually occupy four coordination positions around a metal ion, but the steric requirements of the ligands are such that there is room for only one

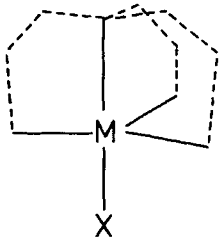


FIGURE 1

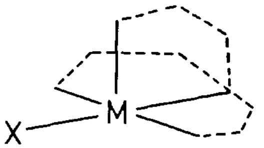


FIGURE 2

other ligand, so that the trigonal bipyramidal structure (Figure 1)[18] or less commonly square-based pyramidal structure (Figure 2)[19] results. The fifth coordination position can be occupied by various charged or uncharged ligands. However, the electronic configuration of the metal ion can bring about a different coordination geometry, particularly when there are 18 valence electrons around the complexed ion. For example, the d^6 ions Cr(O),[20] Mn(I),[21] Fe(II)[22] and Co(III)[23] easily form six-coordinate, diamagnetic octahedral complexes with the ligands QP, pp_3 and np_3, together with a variety of neutral and anionic coligands. The ligand qas behaves similarly with these metal ions, though it has longer tripod legs and less bulky basal substituents.

The tendency of the metal ion to attain a stable electronic configuration accounts for the fact that a 4-D ligand such as QP can bind in a variety of ways: as a tetradentate ligand in $[Co(CO)QP]^+$,[23a] as a tridentate ligand in $[Cr(CO)_3QP]$[20] and as a bidentate ligand in $[MnX(CO)_3QP]$.[21] Similarly, the ligand np_3 is tetradentate in the isoelectronic complexes (Figures 3 and 4) but it is tridentate in the other

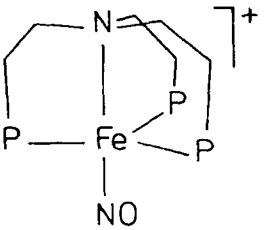


FIGURE 3

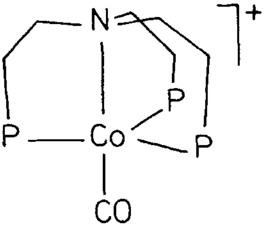


FIGURE 4

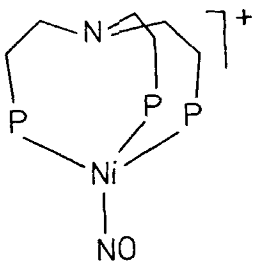


FIGURE 5

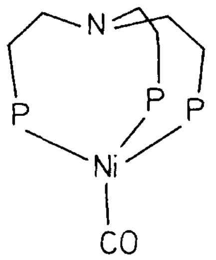


FIGURE 6

isoelectronic pair (Figures 5 and 6) (see also Section IV).[24,25] The importance of the number of valence electrons is also illustrated by the different reactivity of $[FeH(pp_3)]^+$ and $[NiH(np_3)]^+$ towards neutral ligands such as carbon monoxide. The former complex has 16 valence electrons and accepts a CO molecule as an additional ligand under mild conditions[22b] whereas the latter has 18 valence electrons and exchanges CO for H^- under the same conditions.[26]

The 3-D ligands p_3 and as_3 generally occupy a face of the coordination polyhedron of dipositive ions. The resultant steric unsaturation encourages the coligands to occupy more than one coordination site; thus, SO_4^{2-} (Figure 7), NO_3^-, acac$^-$ behave as bidentate ligands.[27] Monodentate ligands can act as bridges in binuclear complexes (Figure 8).[27a,28] With metals in low oxidation states the 3-D ligands form complexes with a single monodentate coligand (Figure 9).[14,29] Clearly, the 3-D ligands donate less electron density to a metal ion than do tetradentate 4-D ligands. Additionally, ligands such as p_3 and as_3 have short tripod legs so that the donor atoms do not easily enter the optimal positions of coordination. Consequently, there is both electronic and steric unsaturation in complexes of the 3-D ligands.

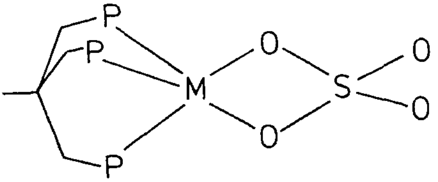


FIGURE 7 M = Co,Ni.

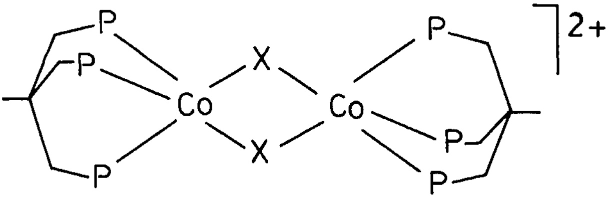


FIGURE 8 X = Cl,Br,OH,SH.

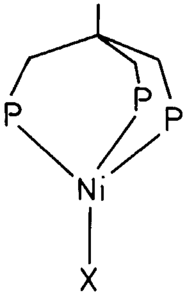


FIGURE 9

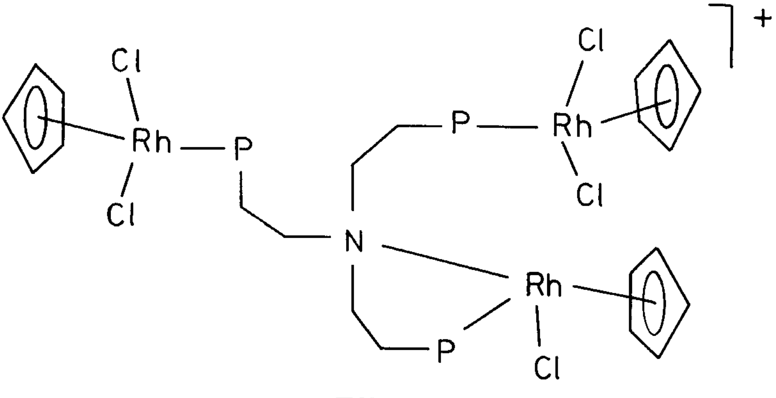


FIGURE 10

All the 4-D ligands with phenyl substituents on the basal donor atoms form mononuclear complexes, with one exception so far: the complexes $[\{Rh(C_5H_5)\}_3Cl_5L]^+$ (Figure 10) (L = np_3 or pp_3) are trimetallic with each ligand bonding to three metal centers.[30] However, when the basal phenyl groups are replaced by the less bulky alkyl groups, the 4-D ligands tend to form polynuclear complexes in which a ligand may coordinate to two or three metal centers. For example, Me_6np_3 forms the radial structure (Figure 11) with both cobalt and nickel, in which each ligand is bound to three metal centers.[6] On the other hand, Et_6np_3[7] forms both mononuclear and trinuclear complexes (Figure 12), with ligands bound to two metal centers in the latter complexes. It is worth noting that QAS and Qas both bind to nickel(II) in the same way,[4,31] presumably because of the lack of flexibility in the tripod legs.

In the case of the 3-D ligands either increasing the length of the tripod legs from C_2 to C_3 (p_3 becomes etp_3) or replacing basal phenyl groups

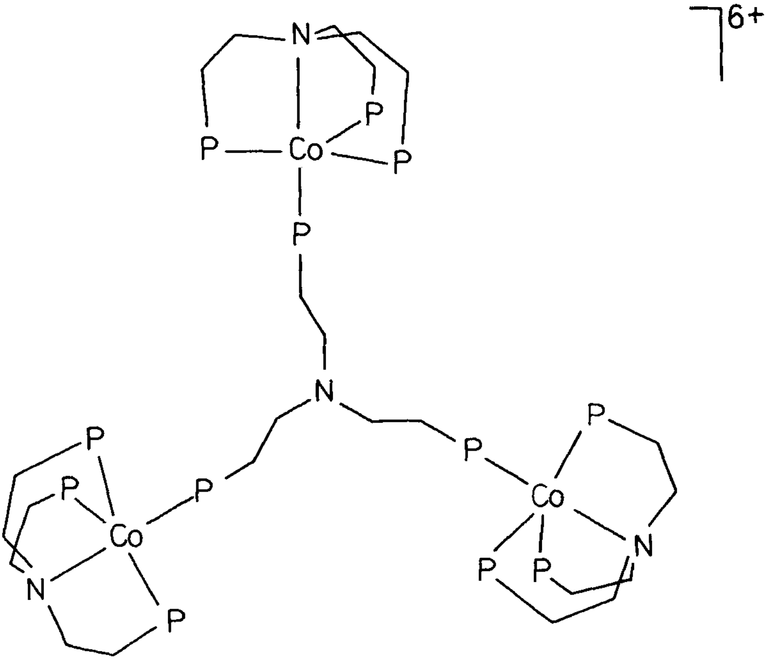


FIGURE 11

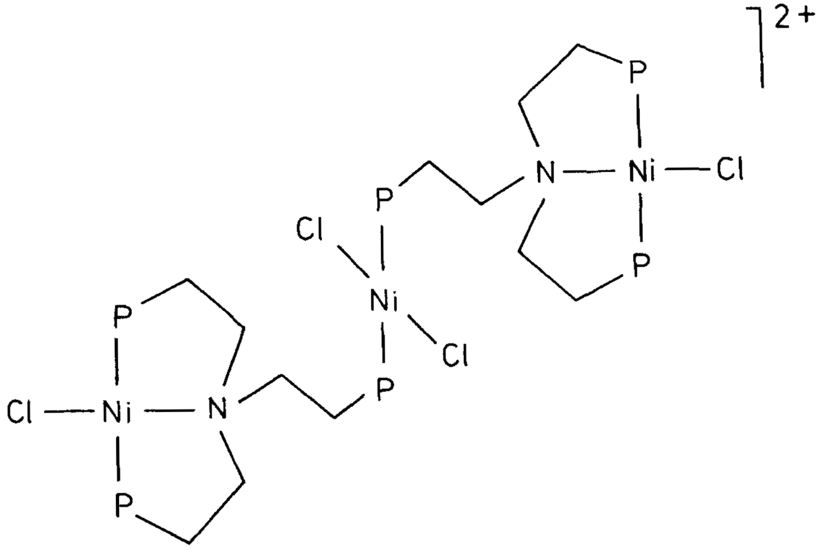


FIGURE 12

by ethyl (p_3 becomes Et_6p_3) is accompanied by the formation of polynuclear rather than mononuclear complexes. The asymmetric ligand ap_3 behaves similarly. The ligands may bond to two (Figures 13 and 14)[16] or three (Figure 15)[17] metal centers.

From the foregoing we may conclude that tripodal ligands with phenyl substitutents on the basal donor atoms invariably form a complex fragment of the form ML^{n+} which is stable to decomposition but unsaturated from the point of view of the coordination of the metal. The ML^{n+}

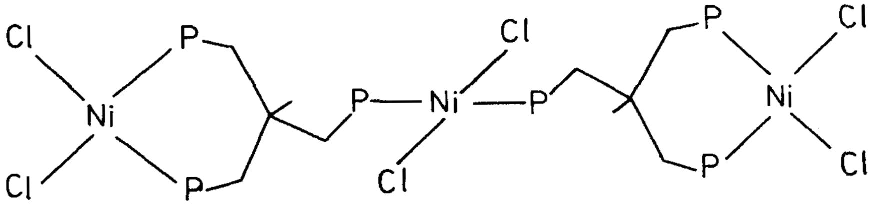


FIGURE 13

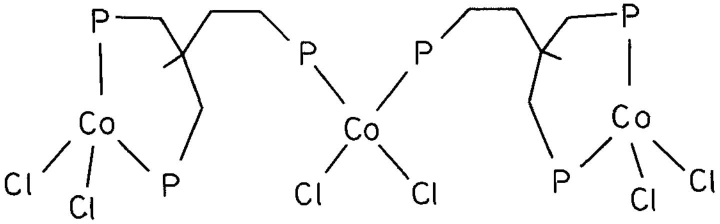


FIGURE 14

fragment is a highly reactive center which may favor reaction with either electrophilic or nucleophilic reagents, according to the electron density on the metal. When suitable reagents are not present in the reaction medium as coligands, as for example happens when one starts with substances such as $[M(H_2O)_6]$ $(BF_4)_2$, the fragment ML^{2+} will react with solvent molecules, water molecules from aquacations, neutral molecules added to the reaction medium, more free ligand molecules and so forth. The fragment ML^{n+} is therefore incorporated intact in the final complex, together with other coligands.

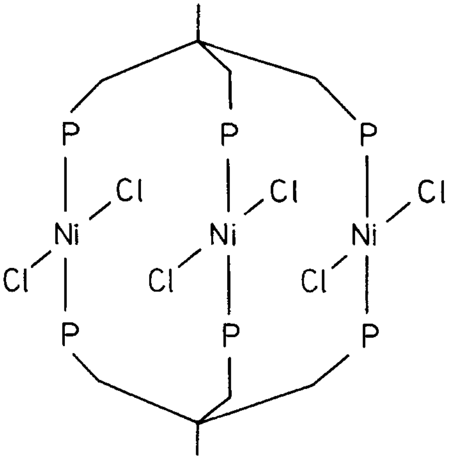


FIGURE 15

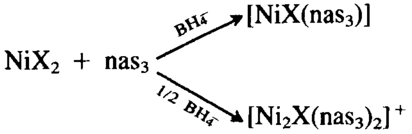
II. THE STABILIZATION OF LOW OXIDATION STATES AND THE FORMATION OF HYDRIDO COMPLEXES

A. Complexes of Metals in Low Oxidation States

In the presence of tripodal ligands transition metal salts can easily be transformed into complexes in which the oxidation state of the metal is low with the assistance of added reducing agents such as BH_4^-, or even without them under mild reaction conditions. The nature of the reduced product depends on the anion present in the starting salt, on the nature of the ligand and to some extent on the reaction conditions. When the anion is a halide or pseudohalide the bipositive metal ions are reduced to the monopositive state and one anion occupies the vacant coordination position (Figures 9 and 16).[26,29,32,33,34] The reduction of the divalent ions from metal iodides can be accomplished by an excess of the ligand, which is itself a sufficiently strong reductant[32]:

$$2\,MI_2 + p_3\,(\text{excess}) \rightarrow 2[MI(p_3)] + p_3I_2, \qquad M = Co, Ni.$$

The reduction of nickel (II) halides in the presence of nas_3 by BH_4^- gives different products according to the amount of BH_4^- used[34,35]:



$$\begin{tikzcd}[column sep=large] & {[NiX(nas_3)]} \\ NiX_2 + nas_3 \arrow[ur, "BH_4^-"] \arrow[dr, "1/2\ BH_4^-"'] & \\ & {[Ni_2X(nas_3)_2]^+} \end{tikzcd}$$

The two complexes of nickel(I) are essentially diamagnetic at ~ 200 K and have $\mu_{eff} = 1.0\ \mu_B$ at 293 K. In the complex $[Ni_2I(nas_3)_2]^+$ the

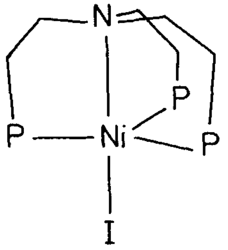


FIGURE 16

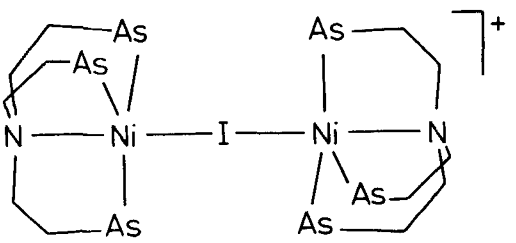


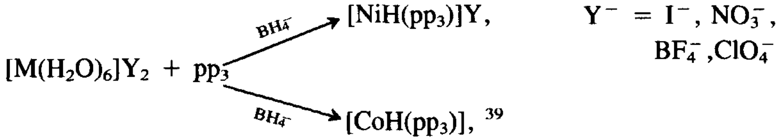
FIGURE 17

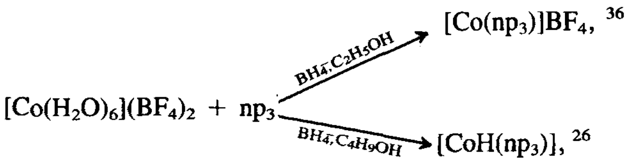
iodide ion forms a linear bridge between the two nickel atoms, which are thus both five-coordinate (Figure 17).

When the anion is noncoordinating (e.g., BF_4^-, ClO_4^-, NO_3^-) borohydride reduction of aquacations leads to trigonal pyramidal complexes $[M(L)]BF_4$ (M = Co, Ni; L = np_3, nas_3),[34,36] $[Ni(np_3)]$ (Figure 18),[26,37] presumably to square planar complexes $[M(p_3)_2]$ (M = Ni, Pd)[38] and also to hydrido complexes.

B. The Formation of Hydrido Complexes

Metal–hydrogen bonds are easily formed in complexes with tripodal ligands such as np_3, pp_3, p_3 and as_3 by the action of hydridic reducing agents and also in their absence. Examples of reactions that lead to hydrido complexes are





$$[Ni(np_3)] + HClO_4 \longrightarrow [NiH(np_3)]ClO_4.^{36}$$

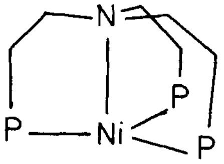
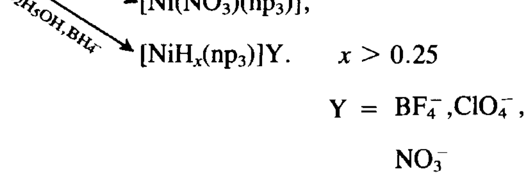


FIGURE 18

We see that with pp_3 nickel(II) and cobalt(I) hydrides are formed under similar reaction conditions, whereas with np_3 more forcing conditions are required for the formation of the cobalt(I) hydrido species, while under the same forcing conditions nickel(II) is reduced to nickel(0).[37] All the hydrido complexes are diamagnetic so it seems that they are favored with low-spin d^8 ions which obtain the 18 valence electron configuration by pentacoordination. The metal–hydride bonds are invariably terminal in complexes of the tetradentate tripod ligands (Figure 19).[26,33b,36,39]

The nonstoichiometric hydrido complexes found with the ligand np_3 are worth particular mention. The reaction of $[Ni(H_2O)_6]Y_2$ with np_3 with or without added BH_4^- depends critically on the nature of the solvent, on the anion Y and on small variations in reaction conditions,[36] and is quite different from the corresponding reactions of $[Co(H_2O)_6]Y_2$ with np_3, or of $[Ni(H_2O)_6]Y_2$ with pp_3:



The compounds which are formulated as $[NiH_x(np_3)]Y$ were found to be made by the paramagnetic nickel(I) species $[Ni(np_3)]Y$ and the

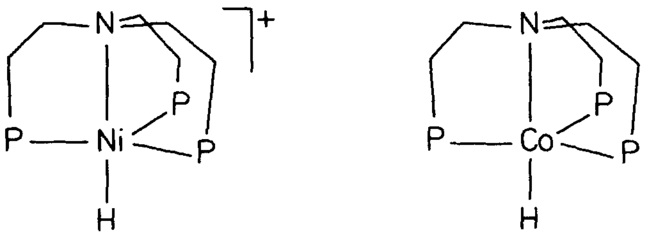


FIGURE 19

diamagnetic nickel(II) species $[NiH(np_3)]Y$, whose relative concentration depended on the conditions of preparation; this conclusion was confirmed by an x-ray study.[36] The reduction of the nickel(II) to the monovalent state can be effected by the ligand

$$2\,[Ni(np_3)]^{2+} + np_3 + H_2O \rightarrow np_3O + 2H^+ + 2\,[Ni(np_3)]^+.$$

Then the formation of hydrido complexes can be explained by the electrophilic nature of the complex $[Ni(np_3)]^{2+}$ which is presumably formed in solution:

$$[Ni(np_3)]^{2+} + RCH_2OH \rightarrow [NiH(np_3)]^+ + H^+ + RCHO.$$

Both the reduction and hydride-forming reactions may be assisted by the basic nature of the ligand and the ease with which it may be protonated (presumably at the nitrogen atom) to remove excess protons from the solution.

Hydrido-bridged dimers of an unusual nature are obtained from Fe(II) and Co(II) with the ligands p_3 and as_3 by borohydride reduction,[40] though with Co(II) an alternative reaction was also found[41]:

$$2[Co(H_2O)_6]^{2+} + 2p_3 + 3BH_4^- \xrightarrow[273\ K]{ether} [Co_2H_3(p_3)_2]^+ + {}^3/_2B_2H_6 + 6H_2O;$$

$$[Co(H_2O)_6]^{2+} + p_3 + 2BH_4^- \xrightarrow[293\ K]{\text{tetrahydrofuran (thf)}} [Co(BH_4)(p_3)] + \tfrac{1}{2}B_2H_6 + \tfrac{1}{2}H_2 + 6H_2O.$$

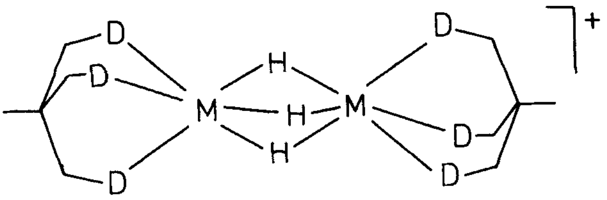


FIGURE 20 M = Co, D = P,As. M = Fe, D = P.

The complex $[Fe_2H_3(p_3)_2]^+$ is diamagnetic while the cobalt complex with p_3 and with its arsenic analog are paramagnetic, $\mu_{eff} = 3.2$ per dimer formula unit. The structures of the binuclear complexes are similar and may be described as made up of two octahedra sharing a face of three hydride ions (Figure 20). Although a qualitative molecular orbital scheme can be used to assign M–M bond orders of three for the iron complex and two for the cobalt complex, it seems more likely that the very short M–M bond lengths (2.34 and 2.37 Å) cannot be correlated to the M–M bond order but are the consequence of the steric requirements of the bridging ligands.

III. DEPROTONATION REACTIONS AND THE FORMATION OF HYDRIDO, THIO, METHYLTHIO AND MERCAPTO COMPLEXES

The tripod ligands can behave as proton acceptors, particularly in ethanolic solutions, and can remove protons from relatively weak acids such as H_2O[42,24a], H_2S and +$HSCH_3$[43,44]. Typical reactions are

$$[Co(H_2O)_6]^{2+} + 2np_3 + HSR \xrightarrow{EtOH} [Co(SR)(np_3)]^+ + Hnp_3^+ + 6H_2O, \quad R = H,CH_3$$

$$[Co(H_2O)_6]^{2+} + 2np_3 \xrightarrow{EtOH} [Co(OH)(np_3)]^+ + Hnp_3^+ + 5H_2O,$$

$$[Co(H_2O)_6]^{2+} + np_3 \xrightarrow{thf} [Co(H_2O)(np_3)]^{2+} + 5H_2O.$$

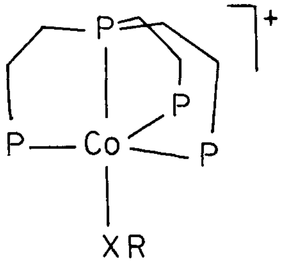


FIGURE 21 $X = O, R = H. X = S, R = H, CH_3$.

The last reaction, which also occurs in acetone, illustrates the fact that the reaction course is once again dependent on solvent and reaction conditions. Deprotonation reactions also occur with the other ligands containing phosphines as donors such as pp_3 (Figure 21), QP and p_3; in the last case dinuclear complexes may be formed[27a,44]:

$$[Ni(H_2O)_6]^{2+} + p_3 + H_2S \xrightarrow[\text{(dmf)}]{\text{dimethyl-formamide}} [NI_2(\mu - S)(p_3)_2]^{2+},$$

$$[Co(H_2O)_6]^{2+} + p_3 \xrightarrow{ButOH,(CH_3)_2CO} [Co_2(\mu - OH)_2(p_3)_2]^{2+}.$$

The dimeric cobalt complex (Figure 22) finds the metal in a distorted square pyramidal configuration, and displays antiferromagnetic behavior deriving from a triplet–singlet equilibrium. Although no complex of the protonated forementioned tripod ligand has yet been isolated, the related complex $[Ni(HS)(Hn_2p_2)] (BF_4)_2$ (n_2p_2 = *N*,*N*-bis(2-diphenylphosphinoethyl)-2′-diethylaminoethylamine) does contain a protonated ligand.[45]

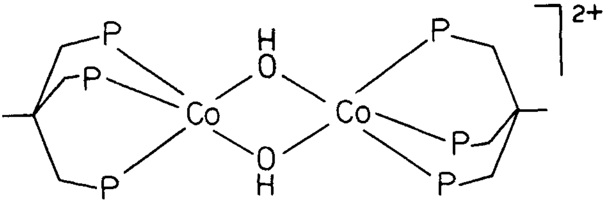


FIGURE 22

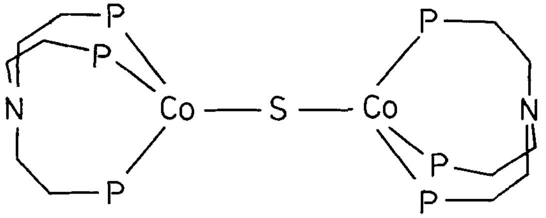
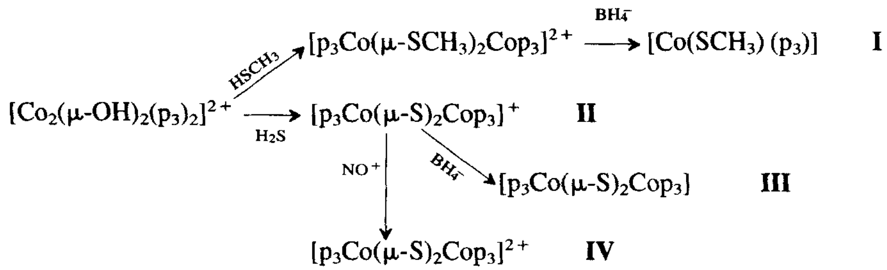


FIGURE 23

Complexes of nickel(I) of the formula [Ni(L)(np_3)] (L = SH, SeH, SCH_3) can be obtained by oxidative addition of the corresponding acid to a nickel(0) complex[44]:

$$[Ni(np_3)] + HSR \rightarrow [Ni(SR)(np_3)] + \tfrac{1}{2} H_2.$$

When the complex $[Co(SH)(np_3)]^+$ is treated with the strong base $NaOC_2H_5$ further deprotonation occurs, but it is accompanied by reduction, to give the binuclear cobalt(I) complex $[Co_2S(np_3)_2]$ (Figure 23).[44] The np_3 ligand acts tridentate so that the complex is structurally similar to the nickel(II) complex $[Ni_2S(p_3)]^{2+}$ (Figure 24).[44] Indeed, both complexes (Figures 23 and 24) have unusual structural and electronic properties. They are diamagnetic and contain a linear M–S–M bridge. Each metal ion is normally four-coordinate. If the sulfide ion donates a pair of electrons to each metal ion, they would have 16 valence electrons. It therefore seems likely that the M–S–M bonds possess substantial double bond character giving each metal ion a share in 18 valence electrons. The M–S bond lengths (Ni–S = 2.034, Co–S = 2.128 Å) are in fact rather short for single bonds. Other binuclear complexes involving the ligand p_3 and two bridging groups have been obtained by the reaction of H_2S or $HSCH_3$ with bis(μ-hydroxo) complexes of cobalt (II) (Figures 25 and 26)[28]:



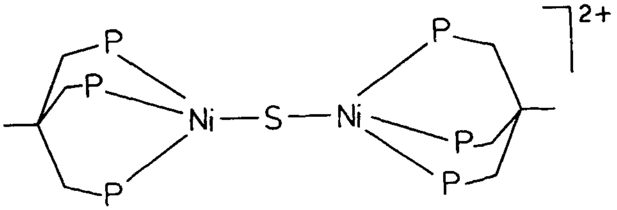


FIGURE 24

The coordination geometry in the four binuclear complexes is distorted square pyramidal. Complex **II** has an odd number of valence electrons (33) and must be paramagnetic; but **I** and **III** which are formally isoelectronic (34 valence electrons) show different magnetic behavior deriving from a singlet–triplet equilibrium. The sulphide ion has a larger exchange coupling constant than the mercaptide ion, and so spin pairing is induced in **III** at ambient temperature, but not in **I**. Complex **IV** is diamagnetic.

The formation of complexes with M–S bonds is generally promoted by the presence of ancillary ligands with π-acceptor ability such as phosphines.[46] However, the tripod ligands give mono and binuclear complexes whereas larger clusters and polymers tend to be formed with the other ligands. The reason for this is that the tripod ligands occupy all but one or two of the coordination sites on the metal ions, and furthermore, the sulfur atoms are surrounded by the phenyl groups attacked to the phosphorus atoms, and are therefore hindered from forming bonds with other metallic centers.

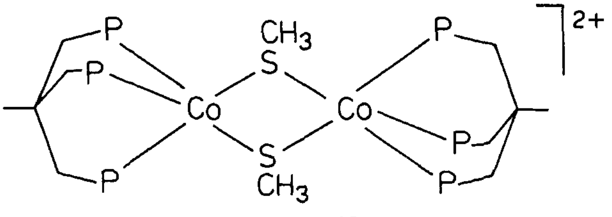


FIGURE 25

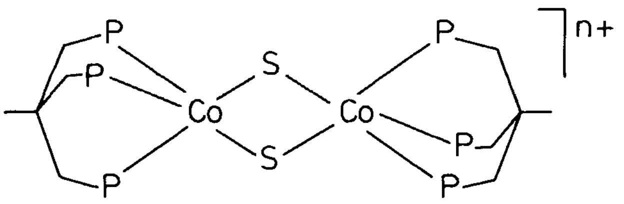
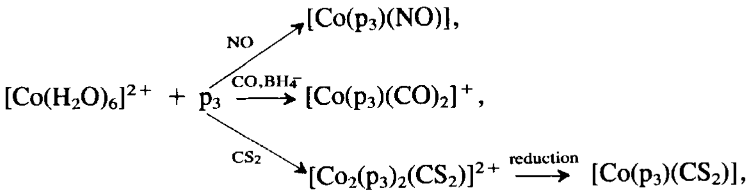


FIGURE 26 $n = 0,1,2$.

IV. REACTIONS WITH NO, CO, SO_2 and CS_2

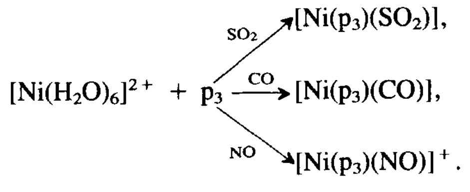
The divalent aquacations of cobalt and nickel react, in the presence of p_3, with the neutral molecules NO, CO, SO_2 and CS_2 under conditions of normal temperature and pressure to give a variety of complexes[41,47]; the metal ions are reduced even in the absence of added reducing agents. Typical examples of these reactions are shown in the following scheme:



$$[Co(H_2O)_6]^{2+} + p_3 \xrightarrow{NO} [Co(p_3)(NO)],$$

$$[Co(H_2O)_6]^{2+} + p_3 \xrightarrow{CO,BH_4^-} [Co(p_3)(CO)_2]^+,$$

$$[Co(H_2O)_6]^{2+} + p_3 \xrightarrow{CS_2} [Co_2(p_3)_2(CS_2)]^{2+} \xrightarrow{\text{reduction}} [Co(p_3)(CS_2)],$$



$$[Ni(H_2O)_6]^{2+} + p_3 \xrightarrow{SO_2} [Ni(p_3)(SO_2)],$$

$$[Ni(H_2O)_6]^{2+} + p_3 \xrightarrow{CO} [Ni(p_3)(CO)],$$

$$[Ni(H_2O)_6]^{2+} + p_3 \xrightarrow{NO} [Ni(p_3)(NO)]^+.$$

The Ni(O) and Co(I) complexes have 18 valence electrons and are diamagnetic. The Co(II) complexes, $[CoX(p_3)(CO)]BPh_4$,[28,48] have 17 valence electrons and are paramagnetic, with $\mu_{eff} = 1.9$–$2.1\ \mu_B$.

The complexes obtained by the action of CS_2 are worth particular mention. In the binuclear complex $[Co_2(p_3)_2(CS)_2]^{2+}$ (Figure 27) the CS_2 group is bonded to one cobalt atom through a π C–S bond and σ

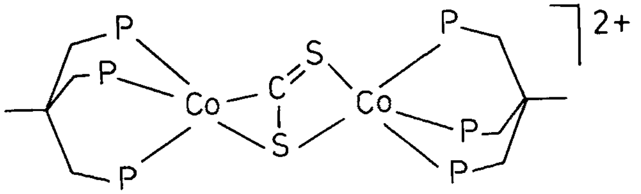
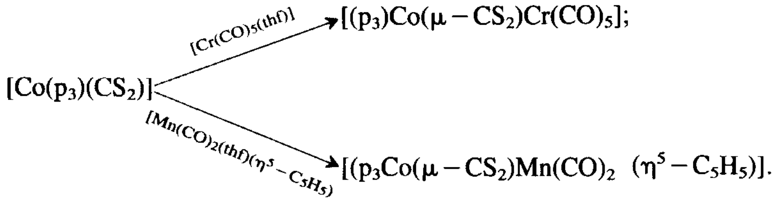


FIGURE 27

bonded through both sulfur atoms to the other cobalt atom.[47a,b] The mononuclear complex (Figure 28) may itself behave as a ligand towards electrophilic species by virtue of the increased electron density on the sulfur atoms in π-bonded CS_2. Heterometallic binuclear complexes are formed as follows[47a,c].



Both complexes have a single unpaired electron (μ_{eff} = 1.95 and 2.18 μ_B).

The reaction of CS_2 with $[Fe(H_2O)_6]^{2+}$ and the ligand Et_6p_3, which differs from p_3 in that the substituents on phosphorus are ethyl rather

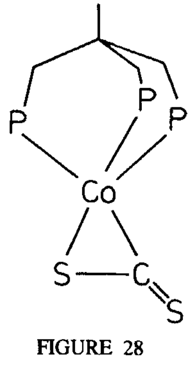


FIGURE 28

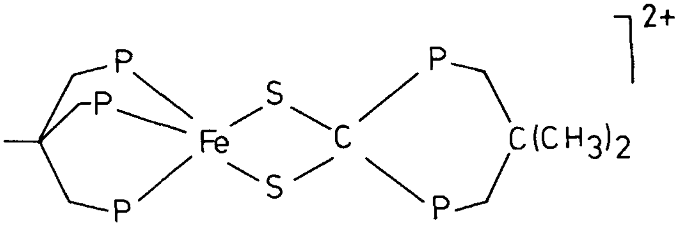
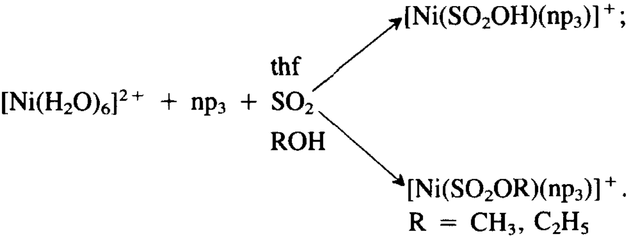


FIGURE 29

than phenyl groups, leads to a diamagnetic complex completely different from the ones previously discussed. This product has a zwitterionic dithiolate ligand coordinated to the metal (Figure 29).[49] This is the first example of a diamagnetic five-coordinate iron(II) complex.

The products formed from SO_2 vary with the nature of the tripod ligand. The 3-D ligand p_3 yields the nickel(0) complex $[Ni(p_3)(SO_2)]$ but the 4-D ligands np_3 and pp_3 yield hydrogenosulfito and alkylsulfito complexes of nickel(II) and cobalt(II) (Figure 30) depending on the reaction solvent[50]:



$$[\mathrm{Ni(H_2O)_6}]^{2+} + \mathrm{np_3} + \mathrm{SO_2} \begin{array}{l} \xrightarrow{\mathrm{thf}} [\mathrm{Ni(SO_2OH)(np_3)}]^{+}; \\ \xrightarrow{\mathrm{ROH}} [\mathrm{Ni(SO_2OR)(np_3)}]^{+}. \\ \quad \mathrm{R} = \mathrm{CH_3}, \mathrm{C_2H_5} \end{array}$$

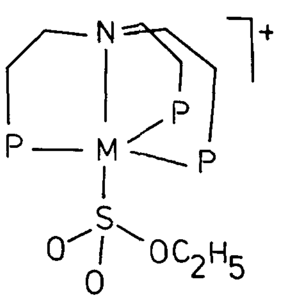


FIGURE 30 M = Ni,Co.

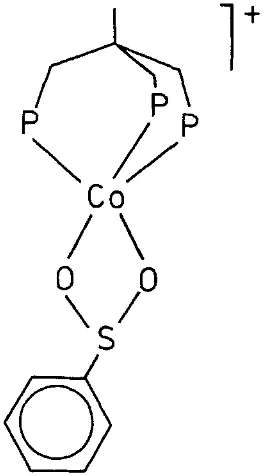


FIGURE 31

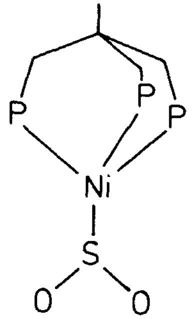


FIGURE 32

The reaction of sodium *p*-toluenesulfinato with the aquacations of Fe(II), Co(II) and Ni(II) and pp_3 or np_3 gives five-coordinate complexes in which the coligand is bound to the metal via one oxygen atom, one sulfur atom or via both oxygen atoms (Figure 31).[51]

It is interesting to compare the way in which SO_2 is bound in the two complexes (Figures 32 and 33)[41] which is obtained by reduction of $[NiBr(np_3)]^+$ with BH_4^- in the presence of sulfur dioxide.[52] In Figure 32 the nickel atom achieves an 18 valence electron configuration by accepting an electron pair from the SO_2; in consequence the Ni–SO_2 grouping is planar. In Figure 33 the 18 electron configuration is already present in the fragment $[Ni(np_3)]$, so that this fragment acts as a Lewis base towards SO_2 and a "bent" Ni–SO_2 bond results.

Three general methods have been used to prepare numerous nitrosyl and carbonyl complexes with tripod ligands. The neutral molecules may be reacted with preformed hydrido complexes[24,26]

$$[NiH(np_3)]^+ + NO \rightarrow [Ni(np_3)NO]^+,$$

or low oxidation state complexes[24,26]:

$$[Ni(np_3)] + CO \rightarrow [Ni(np_3)CO].$$

Alternatively, the ligand may be made to react with metal carbonyl or nitrosyls[10,53]:

$$[Ni(CO)_4] + p_3 \rightarrow [Ni(p_3)(CO)] + 3CO.$$

The complexes formed by all of these methods are diamagnetic and the 18-electron rule determines whether the ligand is bi-, tri- or tetradentate (see Section I.B).

V. σ AND π ORGANOMETALLIC COMPLEXES

The fragments ML^{x+} derived from the 3-D ligands p_3 and as_3 show a marked affinity for unsaturated organic species. They form numerous complexes in which the metal is π bonded to various alkanes (both conjugated and nonconjugated) and alkynes. For the most part these complexes are the counterparts of metal carbonyl complexes in which three CO groups have been replaced by the ligand p_3; indeed some complexes have been prepared by direct substitution of the corresponding carbonyl complex.[54]

The fragments ML^{x+} derived from the 4-D ligands np_3, pp_3 and nas_3 tend to form σ bonds with alkyl and aryl groups. An example of the different behavior of the two types of tripod ligand is the way they react with $[Ni(PPh_3)_2(C_3Ph_3)]ClO_4$ (C_3Ph_3 is the triphenylcyclopropenyl group).[55] The 3-D ligands p_3, Me_6p_3 and as_3 replace the PPh_3 ligands to give the complex $[NiL(C_3Ph_3)]$ ClO_4 (Figure 34).[56] The C_3Ph_3 group is symmetrically η^3 bonded to the nickel to form an elongated tetrahedron. If one considers the neutral C_3Ph_3 as a $3e^-$ donor and nickel

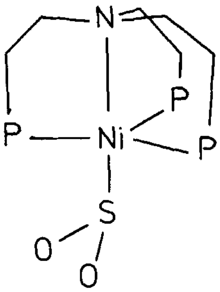


FIGURE 33

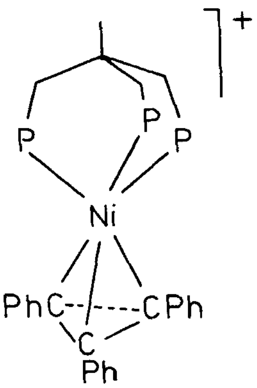


FIGURE 34

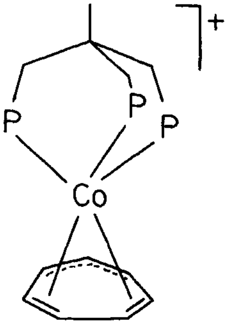


FIGURE 35

monopositive, a valence electron count of 18 results. This would be possible with the 4-D ligands if they were tridentate. Instead they express their full denticity and yield the nickel(I) complex [NiL(PPh_3)]Y (L = np_3, nas) in which the cyclopropenyl group has been replaced.[57]

The 18-electron rule can be used to rationalize the wide variety of structures found in complexes of Fe, Co and Ni involving p_3 and as_3 and polyolefins and acetylenes. Typical examples of these π complexes are compounds of the formula [CoL(p_3)] (L = 1,3-butadiene, 2-methylbutadiene, 1,3-cyclohexadiene, 1,3,5-cycloheptatriene). These compounds are obtained by reacting the olefin with $[Co(H_2O)_6](ClO_4)_2$ in the presence of tripod ligand.[58] The structure of the complex $[Co(p_3)(C_7H_8)]^+$ (Figure 35) shows three phosphorus atoms donating to the cobalt(I); the cycloheptatriene can therefore donate a maximum of four electrons and behaves as a η^4 ligand.

Substitution of carbonyl groups in the complex $[Co_2(Ph_2C_2)(CO)_6]$ by p_3 gave $[Co_2(Ph_2C_2)(CO)_4(p_3)]$ (Figure 36) in which the diphenylacetylene bridges between two cobalt atoms and the p_3 are bidentate.[59] A variety of fluoroalkenes which are η^2 bonded to Ni(as_3) or Ni(p_3) were prepared from Ni(cyclododeca-1,5,9 triene) (Figure 37).[60]

Grignard reagents and organolithium compounds will cause replacement of coligands by σ-bonded alkyl or aryl groups to give a series of low-spin Co(I), Co(II) and Ni(II) complexes[61,62]:

$$[NiX(pp_3)]^+ + MgXCH_3 \rightarrow [Ni(pp_3)(CH_3)]^+ + MgX_2,$$

$$[CoX(np_3)] + LiPh \rightarrow [Co(np_3)(Ph)] + LiX.$$

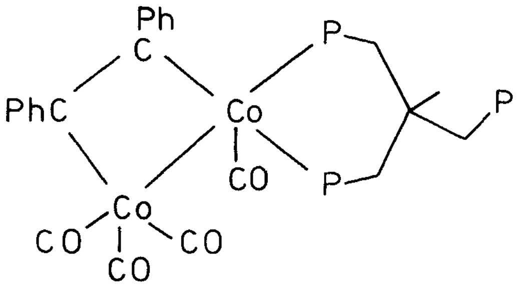


FIGURE 36

The tertiary arsine ligands can promote the extraction of a phenyl group from BPh_4^- in boiling *n*-butanol[63,34] (Figure 38):

$$Ni^{2+} + L + 2BPh_4^- \rightarrow [Ni(L)(Ph)]BPh_4 + BPh_3.$$

$$L = nas_3, QAS, Me_6nas_3$$

The formation of phenyl complexes from BPh_4^- is analogous to the formation of hydrido complexes from BH_4^-:

$$BPh_4^- \rightarrow BPh_3 + Ph^-,$$

$$BH_4^- \rightarrow \tfrac{1}{2}B_2H_6 + H^-.$$

The reaction of carbon monoxide with some of the organometallic complexes of nickel(II) and cobalt(II) leads to acyl derivatives of the

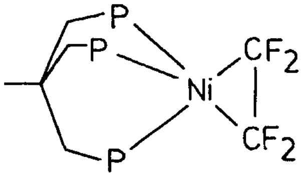


FIGURE 37

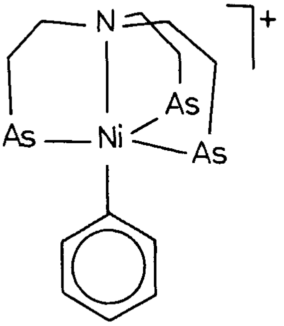


FIGURE 38

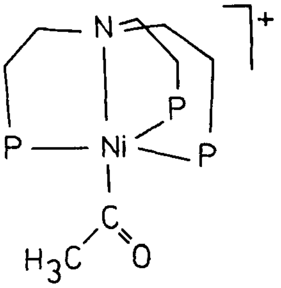


FIGURE 39

formula $[M(COR)L]^+$ (M = Co, Ni, R = CH_3, C_2H_5, CH_2Ph; L = np_3, nas_3)[62] (Figure 39). In the case of np_3 and nickel the first product is a solid solution of the acyl derivative of nickel(II) and the carbonyl derivative of nickel(I) in a ratio 1:1. The analogous reaction with SO_2 leads to the ethyl sulfito complex $[Co(SO_2OC_2H_5)(np_3)]BPh_4$[64] similar to the one formed by nickel (Figure 30). These carbon monoxide insertion reactions can be considered exceptional. Normally, the carbon monoxide and alkyl (or aryl) groups are already both bound to the same metal before the insertion reaction occurs.[65] Such reactions can also occur with tripod ligands[10]:

$$[Mn(CH_3)(CO)_5] + pp_3 \rightarrow [Mn(CH_3CO)(CO)_2(pp_3)] + 2\ CO.$$

VI. COMPLEXES WITH CYCLO-P_3 AND CYCLO-As_3 AS COLIGANDS

The ligands p_3 and np_3 react with the aquacations of cobalt(II) and nickel(II) and white phosphorus or yellow arsenic to give complexes with the cyclic triatomic ligands cyclo-p_3 and cyclo-As_3, such as $[Co(L)(\eta^3\text{-}P_3)]$ (L = p_3, np_3)[66] or the dimeric species $[M_2(p_3)_2\text{-}\mu\text{-}(\eta^3\text{-}D_3)]Y_2$[67] (M = Co, Ni; D = P, As; Y = BF_4, BPh_4). This field of tripod ligand chemistry has been reviewed elsewhere.[68] In the complexes of Figures 40[66a] and 41 [66b] the cobalt is six-coordinate and both p_3 and np_3 act as tridentate ligands. In order to comply with the 18-electron rule the cyclo-P_3 ligand must be designated a trihapto three-electron donor. In the binuclear complexes of cobalt and nickel and P_3 and As_3 moieties bridge

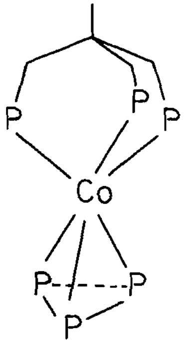


FIGURE 40

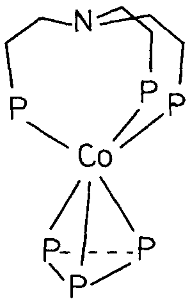


FIGURE 41

between two M(p_3) residues so that each metal atom is again six-coordinate (Figure 42).[67] The interatomic distances in cyclo-P_3 and cyclo-As_3 are only slightly less than in the corresponding tetrahedral molecules P_4 and As_4. The P–P distance in cyclo-P_3 is less in the terminally bonded case than in the bridge-bonded one, and decreases in both types of compound with increasing M–P_3 distance. These structural data would seem to indicate that the three electrons of π symmetry in P_3 are essentially involved in the bonds to the metal atoms, and that bonding within the P_3 moiety is of minimal importance. The mononuclear complexes can also be viewed as substitution products of P_4 in which one vertex is replaced by M(p_3).

The complexes of Figures 40 and 41 are the parents of a long series of mono, bi and polynuclear complexes containing the η^3–P_3 species, the ancillary ligands p_3, Et_6p_3 and various 3*d*, 4*d* and 5*d* metals. The binuclear species were mostly made by reacting the complex $[M(p_3)(\eta^3\text{–}P_3)]$ with the metal aquacation and the ancillary ligand[69]:

$$[M^1(p_3)(\eta^3\text{-}P_3)] + [M^2(H_2O)_6]^{2+} + p_3 \rightarrow [(p_3)M^1\text{-}\mu\text{-}(\eta^3\text{-}P_3)M^2(p_3)]^{2+}$$

$$M^1 = \text{Co, Rh, Ir} \qquad M^2 = \text{Co, Ni}$$

The compounds have a sandwich structure in which cyclo-P_3 is the filling and the two metal atoms may be alike or different. In a sense the terminally bonded η^3-P_3 group acts as a Lewis base in forming these sandwiches. It can also act as a Lewis base by using the nonbonding

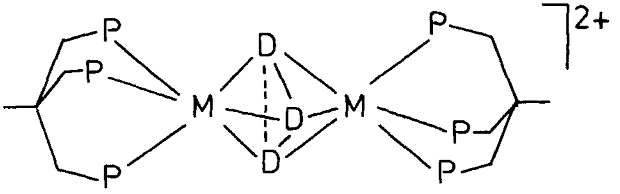


FIGURE 42 D = P,As; M = Co,Ni.

pairs of electrons in the P_3 plane to donate to electrophilic species (Figure 43):

$[Co(p_3)(\eta^3\text{-}P_3)] + [Cr(CO)_6] \rightarrow [(p_3)Co(P_3)\{Cr(CO)_5\}_n]$,
$n = 1,2$[70]

$[Co(p_3)(\eta^3\text{-}P_3)] + [Mn(C_5H_5)(CO)_4] \rightarrow [(p_3)Co(P_3)\{Mn(C_5H_5)(CO)_2\}_3]$.[71]

These reactions are formally analogous to those in which $[Co(p_3)(CS_2)]$ behaves as a ligand itself (Section IV).

Also monocations of general formula $[M(p_3)(\eta^3\text{-}P_3)]^+$ (M = Ni, Pd, Pt) have been obtained using different starting materials and experimental procedures. Interestingly, the nickel complex has been obtained by the reaction of the aquacation of nickel(II) and the ligand p_3 with P_4S_3.[72]

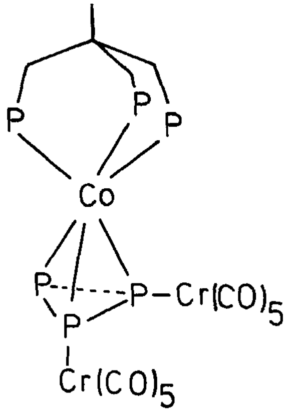


FIGURE 43

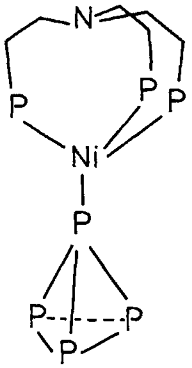


FIGURE 44

Finally, two complexes of the formula $[M(np_3)(P_4)]$ (M = Ni, Pd) (Figure 44)[73,69a] which contain an intact P_4 molecule, have been obtained by reaction of the complexes $[M(np_3)]$ with P_4.

F. MANI
L. SACCONI
Institute of General and Inorganic Chemistry,
University of Florence,
Florence, Italy

References

1. L. Sacconi and F. Mani, *Transition Metal Chemistry* (Marcel Dekker, New York, 1982), p. 179.
2. J. G. Hartley, L. M. Venanzi and D. G. Goodall, J. Chem. Soc. **1963,** 3930 (1963).
3. T. E. W. Howell, S. A. J. Pratt and L. M. Venanzi, J. Chem. Soc. **1961,** 3167 (1961).
4. O. St. C. Headly, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe and L. M. Venanzi, Inorg. Chim. Acta **4,** 93 (1970).
5. L. Sacconi and I. Bertini, J. Am. Chem. Soc. **90,** 5443 (1968).
6. C. Bianchini, C. Mealli, S. Midollini and L. Sacconi, Inorg. Chim. Acta **31,** L433 (1978).
7. C. Bianchini, C. Mealli, A. Meli and L. Sacconi, Inorg. Chim Acta **43,** 223 (1980).
8. L. Sacconi, I. Bertini and F. Mani, Inorg. Chem. **7,** 1417 (1968).
9. L. Sacconi, P. Dapporto and P. Stoppioni, Inorg. Chem. **15,** 325 (1976).
10. R. B. King, R. N. Kapoor, M. S. Saran and P. N. Kapoor, Inorg. Chem. **10,** 1851 (1971); R. B. King and J. C. Cloyd, Jr., *ibid.* **14,** 1550 (1975).
11. G. A. Barclay and A. K. Barnard, J. Chem. Soc. **1961,** 4269 (1961).
12. W. Hewertson, H. R. Watson, J. Chem. Soc. **1962,** 1490 (1962); J. Chatt and F. H. Hart, *ibid.* **1960,** 1378 (1960).
13. D. Berglund and D. W. Meek, Inorg. Chem. **11,** 1493 (1972).
14. S. Midollini and F. Cecconi, J. Chem. Soc. **1973,** 681 (1973).
15. A. S. Kasenally, R. S. Nyholm, M. H. B. Stiddard, J. Am. Chem. Soc. **86,** 1884 (1964); J. R. Phillips and J. H. Vis, Can. J. Chem. **45,** 675 (1967).
16. C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, J. Organomet. Chem. **209,** 219 (1981).
17. F. Cecconi, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chim. Acta **42,** 59 (1980).
18. T. L. Blundell and H. M. Powell, Acta Cryst. **B27,** 2304 (1971); T. L. Blundell, H. M. Powell and L. M. Venanzi, J. Chem. Soc. Chem. Commun. **1967,** 763 (1967); L. Sacconi and M. Di Vaira, Inorg. Chem. **17,** 810 (1978); P. Dapporto and L. Sacconi, J. Chem. Soc. **1970,** 1804 (1970); M. Di Vaira and L. Sacconi, J. Chem. Soc. Dalton **1975,** 493 (1975); L. Sacconi, M. Di Vaira and A. Bianchi, J. Am. Chem. Soc. **92,** 4465 (1970); M. Di Vaira and A. Bianchi Orlandini, Inorg. Chem. **12,** 1292 (1973); M. Di Vaira, J. Chem. Soc. Dalton **1975,** 1575 (1975); F. Mani and L. Sacconi, Inorg. Chim. Acta **4,** 365 (1970).

19. M. Di Vaira, J. Chem. Soc. Dalton **1975,** 2360 (1975); P. L. Orioli and L. Sacconi, J. Chem. Soc. Chem. Commun. **1969,** 1012 (1969); C. Mealli, P. L. Orioli and L. Sacconi, J. Chem. Soc. **1971,** 2691 (1971).
20. I. V. Howell and L. M. Venanzi, J. Chem. Soc. **1967,** 1007 (1967).
21. B. Chiswell and L. M. Venanzi, J. Chem. Soc. **1966,** 417 (1966).
22. (a) M. T. Halfpenny, J. G. Hartley and L. M. Venanzi, J. Chem. Soc. **1967,** 627 (1967); (b) P. Stoppioni, F. Mani and L. Sacconi, Inorg. Chim. Acta. **11,** 227 (1974); M. Bacci, S. Midollini, P. Stoppioni and L. Sacconi, Inorg. Chem. **12,** 1801 (1973).
23. (a) J. G. Hartley, D. G. E. Kerfoot and L. M. Venanzi, Inorg. Chim Acta **1,** 145 (1967); M. Di Vaira, A. Meli and L. Sacconi, Cryst. Struct. Commun. **6,** 727 (1977). G. Kordosky, G. S. Benner and D. W. Meek, Inorg. Chim. Acta **7,** 605, (1973).
24. M. Di Vaira, C. A. Ghilardi and L. Sacconi, Inorg. Chem. **15,** 1555 (1976).
25. C. A. Ghilardi, A. Sabatini and L. Sacconi, Inorg. Chem. **15,** 2763 (1976).
26. L. Sacconi, C. A. Ghilardi, C. Mealli and F. Zanobini, Inorg. Chem. **14,** 1380 (1975).
27. (a) C. Mealli, S. Midollini and L. Sacconi, Inorg. Chem. **14,** 2513 (1975); C. Benelli, M. Di Vaira, G. Noccioli and L. Sacconi, *ibid.* **16,** 182 (1977).
28. C. A. Ghilardi, C. Mealli, S. Midollini, V. I. Nefedov, A. Orlandini and L. Sacconi, Inorg. Chem. **19,** 2454 (1980).
29. P. Dapporto, G. Fallani and L. Sacconi, Inorg. Chem. **13,** 2847 (1974).
30. P. Stoppioni, M. Di Vaira and P. M. Maitlis, J. Chem. Soc. Dalton **1982,** 1147 (1982).
31. G. Dyer, J. G. Hartley and L. M. Venanzi, J. Chem. Soc. **1965,** 1293 (1965).
32. L. Sacconi and S. Midollini, J. Chem. Soc. Dalton **1972,** 1213 (1972).
33. (a) P. Dapporto and L. Sacconi, Inorg. Chim. Acta **39,** 61 (1980).
    (b) A. Orlandini and L. Sacconi, Inorg. Chim. Acta **19,** 61 (1976).
34. L. Sacconi, P. Dapporto and P. Stoppioni, Inorg. Chem. **15,** 325 (1976).
35. L. Sacconi, P. Dapporto and P. Stoppioni, J. Am. Chem. Soc. **97,** 5595 (1975); L. Sacconi, P. Dapporto and P. Stoppioni, Inorg. Chem. **16,** 224 (1977).
36. L. Sacconi, A. Orlandini and S. Midollini, Inorg. Chem. **13,** 2850 (1974), and unpublished results from this laboratory.
37. C. Mealli and L. Sacconi, J. Chem. Soc. Chem. Commun. **1973,** 886 (1973).
38. J. Chatt, F. A. Hart and H. R. Watson, J. Chem. Soc. **1962,** 2437 (1962).
39. C. A. Ghilardi, S. Midollini and L. Sacconi, Inorg. Chem. **14,** 1790 (1975).
40. P. Dapporto, G. Fallani, S. Midollini and L. Sacconi, J. Am. Chem. Soc. **95,** 2021 (1973); P. Dapporto, S. Midollini and L. Sacconi, Inorg. Chem. **14,** 1643 (1975).
41. P. Dapporto, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chem. **15,** 2768 (1976).
42. A. Orlandini and L. Sacconi, Inorg. Chem. **15,** 78 (1976).
43. M. Di Vaira, S. Midollini and L. Sacconi, Inorg. Chem. **16,** 1518 (1977).
44. C. Mealli, S. Midollini and L. Sacconi, Inorg. Chem. **17,** 632 (1978).
45. M. Di Vaira, S. Midollini and L. Sacconi, Inorg. Chem. **17,** 816 (1978).
46. H. Vahrenkamp, Angew. Chem. Int. Ed. Engl. **14,** 322 (1975).
47. (a) C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, Inorg. Chem. **19,** 2968 (1980). (b) C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, Angew. Chem. Int. Ed. Engl. **18,** 673 (1979). (c) C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, Inorg. Chim. Acta **35,** L375 (1979).
48. C. A. Ghilardi, S. Midollini and L. Sacconi, J. Organomet. Chem. **186** 279 (1980).

49. C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, Angew. Chem. Int. Ed. Engl. **19,** 1021 (1980); C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, J. Organomet. Chem. **218,** 81 (1981).
50. C. A. Ghilardi, S. Midollini and L. Sacconi, Inorg. Chem. **16,** 2377 (1977).
51. C. A. Ghilardi, S. Midollini and S. Moneti, J. Organomet. Chem. **217,** 391 (1981).
52. C. Mealli, A. Orlandini, L. Sacconi and P. Stoppioni, Inorg. Chem. **17,** 3020 (1978).
53. M. Bacci and S. Midollini, Inorg. Chim. Acta **5,** 220 (1971); H. Behrens, H. D. Feilner and E. Lindner, Z. Anorg. Allg. Chem. **385,** 321 (1971); H. Behrens and W. Aquila, *ibid.* **356,** 8 (1967); J. Chatt and R. H. Watson, J. Chem. Soc. **1961,** 4980) (1961); J. Chatt and F. A. Hart *ibid.* **1965,** 812 (1965); H. Behrens and K. Lutz, Z. Anorg. Allg. Chem. **356,** 225 (1967).
54. R. B. King, L. W. Hauk and K. H. Pannell, Inorg. Chem. **8,** 1042 (1969); E. O. Fischer and K. Fichtee, Chem. Ber. **94,** 1200 (1961); A. Davidson, M. L. H. Green and G. Wilkinson, J. Chem. Soc. **1961,** 3172 (1961); R. B. King, Inorg. Chem. **1,** 964 (1962); R. Burton, L. Prett and G. Wilkinson, J. Chem. Soc. **1961,** 594 (1961); R. B. King and A. Efraty, Inorg. Chem. **8,** 2374 (1964); W. S. Tsang, D. W. Meek, and W. Wojcicki, *ibid.* **17,** 1264 (1968); D. Rehder and U. Puttfarcken, J. Organomet. Chem. **184,** 343 (1980).
55. C. Mealli, S. Midollini, S. Moneti and L. Sacconi, Angew Chem. Int. Ed. Engl. **19,** 931 (1980).
56. C. Mealli, S. Midollini, S. Moneti and L. Sacconi, J. Organomet. Chem. **205,** 273 (1981).
57. S. Midollini, S. Moneti, A. Orlandini and L. Sacconi, Cryst. Struct. Commun. **9,** 1153 (1980).
58. C. Bianchini, P. Dapporto, A. Meli and L. Sacconi, J. Organomet. Chem. **193,** 117 (1980).
59. C. Bianchini, P. Dapporto, and A. Meli, J. Organomet. Chem. **174,** 205 (1979).
60. P. K. Maples, M. Green, and F. G. A. Stone, J. Chem. Soc. Dalton **1973,** 388 (1973); J. Browing and B. R. Penfold, J. Chem. Soc. Chem. Commun. **1978,** 198 (1978).
61. L. Sacconi, P. Dapporto, P. Stoppioni, P. Innocenti and C. Benelli, Inorg. Chem. **16,** 1669 (1977).
62. P. Stoppioni, P. Dapporto, and L. Sacconi, Inorg. Chem. **17,** 718 (1978).
63. P. Dapporto, and L. Sacconi, Inorg. Chim. Acta **9** L2 (1974).
64. P. Stoppioni and P. Dapporto, Cryst. Struct. Commun. **7,** 375 (1978).
65. T. H. Coffield, R. D. Closson and J. Kozikowski, J. Org. Chem. **22,** 598 (1957); F. Calderazzo and F. A. Cotton, Inorg. Chem. **1,** 30 (1962); R. J. Mawby, F. Basolo and R. G. Pearson, J. Am. Chem. Soc. **86,** 3994 (1964); K. Noack and F. Calderazzo, J. Organomet Chem. **10,** 101 (1967); K. Noack, M. Ruch and F. Calderazzo, Inorg. Chem. **7,** 345 (1968).
66. (a) M. Di Vaira, C. A. Ghilardi, S. Midollini and L. Sacconi, J. Am. Chem. Soc. **100,** 2550 (1978); (b) F. Cecconi, P. Dapporto, S. Midollini and L. Sacconi, Inorg. Chem. **17,** 3292 (1978).
67. (a) M. Di Vaira, S. Midollini, L. Sacconi and F. Zanobini, Angew. Chem. Int. Ed. Engl. **17,** 676 (1978); (b) M. Di Vaira, S. Midollini and L. Sacconi, J. Am. Chem. Soc. **101,** 1757 (1979).
68. L. Sacconi and M. Di Vaira, Angew. Chem. Int. Ed. Engl. **21,** 330 (1982).
69. C. Bianchini, M. Di Vaira, A. Meli and L. Sacconi, J. Am. Chem. Soc. **103,** 1448 (1981); (a) P. Dapporto, L. Sacconi, P. Stoppioni and F. Zanobini, Inorg. Chem. **20,** 3834 (1981); C. Bianchini, M. Di Vaira, A. Meli and L. Sacconi, *ibid.*, 1169

(1981); C. Bianchini, M. Di Vaira, A. Meli and L. Sacconi, Angew. Chem. Int. Ed. Engl. **19,** 405 (1980); C. Bianchini, C. Mealli, A. Meli and L. Sacconi, Inorg. Chim. Acta **37,** L543 (1979); L. Fabbrizzi and L. Sacconi, Inorg. Chim. Acta **36,** L407 (1979).

70. C. A. Ghilardi, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chem. **19,** 301 (1980).
71. C. Mealli, S. Midollini, S. Moneti and L. Sacconi, Cryst. Struct. Commun. **9,** 1017 (1980).
72. M. Di Vaira, L. Sacconi and P. Stoppioni, J. Organomet. Chem., in press.
73. P. Dapporto, S. Midollini and L. Sacconi, Angew. Chem. **91,** 510 (1979).