TRANSITION METAL COMPLEXES CONTAINING BIDENTATE PHOSPHINE LIGANDS

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I. Introduction

The greater stability of complexes of bidentate ligands compared with the corresponding complexes containing similar monodentate ligands is well known. Jorgensen prepared ethylenediamine complexes in 1889, and Blau investigated the bipyridyl and *o*-phenanthroline complexes of iron in 1898. *o*-Phenylenebisdimethylarsine was prepared by Chatt and Mann in 1939, and its complexes have been extensively investigated by Nyholm and co-workers. 1,2-Bis(diphenylphosphino)-ethane (dPe*) was synthesized by Wymore and Bailar in 1956, and the chemistry of the metal diphosphine complexes has since been the subject of a good deal of work. In the relatively short space of 15 years a large number of complexes of diphosphine ligands have been prepared; of these dPe has been most widely used.

At the present time more than sixty diphosphines are known as ligands, but many of these have been only incompletely studied. One of the aims of this review is to focus attention on these less well-studied ligands, and with this in mind, a section has been devoted to references to the synthesis of the various diphosphines.

The coverage is intended to be comprehensive with the exception of organometallic compounds containing diphosphine ligands. Compounds of this type were included when either they were considered to be of particular interest because of the diphosphine ligand, or for comparative purposes. In the last few years a large number of organometallic compounds often containing dPe have been prepared, in which the interest centers on the metal–carbon bond and not the metal–phosphorus bond; these compounds have generally not been included.

There has been one previous review (*30*) in which metal–diphosphine compounds were included, and several other reviews (*110*, *124*, *145*) have included some diphosphine compounds studied from a different viewpoint. Reviews on the ligand preparations have also been published (*97*, *203*).

II. Bonding in Metal–Phosphine Complexes

Until relatively recently concensus of opinion had it that the preference of phosphorus ligands for class (b) cations was due to the formation of π-type bonds between the metal and phosphorus atoms (*30*). A schematic representation of this type of bond (dative π bonding or back-bonding) is shown in Fig. 1.

A revaluation of this model has been stimulated by the work of Venanzi and co-workers, who have reported the ^{195}Pt–^{31}P coupling constants for a series of square-planar Pt(II) complexes (*224*). They found that, as the ligand trans to the phosphine becomes a better trans director, the ^{195}Pt–^{31}P coupling constant decreases. Based on some

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* See Appendix for list of abbreviations used for the diphosphine ligands discussed in this review.

rather vigorous assumptions about the nature of $J(^{195}\text{Pt}-^{31}\text{P})$ (the constancy of ΔE and the constancy of the contribution of the phosphorus $3s$ orbital in the series), these authors related the magnitude of the coupling constant to the s character and strength of the Pt–P bond and concluded that, as the ligand trans to the phosphine becomes a more effective trans director, the s character and the strength of the Pt–P bond decreases. Venanzi *et al.* also concluded that phosphines have a very high trans influence which is entirely due to σ-bonding effects.

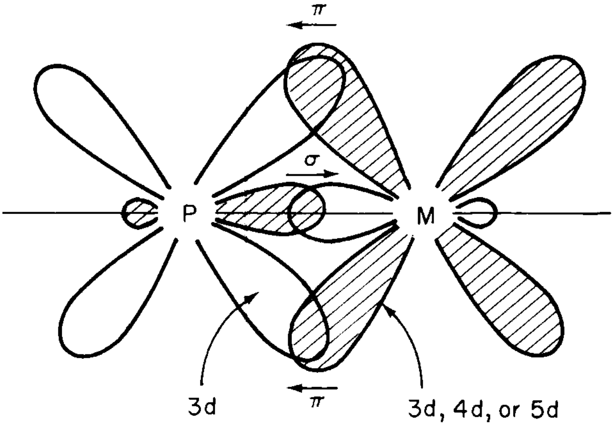


Fig. 1. Bonding in metal-phosphine complexes.

The conclusion by these workers that π bonding was not important in the phosphine complexes which they studied was mainly based on the fact that the ratio of the $^{195}\text{Pt}-^{31}\text{P}$ coupling constant in the cis complex to that in the trans complex is the same for both Pt(II) and Pt(IV) complexes. It was suggested that since π bonding is expected to be much less in Pt(IV) than in Pt(II) complexes, the similar coupling constant ratios for the two types of complexes indicate that π bonding is unimportant in both the Pt(II) and Pt(IV) complexes. Because of the difficulties, already mentioned, in interpreting J, and in the absence of any other information, this conclusion seems far from certain.

However, Zumdahl and Drago have done some extended Hückel M.O. calculations in order to investigate the π bonding in Pt(II) complexes (*269*). The extent of $d\pi$–$d\pi$ interactions between the Pt and P atoms in these complexes is hard to estimate because the energy and the Slater exponent for the phosphorus set of $3d$ orbitals are very uncertain.

However, a calculation was performed on *trans*-$PtCl_2(PH_3)(NH_3)$ in which was included a set of phosphorus 3*d* orbitals with a Slater exponent of 0.7 and an energy of −5.0 eV, and it was felt that these parameters would overemphasize any Pt–P $d\pi$–$d\pi$ bonding. The results showed that the Pt–P π-bond order is ~15% of the σ-bond order.

Thus, although it would seem that the postulation of π bonding in metal–phosphine complexes is no longer fashionable, this may only apply to metal ions in their usual oxidation states. It is possible, even likely, that π bonding may become important when ligands with strong electronegative substituents such as PF_3 are used in conjunction with Lewis acids of very low formal oxidation state, as in the complex $[Pt(PF_3)_4]$. It is also likely that π bonding may be of significance in transition states (*258*).

III. Techniques Used to Study Metal–Phosphine Complexes

A variety of physical techniques have been used to characterize transition metal diphosphine complexes. Several of these, namely, conductivity, magnetic, and dipole moment measurements, are standard methods and will not be discussed. Much information has been obtained by application of various spectroscopic methods to these complexes, and some examples of the kind of information obtained are mentioned below.

A. MASS SPECTROSCOPY

This technique has not been widely used. Lewis and co-workers obtained the mass spectra of a number of diphosphine and phosphido-bridged dinuclear carbonyls of Cr, Mo, W, Fe, and Mn (*191*). Observation of the parent ions, e.g., $[(OC)_5Cr(PMe_2)_2Cr(CO)_5]^+$, confirmed the dimeric formulas. The parent ions lose carbonyl groups progressively before appreciable fragmentation of the $M_2P_2R_4$ moiety occurs. In the diphosphine complexes the monomeric ions $M(CO)_nP_2R_4{}^+$ and $MP_2R_4{}^+$ are observed in low abundance, but such ions do not appear in the spectra of the phosphido-bridged complexes. This difference has been proposed as a method of distinguishing between the two types of complexes.

Mass spectroscopy has been used to study a number of other substituted carbonyl complexes. For example, Cullen *et al.* (*103*) found that the ffos and $f_6$fos complexes of iron lost carbonyl groups progressively until $Fe_2(diphos)^+$ remained.

B. INFRARED SPECTROSCOPY

The metal–phosphorus vibrational frequencies occur in the far-infrared, and few assignments have been reported. Many workers have instead studied the infrared frequencies of other ligands in the complex, whose absorptions occur in regions of the spectrum where assignments are easier, e.g., carbonyl and metal–hydride vibrations. The infrared spectra of carbonyl complexes (*136*) and metal–halogen vibrations (*86*) have recently been reviewed. The few examples of metal–phosphorus vibrational assignments which have been made and some data from the study of metal–hydride frequencies and from the spectra of the free and complexed ligands are discussed next.

1. *Metal–Hydride complexes*

The ν(M–H) frequency occurs in the range 2250–1600 cm^{-1}, and is easily observed and assigned, usually by comparing with deuteriated analogs. The δ(M–H) vibrations have only rarely been assigned. The ν(M–H) band is very sensitive to the nature of the trans ligand, and when H is trans to H, the ν(M–H) occurs at a particularly low frequency

TABLE I

EXAMPLES OF METAL–HYDROGEN VIBRATION FREQUENCIES

Compound	ν(M–H)[a] (cm^{-1})	δ(M–H) (cm^{-1})	Ref.
trans-[$\mathrm{OsHCl(dee)_2}$]	2039	—	(*69*)
trans-[$\mathrm{OsH_2(dee)_2}$]	1721	—	(*69*)
trans-[$\mathrm{OsH_2(PEE)_2}$]	1720[b]	—	(*69*)
trans-[$\mathrm{RuHCl(dme)_2}$]	1891[c]	—	(*69*)
trans-[$\mathrm{RuHCl(dee)_2}$]	1938[c]	—	(*69*)
trans-[$\mathrm{RuHCl(dPm)_2}$]	1978	—	(*69*)
trans-[$\mathrm{RuHCl(PEE)_2}$]	1726[b]	—	(*69*)
cis-[$\mathrm{RuH_2(dme)_2}$]	1806	—	(*69*)
trans-[$\mathrm{RuH_2(dee)_2}$]	1615	—	(*58*)
trans-[$\mathrm{FeHCl(dee)_2}$]	1849	656	(*66*)
trans-[$\mathrm{FeH_2(PEE)_2}$]	1726	716	(*66*)
trans-[$\mathrm{FeD_2(PEE)_2}$]	1259 ν(Fe–D)	—	(*70*)
trans-[$\mathrm{FeDCl(dee)_2}$]	1336 ν(Fe–D)	—	(*70*)
$\mathrm{ReH_4(dPe)_2Cl}$	1950	850?	(*120*)
$\mathrm{ReH_3(dPe)_2}$	1860	850?	(*120*)

[a] All solid mulls.

[b] Benzene solution.

[c] Hexane solution.

(~1600 cm^{-1}). ν(M–H) are usually solvent-sensitive, except when H is trans to P, when little change is observed on varying the solvent (*4*).

In the $RuHX(diphos)_2$ complexes ν(Ru–H) increases with increasing electronegativity of the diphosphine (*69*). ν(Ru–H) rises in the order o-$C_6H_4(AsMe_2)_2$ < dme < dee < dPm ~PEE. Table I contains more examples of M–H vibrational frequencies.

2. *Metal–Phosphorus Frequencies*

ν(M–P) frequencies occur in the range ~460–150 cm^{-1} (*218*). There has been a moderate number of assignments of ν(M–P) in tertiary phosphine complexes, but hardly any in diphosphine complexes. With the increasing availability of infrared instruments that cover this region of the spectrum, an increasing number of reports of far-infrared spectra have appeared; but owing to the difficulty of assigning particular bands, most authors have assigned ν(M–X) (X = halogen) (which frequencies often fall in the same region), stating that some at least of the remaining bands must be ν(M–P). A major complication in diphosphine complexes is the relative complexity of the ligands. Boorman and Carty (*26*) studied the far-infrared region of a number of Ni(II) complexes, but were unable to assign ν(M–P) in the diphosphine compounds, since the free ligands had several absorption bands in the range in which ν(M–P) was expected.

3. *IR Spectra of Free and Coordinated Ligands*

When a diphosphine complexes with a metal ion, the electron density on the phosphorus atom changes, and the ligand is restricted in the conformation it can assume. Thus the vibrational spectra of the free and coordinated ligands differ. Ligands containing multiple bonds, VPP, DPPA, etc., are particularly suited to this kind of study since changes in C=C and C≡C bonds are easy to observe. For example, IR studies indicate that the C≡C bond does not coordinate in metal complexes of DPPA (*10*, *47*, *193*). Similarly, Cullen *et al.* (*99*, *100*, *103*) have used IR spectra to show that ffos and $f_6$fos forms complexes in which the C=C is coordinated, e.g., $Fe_2(CO)_6$ffos, or is not coordinated, e.g., $PtCl_2$ffos. Vibrational spectra have also been used to distinguish between diphosphines behaving as monodentate or bidentate ligands (*47*).

C. NUCLEAR MAGNETIC RESONANCE

1. *Proton NMR*

Proton NMR has been widely used in the study of hydrido complexes. Hydrogen bonded to a transition metal exhibits a chemical shift in the range ~17–~45τ, the majority falling between 20–35τ (see Table II).

TABLE II

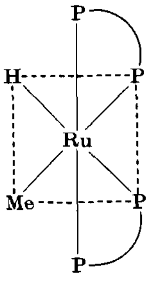
EXAMPLES OF PROTON NMR OF DIPHOSPHINE COMPLEXES

Compound	τ(M–H)[a]	J(P–H) (Hz)	Ref.
trans-$[FeH_2(PEE)_2]$	23.1	—	*(66)*
trans-$[FeHCl(PEE)_2]$	41.2	49 (cis)	*(70)*
trans-$[RuHBr(dee)_2]$	31.5	19 (cis)	*(69)*
trans-$[OsHI(dee)_2]$	31.6	16 (cis)	*(69)*
trans-$[RuHMe(dee)_2]$	18.4		*(72)*
cis-$[RuHMe(dee)_2]$	18.9	19 (cis) 76 (trans)	*(72)*
trans-$[IrHCl(dme)_2]BPh_4$	32.2	17.5 (cis)	*(180)*
trans-$[FeH(CO)(dee)_2]BPh_4$	20.9	47 (cis)	*(16)*
cis-$[MnH(CO)_3(dPe)]$	17.8	45 (cis)	*(29)*

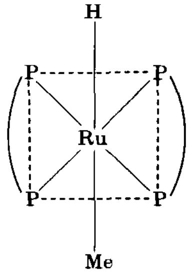
[a] Relative to T.M.S. internal standard.

The J(P–H) values in the range 10–50 Hz are characteristic of *cis*-P–H, whereas J(P–H) values of 75–160 Hz are found for *trans*-P–H.

For the *trans*-hydrohalides of Fe, Ru, and Os the splitting pattern is a 1:4:6:4:1 quintet, which requires the presence of four equivalent ^{31}P nuclei. This indicates that the structure is indeed trans. For *trans*-$FeH_2(PEE)_2$ only three bands were observed *(66)*. The compound $RuHMe(dee)_2$ occurs in two forms; one has a quartet 1:3:3:1 and is thus the cis isomer (I), the other has a more complex pattern, probably due to coupling between the proton and the *trans*-methyl group (II).



(I)



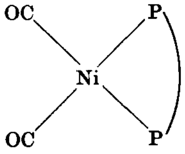
(II)

The ^1H NMR spectra of diphosphine complexes show a number of absorptions due to the magnetically different protons in the molecule. The spectrum of a coordinated diphosphine will differ from that of the uncoordinated ligand in that the magnetic equivalence of some of the protons may be changed, and the extent of shielding will change. The coupling between the phosphorus and the protons in the diphosphine may also change. Recently, several groups have begun to study these effects. In VPP the absorption of the olefinic protons is hidden by that due to the phenyl protons, but in coordinated VPP the olefinic protons are clearly distinguishable from the phenyl protons. This is a reflection of the greater effect of coordination on the olefin protons compared with the phenyl protons (*194*). King and Efraty observed that in DPPB the CH_2 protons are coupled to both phosphorus atoms. On formation of $(PtCl_2DPPB)_2$ coupling decreases; the CH_2 protons are only coupled with the phosphorus to which it is bonded. An intermediate degree of coupling is observed in the compound $(AuCl)_2DPPB$ (*193*).

2. ^{31}P *NMR*

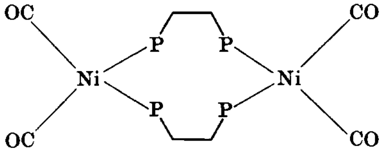
The utility of NMR spectra of the phosphorus isotope ^{31}P in chemical studies of both organic and inorganic compounds containing phosphorus has been well established (*240*), and metal complexes containing phosphine ligands are receiving an increasing amount of attention (*134, 221*). However, diphosphine complexes have not been well investigated.

High-resolution ^{31}P NMR spectra of a large number of nickel carbonyl–phosphine complexes have been obtained by Meriwether and Leto (*216*). It was pointed out that complex formation always causes a shift in the phosphorus resonance, δ^{P}, to a new value δ^{P-M}. In most cases δ^{P-M} is more negative than δ^{P}, agreeing with the intuitive assumption that the formation of a donor bond from phosphorus to nickel results in a decrease in electron density on the phosphorus atom and thus a decrease in the shielding and in the δ value. Three monomeric diphosphine complexes (III) were studied. The values of $\delta^{P-M}-\delta^{P}$ for



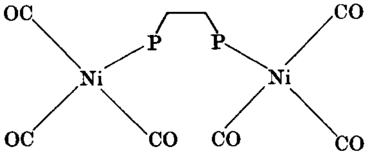
P–P = dee, dne, PEE

(III)



P–P = dne

(IV)



P–P = dee

(V)

these complexes (−68 to −52 ppm) were much more negative than those obtained for the unchelated complexes of similar monodentate complexes (−42 ppm). This was attributed to the presence of the phosphorus atoms in a planar 5-membered ring, in which the C–P–C and Ni–P–C bond angles are distorted from the approximately tetrahedral angles which obtain in the unchelated complexes. The reaction with dne also yielded a small amount of (IV). In this complex the $\delta^{P-M}-\delta^{P}$ was −42 ppm, proving the absence of a chelate ring. Complex (V) also exhibited $\delta^{P-M}-\delta^{P}$ in the unchelated range. The *cis*-Mo(dne)(CO)$_4$ exhibits a large $\delta^{P-M}-\delta^{P}$ (−74.4 ppm) value (*216*).

Grim *et al.* have measured the $^{31}P-^{31}P$ coupling constant in the novel *trans*-[(EtO)$_3$PMo(CO)$_3$dPe] ($J_{P-P} = 104$ Hz) (*133*). The $^{183}W-^{31}P$ nuclear spin coupling constant has also been measured for [W(CO)$_4$·dPe] ($J_{W-P} = 239.0$) (*209*).

D. Electronic Spectroscopy

The observation and interpretation of "*d–d*" bands in the visible spectra of metal complexes have now become refined tools for "fingerprinting" structural types. This is particularly true for $3d^7$ and $3d^8$ complexes, and it is for ions with these configurations that the main application of visible spectroscopy has been made.

Horrocks and co-workers, have identified a planar-tetrahedral equilibrium in complexes of nickel(II) halides with dPp (*150*). These workers have also identified the structures of [CoLX$_2$] (L = dPe, dPp; X = Cl, Br, I) as tetrahedral, and that of [CoL$_2$X$_2$] as pentacoordinate on the basis of electronic spectra (*167*). Dyer *et al.* have also used this technique in assigning structures to the pentacoordinate [Co(VPP)$_2$X]$^+$ (X = Cl, Br, I) cation, and to the [Co(VPP)$_2$(NCS)]$_2$[Co(NCS)$_4$] complex which contains a pentacoordinate cation and a tetrahedral anion (*111*). McAuliffe and Meek assigned square-planar structures to [Ni(VPP)X$_2$] (X = Cl, Br, I, NCS), and square-pyramidal structures to [Ni(VPP)$_2$X]$^+$ (X = Cl, Br, I) using visible spectroscopy (*212*).

E. Electron Spin Resonance

Horrocks *et al.* obtained the electron spin resonance spectra of Co(dPe)$_2$Cl$_2$ (*167*), Co(dPe)$_2$Br$_2$ (*167*), and Ni(dPp)Br$_3$ (*150*). For Ni(dPp)Br$_3$ $g = 2.218$ was obtained, corresponding to a magnetic moment of 1.92 B.M. The g values for the Co complexes were:

Co(dPe)$_2$Cl$_2$	$g_1 = 2.257$	$g_2 = 2.056$	$g_3 = 2.041$
Co(dPe)$_2$Br$_2$	$g_1 = 2.258$	$g_2 = 2.075$	$g_3 = 2.037$

which leads to $\mu = 1.84$ B.M. The ESR spectra are consistent with the ground state configuration for the pentacoordinate complexes of $|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(x^2-y^2)}\rangle$, in agreement with electronic spectral data (*167*).

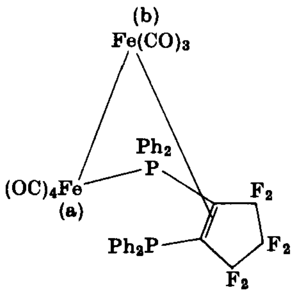
The reaction of $Co(dPe)_2Cl_2$ or $Co(dee)_2Cl_2$ with MeMgCl in 1,2-dichloroethane gave no ESR signal at a Mg : Co ratio >8, consistent with the formation of Co^{I}. The reappearance of Co^{II} was observed. The suggested explanation was that the signal was produced by Co–H interaction, i.e., that a proton from the phosphine was exchanged for a chloride ion (*151*).

F. MÖSSBAUER SPECTROSCOPY

Only diphosphine complexes of iron have so far been studied by this technique, although it is potentially capable of extension to a number of other transition metals, e.g., Ni, Ir, or Pt.

Bancroft *et al.* (*15*) studied a number of low-spin iron(II) complexes of the type $FeX_2(diphos)_2$. They found an inverse correlation between the partial center shifts of the various ligands and their position in the spectrochemical series. The partial center shifts for the ligands dee, dme, and PEE were obtained, and the results discussed in terms of the σ-donor and π-acceptor properties of these ligands. The quadrupole splitting values have been used as a means of assigning structure in some iron complexes, but in the cases discussed, the Mössbauer data did not clearly indicate the configuration.

Cullen *et al.* (*103*, *105*) have obtained some interesting results from the $f_6$fos complexes. $Fe_2(CO)_7f_6$fos and $Fe_2(CO)_6f_6$fos are believed to have the structures (VI) and (VII), respectively. The Mössbauer spectra are in agreement with these structures and exhibit several interesting features. The isomer shifts for Fe(b) in both compounds are



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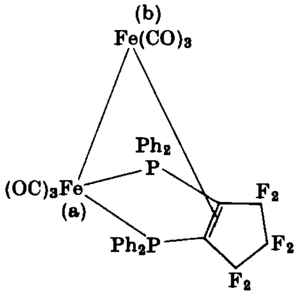
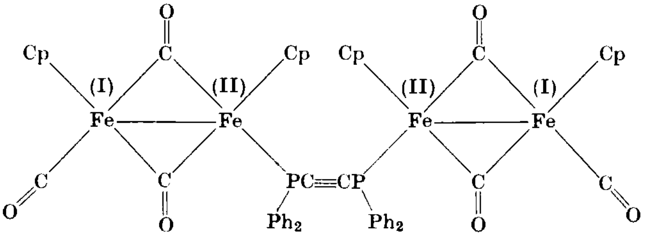


(VII)

identical, but Fe(a) is slightly lower in the $Fe_2(CO)_7$ complex than in the $Fe_2(CO)_6$ complex (lower shift corresponding to higher *s*-electron density). This was attributed to the greater $d\pi$-acceptor properties of the extra carbonyl group compared with Ph_2P–. In both complexes the isomer shift of Fe(a) is smaller than that of Fe(b), indicating a deficiency of *s*-electron density on the Fe(b) nucleus. The quadrupole splitting of Fe(a) in $Fe_2(CO)_6f_6fos$ is greater than that of Fe(a) in $Fe_2(CO)_7f_6fos$. When both phosphorus atoms are coordinated to Fe(a), the P–Fe(a)–P angle is fixed, which means a distortion of the octahedron around Fe(a). In $Fe_2(CO)_7 \cdot f_6fos$ the presence of one coordinated phosphorus only allowed this distortion to be minimized. Mössbauer spectra then can give information about the environment of the metal atom and the electron density on the atom.



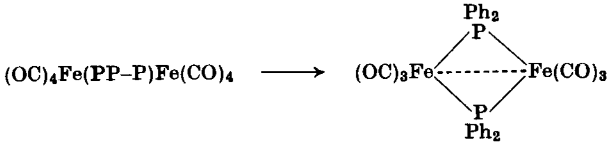
(VIII)

An interesting case is that of $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3]_2DPPA$ (*52*). An X-ray structural determination showed it to be (VIII), but a Mössbauer study failed to detect the nonequivalence of the iron atoms, the difference in isomer shift between Fe^{I} and Fe^{II} being too small to be resolved.

IV. X-Ray Crystallography Studies

Several diphosphine complexes have had full crystallographic structures determined, and a section is devoted to them here in order to illustrate some especially interesting features of diphosphine complexes.

Mais and co-workers have determined the structure of $[(OC)_3Ni(PP\text{–}P)Ni(CO)_3]$ (*206*). Nickel is in a tetrahedral environment, and the diphosphine link has the catenary form. The molecule consists of two identical halves related by a center of symmetry. The P–P bond (2.777 Å) is longer than normal, and this was attributed to steric strain resulting from repulsion between the phenyl groups and between the phenyl and carbonyl groups. The increased length of the P–P bond suggests that this bond may be weak, and when PP–P is complexed in the analogous iron carbonyl complex, cleavage of the P–P bond occurs.



(IX)

However, the iron carbonyl complex containing MP–P is stable, and Jarvis *et al.* have published the structure of $[(OC)_4Fe(MP\text{–}P)Fe(CO)_4]$ (*187*). This has the centrosymmetric pi-catenary form; a "staggered" conformation of substituents (methyl or carbonyl) about the Fe–P and P–P bonds which produce the main steric interactions. However, these steric interactions are not at all severe, and the P–P bond length (2.231 Å) is quite normal. The Fe atoms are not in an "ideal" trigonal-bipyramidal environment (two equatorial bond angles = 116°–117°, and one equatorial bond angle = 127°, instead of three at 120°). The Fe–P bond length (2.25 Å) is less than the radius sum (2.35–2.40 Å, taking 1.25–1.30 Å as the radius for iron) by about 0.10–0.15 Å, and suggests that there is appreciable double bonding in the Fe–P bond.

Adam *et al.* investigated the structure of $[MoOCl(dPe)_2][ZnCl_3\cdot(OCMe_2)]$ (*3*). The molybdenum atom is in a fairly regular octahedral environment, with bond lengths of Mo–O (1.69 Å), Mo–Cl (2.46 Å), and Mo–P (2.57 Å, mean).

The planar $[Rh(dPe)_2](ClO_4)$ structure was elucidated by Hall *et al.* (*138*) and these workers included a valuable discussion of the torsion included in the bond angles of this and several other diphosphine complexes. The mean Rh–P bond length is 2.306 Å, and the P–Rh–P angles are 82.7°.

The oxygen adduct of $[Rh(dPe)_2]^+$, $[Rh(O_2)(dPe)_2]PF_6$, and the analogous iridium complex have been studied crystallographically by McGinnety *et al.* (*215*). The complexes have been assigned distorted trigonal-bipyramidal structures. The mean Rh–P distance (2.342 Å) is longer than in the parent complex, and the mean Ir–P distance is 2.283–2.452 Å. The bond lengths associated with the oxygen molecule are very interesting. The Rh complex can be reversibly oxygenated and the mean Rh–O distance is 2.2025 Å and O–O distance is 1.418 Å (the O_2 molecule is bonded "sideways on" to the Rh and Ir). However, oxygenation is irreversible in the Ir complex, the Ir–O bond (1.976 Å) is distinctly shorter, and the O–O bond (1.625 Å) has lengthened compared with the Rh complex.

The complex "Ru(dme)$_2$(naphthalene)" was originally thought to be a complex of Ru(0), but the I.C.I. crystallographers have shown this to be a Ru(II)-hydrido complex, *trans*-[Ru(H)(naphthyl)(dme)$_2$]. The complex is a fairly regular octahedron, with Ru–P (2.28–2.33 Å) and an estimated Ru–H bond length of 1.7 Å (*169*).

The phenomenon of diphosphine ligands promoting the coordination of both thiocyanato and isothiocyanato groups in [Pd(diphos)(NCS)(SCN)] complexes has been investigated by Meek and McAuliffe and co-workers (*84*). Palenik has X-rayed the complex prepared by Meek [Pd(dPe)(SCN)(NCS)] and shown the complex to be approximately square-planar (*24*). The complex does indeed contain both S- and N-bonded groups. The Pd–P bond trans to –SCN is significantly longer (2.260 Å) than the Pd–P bond trans to the –NCS group (2.245 Å).

[Ni(POPO)Cl$_2$] contains a distorted tetrahedral environment about the Ni atom (Cl–Ni–Cl = 127.1°, P–Ni–P = 107.1°). The mean Ni–Cl distance is 2.20 Å, and the mean Ni–P distance is 2.315 Å. The oxygen atom in the chelate is 3.64 Å from the metal and is thus not coordinated. This complex is therefore a rare example of an eight-membered chelate ring (*132*).

V. Syntheses of Diphosphines

The synthetic methods have been reviewed and will not be discussed. For completeness, references to synthesis are included in the Appendix alongside the abbreviations.

VI. Diphosphine Complexes

A. LANTHANIDES AND ACTINIDES

A light tan complex UCl$_4$·dme was reported (*207*) in 1963, but its existence has since been questioned (*247*). A light green complex (UCl$_4$)$_2$·dPe produced by mixing UCl$_4$ and dPe in THF seems authentic (*247*). The IR spectrum of this complex shows no evidence of P═O, P–H, or UO_2^{2+}; $\mu_{eff} = 3.2$ B.M.

A pale green U^{V} complex, UCl$_5$·dPe, $\mu_{eff} = 2.7$ B.M., was synthesized by mixing UCl$_5$·tcac with dPe in benzene (tcac = Cl$_2$C═CCl—COCl) with exclusion of oxygen and moisture (*246*).

B. GROUP IVA (Ti, Zr, AND Hf)

A complex of Ti^0 (analogous to the V, Cr, Mo, and W complexes) could not be obtained; reduction of $TiCl_4$·dme gave a black solid—probably metallic titanium (*82*).

Titanium tetrachloride reacts with dme, dee, and PEE in dry benzene under nitrogen to give red or orange 1:1 adducts, $TiCl_4$·L (*71*). By reacting $TiCl_4$ with dPe in various ratios in benzene three red solids were obtained: $TiCl_4$·dPe (*119*, *260*), $(TiCl_4)_2$·dPe, and $(TiCl_4)_3(dPe)_2$ (*260*); their IR spectra were recorded. All are extremely moisture-sensitive. The ligand PMM reacted with $TiCl_4$ in a 2:1 ratio to produce the eight-coordinate, orange $TiCl_4(PMM)_2$ (*88*). Titanium tetrabromide is reported to be reduced to Ti^{III} by dPe (*119*).

The complexes $[CH_3TiCl_3(dPe)]$ (*87*) and $[Ti(CH_3)_4(dme)]$ (*254*) have been prepared. A compound thought to be $TiCl_3$(dee) was obtained as a dark brown solid by refluxing the ligand with $TiCl_3$ in benzene (*71*).

Fowles could not obtain pure complexes from the reaction of zirconium halides with dPe (*119*); but the compounds $[Zr(dPe)Cl_4]$, $[Zr(dpe)Br_4]$, and $[Hf(dPe)Cl_4]$ have been obtained from MX_4 and dPe in benzene, and their IR spectra in the range 460–250 cm^{-1} reported (*227*).

C. GROUP VA (V, Nb, AND Ta)

Brown-black crystals of $V(dme)_3$ were obtained by reducing a mixture of VCl_3 and dme in THF with sodium naphthalenide (*82*). It is paramagnetic, $\mu_{eff} = 2.1$ B.M. A similar reaction with $NbCl_5$ gave only a black carbon-free sludge, presumably niobium metal.

Reaction of $V(CO)_6$ with dPe produced three different products depending on the ratio of the reactants and the temperature: the red-brown $[VL_3][V(CO)_6]$, $\mu_{eff} = 4.01$ B.M.; the dark-green $[V(CO)_4L]$, $\mu_{eff} = 2.23$ B.M.; and the red *trans*-$[V(CO)_2L_2]$, $\mu_{eff} = 1.77$ B.M. The anion $[V(CO)_4L]^-$ was also obtained (*20*). $V(CO)_6$ gives a phosphido derivative with PP–P, but vanadium nitrosyl carbonyl forms $[(CO)_4(NO)V(PP\text{–}P)V(NO)(CO)_4]$ (*159a*).

Vanadium trichloride reacted with dme in THF to produce an apple-green solution, but no complex was isolated (*82*). VCl_4 is reduced by dPe (*34*).

Selbin investigated the reaction of $VOX_2 \cdot xH_2O$ (X = Cl, Br) with dPe and dPm. Green complexes $[VOBr_2(dPe)\cdot H_2O]$, $[VOBr_2(dPm)\cdot H_2O]$, and $[VOCl_2(dPe)\cdot H_2O]$ were obtained. Their electronic and IR spectra were characteristic of the VO^{2+} group. Some blue-green compounds, apparently phosphine oxide complexes, produced by ligand oxidation by V^{IV}, were also formed (*248*).

D. GROUP VIA (Mo, Cr, AND W)

The compounds $Cr(dme)_3$, $Mo(dme)_3$, and $W(dme)_3$ were formed as yellow solids by reducing $CrCl_3$, $MoCl_5$, and WCl_6, respectively, with $LiAlH_4$ or sodium naphthalenide in THF (*82*). Mo^0 complexes $[Mo(dme)_3]$, $[Mo(dPe)_3]$, and $[Mo(PEE)_3]$, were obtained by heating dibenzenemolybdenum with the ligand in a sealed tube (*80*). $K_6Cr(CN)_6$ reacts with dpm and dPe in liquid ammonia to give $[Cr(dpm)_3]$ and $[Cr(dPe)_3]$ (*21*). $[Mo(dme)_3]$ is monomeric in chloroform. All the complexes readily oxidize in the order $Cr > Mo \gg W$. An essentially octahedral structure has been proposed for these unique MP_6 compounds (see Table III).

TABLE III

GROUP VIA DIPHOSPHINE COMPLEXES

Compound	Color	M.p.[a] (°C)	Properties	Ref.
$[Cr(dme)_3]$	Yellow	293 (d)	—	(*82*)
$[Mo(dme)_3]$	Yellow	397	—	(*80, 82*)
$[W(dme)_3]$	Yellow	396 (d)	—	(*82*)
$[Mo(dPe)_3]$	Red-orange	281	—	(*80*)
$[Mo(PEE)_3]$	Red-black	236	—	(*80*)
$[WCl_3(dPe)]$	Brown		IR, $\mu = 1.29$	(*27*)
$WCl_3(dPe)_2$	Yellow		IR, $\mu = 1.48$	(*27*)
$[WCl_4(dPe)]$	Yellow-brown		IR, $\mu = 1.74$	(*27*)
$WCl_5(dPe)$	Pale green		IR, $\mu = 0.90$	(*28*)
$[WCl_2(dPe)_2][WCl_6]$	—		IR, $\mu = 1.09$/W atom	(*27*)
$[MoCl_4(dPe)]$	Red-brown		$\mu = 2.18$	(*36*)
$[MoCl_4(VPP)]$	Red-brown		$\mu = 2.26$	(*36*)
$[(Mo_6Cl_8)Cl_3(dPe)]Cl$	—		Vis.[b]	(*116*)
$[(Mo_6Cl_8)Cl_3(dPe)py]Cl$	—		Vis.	(*116*)

[a] (d), decomposes.
[b] Vis., visible.

The substituted carbonyls have been extensively studied [see Table IV (*110*)]. Although the $M(diphos)_3$ compounds can be prepared directly, complete substitution of the CO in the carbonyls has not been achieved. Three main types of complexes are known: $[M(CO)_4\text{-}diphos]$, $[M(CO)_2(diphos)_2]$, and $[M_2(CO)_6(diphos)_3]$. The compounds

TABLE IV

SUBSTITUTED CARBONYLS OF GROUP VIA

Compound	Color	M.p.^{a}(°C)	Physical properties	Ref.
$[Cr(CO)_4(dPe)]$	White	211–212	IR	(*81*)
$[Mo(CO)_4(dPe)]$	White	193–194	IR	(*81*)
$[W(CO)_4(dPe)]$	Pale yellow	208–209	IR, ^{31}P NMR	(*81, 209*)
$[Cr(CO)_4(dee)]$	White	116	IR	(*81*)
$[Mo(CO)_4(dee)]$	White	107	IR	(*81*)
$[W(CO)_4(dee)]$	Pale yellow	122	IR	(*81*)
$[Cr(CO)_4(dPm)]$	Yellow	171	IR	(*81*)
$[Mo(CO)_4(dPm)]$	Yellow	195	IR	(*81*)
$[W(CO)_4(dPm)]$	Yellow	201	IR	(*81*)
$[Cr(CO)_4(PEE)]$	White	163	IR, D.M. = 7.6	(*81*)
$[Mo(CO)_4(PEE)]$	White	181	IR, D.M. = 7.8	(*81*)
$[W(CO)_4(PEE)]$	White	190	IR, D.M. = 8.3	(*81*)
cis-$[Cr(CO)_2(PEE)_2]$	Orange	265	IR	(*81*)
cis-$[Mo(CO)_2(PEE)_2]$	Bright yellow	257	IR, D.M. = 6.4	(*81*)
cis-$[W(CO)_2(PEE)_2]$	Bright yellow	271	IR, D.M. = 6.6	(*81*)
cis-$[Cr(CO)_2(dPe)_2]$	Pale orange	280	IR	(*81*)
cis-$[Mo(CO)_2(dPe)_2]$	Yellow	324	IR, D.M. = 6.2	(*81*)
cis-$[W(CO)_2(dPe)_2]$	Yellow	321	IR, D.M. = 6.7, ^{31}P NMR	(*81, 209*)
trans-$[Cr(CO)_2(dPe)_2]$	Vermillion	279	IR	(*81*)
cis-$[Cr(CO)_2(dPm)_2]$	Orange	289	IR	(*81*)
trans-$[Mo(CO)_3(dPe)P(OEt)_3]$	Yellow	117	IR, ^{31}P NMR	(*133*)
$[Cr_2(CO)_{10}(MP\text{–}P)]$	Pale yellow	130	IR, UV, NMR, D.M. = 4.6	(*78, 146*)
$[Mo_2(CO)_{10}(MP\text{–}P)]$	Colorless	143	IR, UV, NMR, D.M. = 4.8	(*78, 79, 146*)
$[W_2(CO)_{10}(MP\text{–}P)]$	Colorless	163	IR, UV, NMR, D.M. = 4.6	(*78, 79, 146*)
$[Mo_2(CO)_{10}(EP\text{–}P)]$	Colorless	158(d)	IR	(*79*)
$[W_2(CO)_{10}(EP\text{–}P)]$	Colorless	188	IR	(*79*)

$[\mathrm{Cr_2(CO)_6(dPe)_3}]$	Yellow	263(d)	IR	(*266*)
$[\mathrm{Mo_2(CO)_6(dPe)_3}]$	Colorless	210(d)	IR	(*266*)
$[\mathrm{W_2(CO)_6(dPe)_3}]$	Yellow	194(d)	IR	(*266*)
$[\mathrm{Cr(CO)_4(ffos)}]$	Orange	217	IR	(*99*)
$[\mathrm{Mo(CO)_4(ffos)}]$	Yellow	194	IR	(*99*)
$[\mathrm{W(CO)_4(ffos)}]$	Yellow	208(d)	IR	(*100*)
$[\mathrm{Cr(CO)_4(f_6fos)}]$	Orange-brown	189(d)	IR	(*100*)
$[\mathrm{Mo(CO)_4(f_6fos)}]$	Yellow	192(d)	IR	(*100*)
$[\mathrm{W(CO)_4(f_6fos)}]$	Yellow	216(d)	IR	(*100*)
$[\mathrm{Cr(CO)_4(f_8fos)}]$	Amber	209(d)	IR	(*100*)
$[\mathrm{Mo(CO)_4(f_8fos)}]$	Orange	202(d)	IR	(*100*)
$[\mathrm{W(CO)_4(f_8fos)}]$	Orange	211(d)	IR	(*100*)
$[\mathrm{Cr(CO)_4(dHe)}]$	Cream	—	ν(P–H) 2330 cm^{-1}	(*109*)
$[\mathrm{Mo(CO)_4(dHe)}]$	White	—	ν(P–H) 2345, 2315 cm^{-1}	(*109*)
$[\mathrm{Mo(CO)_4(VPP)}]$	Yellow	174(d)	IR, NMR	(*194*)
$[\mathrm{W(CO)_4(VPP)}]$	Yellow	179	IR, NMR	(*194*)
$[\mathrm{Cr(CO)_4(VPP)}]$	Yellow	152	IR, NMR	(*194*)
$[\mathrm{Mo(CO)_2(dPe)_2}]\mathrm{I_3}$	Red	201(d)	$\mu = 1.66$	(*199*)
$[\mathrm{W(CO)_2(dPe)_2}]\mathrm{I_3}$	Red	216(d)	$\mu = 1.86$	(*199*)
$[\mathrm{Mo(CO)_2(dPe)_2}]\mathrm{ClO_4}$	Pink	160	$\mu = 1.61$	(*199*)
$[\mathrm{W(CO)_2(dPe)_2}]\mathrm{ClO_4}$	Orange	—	—	(*199*)
$[\mathrm{Mo(CO)_3(dPe)\cdot I_2}]$	Orange-brown	208(d)	IR, $\mu = 0$	(*12, 199*)
$[\mathrm{W(CO)_3(dPe)\cdot I_2}]$	Yellow	237(d)	IR, $\mu = 0$	(*12, 199*)
$[\mathrm{Mo(CO)_3(dPe)\cdot Br_2}]$	Yellow	217(d)	IR	(*12, 199*)

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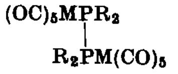
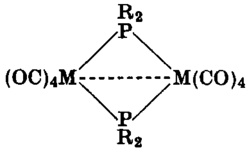
[a] (d), decomposes.

[$M(CO)_4$diphos] result from heating $M(CO)_6$ with a slight deficit of the diphosphine in a sealed tube (*81*). The disubstituted $M(CO)_2$(diphos)$_2$ compounds are obtained similarly with two equivalents of the diphosphine, but [$Cr(CO)_2$(diphos)$_2$] compounds are better prepared from tricarbonylmesitylenechromium (*81*). This latter method also produced the only trans isomer, *trans*-[$Cr(CO)_2$(dPe)$_2$]. The corresponding cis isomer is obtained by recrystallization of the trans isomer from methanol. Infrared and dipole moment measurements have shown that the chromium compounds [$Cr(CO)_2$(diphos)$_2$] exhibit cis-trans isomerism in solution, but this is not observed with the molybdenum and tungsten analogs (*81*). *trans*-[$Mo(CO)_2$(dPm)$_2$] results on refluxing $Mo(CO)_6$ with dPm in *n*-decane (*92*). The dinuclear $M_2(CO)_6$(diphos)$_3$ compounds were obtained by Zingales and Canziani from the reaction of [$M(CO)_3$-(cycloheptatriene)] with the diphosphines (*266*). Some diphosphine-bridged complexes are known, e.g., [$M(CO)_5$]$_2$·dPe (M = Cr, Mo); they react with dPe to form the [$M(CO)_4$(dPe)] compounds (*17*).

Diphosphines containing a direct P–P bond react rather differently from their C-linked analogs. At 180°–200° in sealed tubes, these ligands react with the hexacarbonyls to produce yellowish compounds (X) in which the P–P bond is retained. At higher temperatures the P–P bond ruptures and phosphido-bridged complexes result (XI) (*147*).



(X)



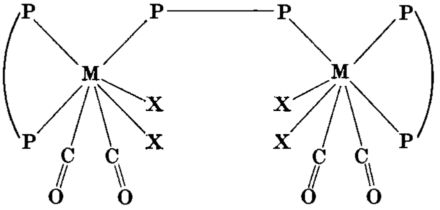
(XI)

M = Cr, Mo, or W

Phosphido-bridged [$Mo_2(CO)_8(PMe_2)_2$] reacts with dPm, dPe, and dPb to produce compounds, $Mo_2(CO)_6(PMe_2)_2$(diphos), of unknown structure (*205*). With P_fP–P molybdenum and chromium form white polymers [$Mo(P_fP$–$P)(CO)_4]_n$, and also low-melting white or yellow compounds [$Mo(P_fP$–$P)(CO)_5$], in which the diphosphine acts as a monodentate ligand (*131*). The di(primary)phosphine,$C_2H_4(PH_2)_2$ (dHe), displaced weakly bonded bidentates from [M(bid.)$(CO)_4$] (M = Cr, Mo, W) to produce [M(dHe)$(CO)_4$] (*109*). Diphosphine, P_2H_4, has been reacted with (norbornadiene)$Mo(CO)_4$ to produce [$Mo(P_2H_4)(CO)_4]_n$ (*17*). In no case is the $\rangle C{=}C\langle$ involved in coordination in the complexes [$M(CO)_4$(diphos)] (M = Cr, Mo, W; diphos = ffos, $f_6$fos, $f_8$fos) (*99, 100*). A large number of compounds containing other ligands as well as diphosphines are known, e.g., [$(C_5H_5)Mo(CO)_2$(dme)]Cl and [(C_5H_5)-

$Mo(CO)_2(VPP)]PF_6$ (*195*, *196*), and the reader is referred to reviews of carbonyl compounds (*1*) for coverage of these.

The complexes $[M(CO)_2(dPe)_2]$ react with three equivalents of iodine to give M^I complexes. The presence of univalent metal is confirmed by the preparation of the perchlorates $[M(CO)_2(dPe)_2]ClO_4$ ($M = Mo, W$). Lewis and Whyman observed that excess chlorine or bromine decomposed the substituted carbonyl complexes with formation of Mo^V, W^{VI}, and phosphine oxide complexes (*199*). Under controlled conditions they isolated $[M(CO)_3(dPe)X_2]$ ($X = Br, I$), and these nonelectrolyte complexes were assigned a seven-coordinate structure. Recently, Colton and co-workers have prepared a number of complexes of the types $[M(CO)_2(diphos)_2X_2]$, $[M(CO)_3(diphos)X_2]$, and $[M(CO)_2(diphos)_{1.5}X_2]_2$ ($M = Mo, W$; diphos = dPm, dPe; $X = Cl, Br, I$) (*12*, *13*, *91–93*). The $M(CO)_2(diphos)_2X_2$ ($X = Cl, Br$) are neutral diamagnetic, seven-coordinate complexes, in which one of the diphosphines behaves as a monodentate ligand. The structures of the $[M(CO)_2(diphos)_{1.5}X_2]_2$ compounds are probably given by (XII). The general methods of preparation are from $M(CO)_4X_2$ + diphosphine, from $[M(CO)_4X_3]^-$ and dPm, or by the method of Lewis and Whyman. The iodo complexes are different in several respects from the chloro and bromo complexes. $M(CO)_2(diphos)_2I_2$ are 1 : 1 electrolytes and react reversibly with CO (*13*, *92*, *93*). They may be seven-coordinate, but it is more likely that they are six-coordinate, with one diphosphine behaving as a monodentate ligand. Two isomers of $M(CO)_3(diphos)I_2$ and three of $M(CO)_2(diphos)_2I_2$ have been isolated (*92*, *93*). The apparently irreversible isomerism occurs on dissolution of the yellow $[Mo(CO)_2(dPm)_2Cl_2]$ under reflux in an inert solvent (*91*). The differences between the complexes formed with the different halogens and those of dPm and dPe are believed to be largely due to steric factors (*91*).



(XII)

$$[Mo(CO)_2(dPm)_2Cl_2] \longrightarrow [Mo(CO)_2(dPm)_2Cl]Cl$$

A *trans*-dinitrogen complex $[Mo(N_2)_2(dPe)_2]$ was obtained as orange-yellow crystals by reducing molybdenum(III) acetylacetonate with iso-Bu_3Al in the presence of nitrogen and dPe (*153*). The ν(N–N) occurs at 1970 cm^{-1}, indicative of the trans configuration. The orange $[W(N_2)_2(dPe)_2]$, ν(N–N) at 1953 cm^{-}, has also been obtained (*22*).

Complexes analogous to Reinecke's salt result from the reaction of $K_3Cr(NCS)_6$ (*175*) and $K_3Mo(NCS)_6$ (*171*) with dCye and dee. The products are $[R_2PH(CH_2)_2PHR_2][M(SCN)_4(diphos)]$ (M = Cr, Mo). A similar complex was obtained with dPm and $K_3Mo(NCS)_6$, but this ligand did not react with $K_3Cr(NCS)_6$. Salts of the $[M(SCN)_4(diphos)]^{2-}$ anions with Cd^{2+}, Cu^{2+}, Zn^{2+}, and Cs^{+} have also been prepared.

The 1 : 1 electrolyte $[(Mo_6Cl_8)(dPe)Cl_3]Cl$ was obtained from Mo_6Cl_{12} and excess dPe in THF. It forms $[(Mo_6Cl_8)(dPe)(py)Cl_3]Cl$ upon recrystallization from pyridine (*116*).

Molybdenum(IV) complexes $[Mo(dPe)Cl_4]$ and $[Mo(VPP)Cl_4]$ were obtained by Butcher and Chatt by adding the ligand in benzene to $[MoCl_4(EtCN)_2]$ in boiling benzene (*36*).

Several dPe complexes of tungsten are known (*27*). $[W(dPe)Cl_3]$ is formed from $[WCl_4(MeCN)_2]$ and dPe, or from K_2WCl_6 and dPe in acetonitrile. $WCl_3(dPe)_2$ results from fusing $[WCl_4(PrCN)_2]$ with dPe. It is a 1:1 electrolyte in nitromethane, $[WCl_2(dPe)_2]Cl$, but a non-electrolyte in chloroform. Fusion of K_2WCl_6 with dPe produces yellow-brown $WCl_4(dPe)$. The green solid, $WCl_5(dPe)$, formed from WCl_6 and excess dPe in benzene, rapidly decomposes in air (*28*). A complex which, on the basis of molecular weight and IR measurements, was formulated as $[WCl_2(dPe)_2][WCl_6]$, was obtained from $[WCl_4(MeCN)_2]$ and dPe in acetonitrile (*28*).

Complexes $[MoOCl(diphos)_2]X$ (diphos = dme, dPe, VPP; X = Cl, BPh_4, BF_4) are obtained as violet or purple solids from $[MoOCl_2(PR_3)_3]$ and excess diphosphine in ethanol (*14*). With a stoichiometric amount of diphosphine $[MoOCl_2(PR_3)(diphos)]$ can be isolated. The THF in $MoOCl_3(THF)$ is easily replaced by dPe giving red $[MoOCl_3(dPe)]$, which can be reduced with zinc in THF to the $[MoOCl(dPe)_2]^{+}$ ion, isolated as $[MoOCl(dPe)_2][ZnCl_3{\cdot}OCMe_2]$ upon recrystallization from acetone (*3*).

E. GROUP VIIA (Mn, Tc, AND Re)

Diphosphine complexes of manganese are only formed in low oxidation states. Manganese(III) is readily reduced by phosphines.

Hieber and Freyer obtained $Mn_2(CO)_8(dPe)$ as yellow crystals by reaction of $Mn_2(CO)_{10}$ and dPe (*155*). Sacco reacted dPe and $Mn_2(CO)_{10}$

in benzene when paramagnetic [$Mn(CO)_3(dPe)$] and [$Mn(CO)(dPe)_2$], and diamagnetic [$Mn(CO)_2(dPe)_2$][$Mn(CO)_5$] and [$Mn(CO)_2(dPe)_2$]Cl were obtained (*232*). [$Mn(CO)_2(dPe)_2$]Cl can be oxidized to the green [$Mn(CO)_2(dPe)_2$]$^{2+}$, which has been isolated as the perchlorate; IR evidence suggests a trans structure (*252*).

Interaction of $HMn(CO)_5$ and dPe in benzene produced the yellow [$HMn(CO)_3(dPe)$]; the NMR spectrum (triplet 1:2:1, $\tau = 17.8$, $J = 45$ Hz) is indicative of a cis structure (*29*). The carbonyl halides $Mn(CO)_5X$ (X = Br, I) produce monomeric, diamagnetic, octahedral [$Mn(CO)_3$(dPe)X] complexes (*222*). Pale cream [$Mn(CO)_3$(PPP)Cl] was similarly obtained in diglyme (*83*). Farona and Wojcicki reported that the S-bonded thiocyanate complex [$Mn(CO)_5(SCN)$] produced an N-bonded isomer upon reaction with dPe to form [$Mn(CO)_3$(dPe)(NCS)] (*112*).

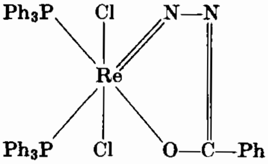
There are several examples of organometallic complexes in which the diphosphine behaves either as a bridging or a chelating ligand depending on reaction conditions. On irradiation of [$C_5H_5Mn(CO)_3$] and dPe in cyclohexane, the bridged [$C_5H_5Mn(CO)_2$]$_2$dPe is formed as yellow crystals, while prolonged irradiation of the mixture in benzene produces the chelate-containing [$C_5H_5Mn(CO)$(dPe)] as orange crystals (*220*). Similarly, [$CH_3COMn(CO)_5$] and dPe produce either [$CH_3COMn(CO)_4$]$_2$dPe or [$CH_3COMn(CO)_3$(dPe)] depending on the conditions (*210*). The same types of complexes are obtained from [$CH_3Mn(CO)_5$], but [$PhMn(CO)_5$] produces *cis*-[$PhMn(CO)_3$(dPe)] (*16a*). The structures of the diphosphine complexes derived from methylmanganese carbonyl have been discussed (*197*).

VPP displaced carbon monoxide from [$C_5H_5Mn(CO)_2(NO)$]PF_6 to form [$C_5H_5Mn(NO)$(VPP)]PF_6 (*192*). [$C_5H_5Mn(CO)$(VPP)] was obtained from [$C_5H_5Mn(CO)_3$] (*194*). Several diphosphines (dPe, DPPA, and DPPB) react with [$C_5H_5Mn(CO)_2NO$]PF_6 to form either monodentate [$C_5H_5Mn(CO)(NO)$(diphos)]PF_6 or bidentate, bridged [{$C_5H_5Mn(CO)(NO)$}$_2$(diphos)]$(PF_6)_2$ complexes (*192*).

A number of diphosphine complexes of rhenium have been prepared by Freni *et al.* by reaction of $Re(CO)_5X$ or $Re_2(CO)_{10}$ with diphosphines (*121*, *123*) [$Re(CO)_5I$] reacts with dPe in benzene to give *cis*-$Re(CO)_3$(dPe)I. A further molecule of carbon monoxide is lost on heating with dPe in a sealed tube, and on recrystallization from CH_2Cl_2, *cis*-[$Re(CO)_2(dPe)_2$]I·CH_2Cl_2 is obtained. By the reaction of *cis*-[$Re(CO)_2(dPe)_2$]I·CH_2Cl_2 with excess dPe, again in a sealed tube, $Re(CO)(dPe)_2I$ is produced (*123*). $Re_2(CO)_{10}$ and dPe react *in vacuo* to produce two isomers of $Re(CO)_3$(dPe): a diamagnetic, nonelectrolytic, and a paramagnetic isomer. Because of magnetic and IR evidence the former is assigned as *cis*-[$Re(CO)_3$(dPe)]$_2$, and the latter as *trans*-[$Re(CO)_3$(dPe)] (*121*). At higher temperatures the reaction of $Re_2(CO)_{10}$ and dPe produces $Re(CO)_2(dPe)_2$ and $Re(CO)(dPe)_2$. Both forms of $Re(CO)_3(dPe)$ react with iodine. The trans isomer behaves normally, forming *trans*-$[Re(CO)_3(dPe)I]$, but the cis isomer reacts with two equivalents of iodine to produce an ill-defined product. $Re(CO)_2(dPe)_2$ reacts with three equivalents of iodine to form a diamagnetic, nonelectrolyte $[Re(CO)_2(dPe)_2I_3]$. Freni *et al.* suggest (*121*) that, rather than nine-coordinate Re(III), this is a Re(I) compound in which one dPe is monodentate, and the uncoordinated phosphorus has been oxidized to P(V), i.e., $Re(CO)_2(dPe)[Ph_2PCH_2CH_2P(I)_2Ph_2]I$. On hydrolysis a compound $Re(CO)_2(dPe)\{Ph_2PCH_2CH_2P(O)Ph_2\}I$ is formed, a formulation supported by the presence of two bands assigned as P–O stretching IR modes.

Upon heating $[Re(CO)_6]ClO_4$ with dPe, $[Re(CO)_4(dPe)]^+$ is formed; it is also formed by the high-pressure carbonylation of *cis*-$[Re(CO)_3(dPe)Cl]$ (*2*). $Re(CO)_5I$ reacts with PP–P to form $[(PP\text{–}P)Re(CO)_4I]$, in which the PP–P behaves as a monodentate ligand (*161*).

Some dinitrogen complexes of rhenium, $[Re(N_2)(diphos)_2Cl]$ (diphos = dPm, dPe, VPP), have been obtained by the reaction of (XIII) with



(XIII)

diphos in methanol, or from $[Re(N_2)(PPh_3)_4Cl]$ and the diphosphine in boiling toluene (*59*). The dinitrogen is probably trans to the chlorine. The N_2 is displaced by chlorine in chloroform, but in CCl_4 $[ReCl(N_2)(dPe)_2]$ forms a purple solid, probably $[ReCl(N_2)(dPe)_2]Cl$.

The rhenium hydrido complexes have been studied by Chatt and Coffey (*57*), and Freni *et al.* (*120*). $[ReH_7(dPe)]$ and $[ReH_5(dPe)_2]$ were obtained on reducing $[ReOCl_3(dPe)]$ with excess dPe and $LiAlH_4$. In the presence of PPh_3, $[ReH_5(dPe)(PPh_3)]$ results. The NMR spectrum of $[ReH_5(dPe)_2]$ indicates that one dPe is acting as a monodentate ligand (*57*). $[ReH_3(dPe)(PPh_3)_2]$ is formed by displacement of PPh_3 from $[ReH_5(PPh_3)_3]$ by dPe in benzene (*120*). In a sealed, evacuated tube dPe displaces all the PPh_3 to form $[ReH_3(dPe)_2]$. Both $[ReH_3(dPe)(PPh_3)_2]$ and $[ReH_3(dPe)_2]$ can be protonated by acids to give $[ReH_4(dPe)(PPh_3)_2]^+$ and $[ReH_4(dPe)_2]^+$ cations, the reaction being reversed by alkali. With halogens in benzene solution the following reactions

$$2ReH_3(PPh_3)_2(dPe) + X_2 \longrightarrow [ReH_4(PPh_3)_2(dPe)]X + ReH_2(PPh_3)_2(dPe)X$$

$$2ReH_3(dPe)_2 + X_2 \longrightarrow [ReH_4(dPe)_2]X + ReH_2(dPe)_2X$$

occur. Freni *et al.* also reported the formation of $ReH_2(dPe)_2X$ from reduction of $[Re(dPe)_2X_2]$ or $[ReO_2(dPe)_2]X$ with $LiAlH_4$, but Chatt and Coffey were only able to isolate $[Re(dPe)_2X_2]$ from the reaction mixture. $[ReH_3(dPe)(PPh_3)_2]$ reacts with chlorine to give $[Re(dPe)Cl_4]$ and PPh_3O, but $[ReH_3(dPe)_2]$ forms $[Re(dPe)_2Cl_2]Cl$ (*120*). Some properties of these hydrides are shown in Table V.

There was a good deal of confusion in the older literature about the formulation of rhenium complexes, due to the failure to recognize the presence of oxygen in many complexes prepared by reduction of Re_2O_7 or $KReO_4$. $[ReCl_2(dPe)_2]$ was produced by reducing $[ReCl_2(dPe)_2]Cl$ with $NaBH_4$ in ethanol (*75*). A red complex of approximate composition $Re_3Cl_9(dPe)_{1.5}$ has been obtained, but its structure is uncertain (*96*, *114*).

The compound $[ReCl_3(dPe)(PEt_2Ph)]$ is formed on boiling *cis*-$[ReOCl_3(PEt_2Ph)_2]$ with dPe in propanol (*75*). $[ReCl_2(dPe)_2]Cl$ was obtained by Chatt and Rowe by reduction of $KReO_4$ with concentrated hydrochloric acid and dPe in propanol (*75*); Cotton *et al.* obtained this compound from $[Re_2Cl_8]^{2-}$ (*95*). The latter workers found that $[Re_2Cl_8]^{2-}$ and dPe react in acetonitrile to give a very insoluble red isomer $[ReCl_3(dPe)_2]$. The $[ReX_2(dPe)_2]X$ ($X = Br$, Cl) compounds are converted to $[ReX_2(dPe)_2]ClO_4$ by $HClO_4$ or $NaClO_4$ in methanol. The red $[ReCl_3(dPe)_2]$ absorbs oxygen when refluxed in CH_2Cl_2 with free access of air to form green $[Re(dPe)OCl_3]$ (*95*). A blue $[Re(dPe)OCl_3]$ had previously been obtained (*75*), and it is possible that these are cis and trans isomers. A blue $[Re(dee)OCl_3]$ is also known (*75*).

On boiling $[n\text{-}Bu_4N]_2[Re_2Br_8]$ with dPe and 70% $HClO_4$ in methanol $[ReO_2(dPe)_2](ClO_4)$ is formed (*95*). $HReO_4$ reacts with dPe to form *trans*-$[ReO_2(dPe)_2]^+$, which can be isolated as the Cl^-, Br^-, I^-, I_3^-, ClO_4^-, ReO_4^-, or NO_3^- salts (*122*) (see Table VI). Acids in acetone solution form Re(V) derivatives $[ReO(OH)(dPe)_2]^{2+}$, but in ethanol diamagnetic $[ReO(OEt)(dPe)_2]^{2+}$ is formed. $ReO(dPe)X_3$ and $[Re(dPe)X_2]X$ were also prepared.

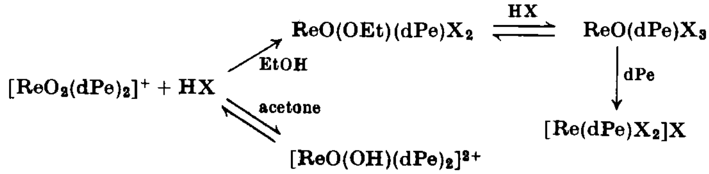


TABLE V

RHENIUM–HYDRIDO COMPLEXES (*57*, *120*)

Compound	Color	M.p.(°C)	ν(Re–H) (cm^{-1})	τ(Re–H)	J(P–H) (Hz)	Dipole moment (D)
$ReH_7(dPe)$	White	161	1967, 1916	Triplet 15.71[a]	13.5	6.57
				Triplet 15.77	13.0	—
				Triplet 16.60	13.0	—
$ReH_5(PPh_3)(dPe)(THF)$	White	190(d)	1943, 1926	Quartet 15.73	16.0	3.59
				Quartet 16.36		
$ReH_5(dPe)_2(THF)$	White	197(d)	1972, 1934, 1890	Quartet 16.76	17.2	3.06
$ReH_3(dPe)(PPh_3)_2$	Yellow	164	1960, 1900, 1820	Singlet 16.27[b]	24	8.26
				quintet 16.75		
$ReH_3(dPe)_2$	Yellow	202	1860	Quintet 17.97[c]	17	4.95
$[ReH_4(dPe)(PPh_3)_2]Cl$	White	170	1970	Quintet 13.88[c]	22.1	—
$[ReH_4(dPe)_2]Cl$	White	172	1950	Quintet 15.34[d]	19.9	—
$ReH_2(dPe)_2Cl$	Yellow	172(d)	2040, 2020	Quintet 17.9[e]	14.4	4.20
$ReH_2(dPe)_2Br$	Yellow	178	2010, 2030	Quintet 20	16	4.43
$ReH_2(dPe)_2I$	Yellow	185(d)	2050	Quintet 21.6	24	4.89

[a] THF.

[b] 100 MHz CS_2.

[c] 60 MHz CS_2.

[d] 100 MHz $(CD_3)_2CO$.

[e] 60 MHz C_6D_6.

TABLE VI

RHENIUM AND TECHNETIUM DIPHOSPHINE COMPLEXES

Compound	Color	M.p. (°C)	Physical Properties	Ref.
cis-$\mathrm{Re(CO)_3(dPe)I}$	White	133	IR, D.M. = 6.9	(*123*)
cis-$\mathrm{[Re(CO)_2(dPe)_2]I}$	White	282	IR, D.M. = 5.6	(*123*)
cis-$\mathrm{[Re(CO)_3(dPe)]_2}$	Cream	195	IR	(*123*)
trans-$\mathrm{Re(CO)_3(dPe)}$	Pale yellow	325(d)	IR	(*121*)
cis-$\mathrm{Re(CO)_2(dPe)_2}$	White	136	IR, D.M. = 5.01	(*121*)
$\mathrm{Re(CO)(dPe)_2}$	White	308(d)	IR	(*121*)
trans-$\mathrm{Re(CO)_3(dPe)I}$	Orange	335	IR	(*121*)
cis-$\mathrm{Re(CO)_2(dPe)(dPeI_2)I}$	Yellow	172	IR	(*121*)
cis-$\mathrm{Re(CO)_2(dPe)(dPeO)I}$	White	152	IR, D.M. = 6.30	(*121*)
$\mathrm{[Re(CO)_4(dPe)]ClO_4}$	White	—	IR, ^{1}H NMR	(*2*)
$\mathrm{[ReCl_2(dPe)_2]}$	Yellow	225	—	(*63*)
$\mathrm{Re_3Cl_9(dPe)_{1.5}}$	Red	—	UV, $\mu = 0.63$/Re	(*96, 114*)
$\mathrm{[ReCl_3(PEt_2Ph)(dPe)]}$	Yellow	195(d)	—	(*63*)
$\mathrm{[ReCl_2(dPe)_2]}$	Yellow	219(d)	Vis.[a]	(*63, 95*)
$\mathrm{[ReCl_3(dPe)_2]}$	Purple-red	—	Vis.	(*95*)
$\mathrm{[ReCl_2(dPe)_2]ClO_4}$	Yellow	—	Vis.	(*95*)
$\mathrm{[ReBr_2(dPe)_2]Br}$	Red-orange	—	Vis.	(*95*)
$\mathrm{[ReBr_2(dPe)_2]ClO_4}$	Orange	—	Vis.	(*95*)
$\mathrm{[ReCl_2(dPe)_2]Cl}$	Orange	245	—	(*122*)
$\mathrm{[ReI_2(dPe)_2]I}$	Violet	236	—	(*122*)
$\mathrm{[Re(NPh)(dPe)Cl_3]}$	Blue-green	291	—	(*60, 95*)
$\mathrm{[Re(NMe)(dPe)Cl_3]}$	Blue-violet	261	IR	(*60*)
$\mathrm{[Re(NPh)(dee)Cl_3]}$	Green	248	IR	(*63*)
$\mathrm{[ReOCl_3(dPe)]}$	Blue	260(d)	ν(Re–O) 976 cm^{-1}	(*63*)
$\mathrm{[ReOCl_3(dPe)]}$	Green	—	ν(Re–O) 980 cm^{-1}	(*95*)
$\mathrm{[ReOCl_3(dee)]}$	Blue	241(d)	ν(Re–O) 984 cm^{-1}	(*63*)
$\mathrm{[ReO_2(dPe)_2]ClO_4}$	Orange	Explodes	ν(Re–O) 789 cm^{-1}	(*95, 122*)
$\mathrm{[ReO(OEt)(dPe)_2]Cl_2}$	Violet	234	ν(Re–O) 958 cm^{-1}	(*122*)
$\mathrm{[ReO_2(dPe)_2]ReO_4}$	Yellow	250(d)	ν(Re–O) 785 cm^{-1}	(*122*)
$\mathrm{[ReO_2(dPe)_2]Cl}$	Yellow	230	ν(Re–O) 790 cm^{-1}	(*122*)
$\mathrm{[ReO_2(dPe)_2]Br}$	Yellow	239	ν(Re–O) 790 cm^{-1}	(*122*)
$\mathrm{[ReO_2(dPe)_2]I}$	Yellow	232(d)	ν(Re–O) 788 cm^{-1}	(*122*)
$\mathrm{[ReO_2(dPe)_2]NO_3}$	Yellow	245	ν(Re–O) 787 cm^{-1}	(*122*)
$\mathrm{[ReO(dPe)Br_3]}$	Green	258	—	(*122*)
$\mathrm{[ReO(OH)(dPe)_2]Cl_2}$	Orange	194	—	(*122*)
$\mathrm{[ReO(OH)(dPe)_2]Br_2}$	Orange	189	—	(*122*)
$\mathrm{[ReO(OH)(dPe)_2]I_2}$	Orange	202(d)	—	(*122*)
$\mathrm{[ReO(OH)(dPe)_2](ReO_4)_2}$	Orange	230	—	(*122*)
$\mathrm{[TcCl_2(dPe)_2]}$	Yellow-green		$\mu = 2.05$ B.M.	(*115*)
$\mathrm{[TcBr_2(dPe)_2]}$	Yellow		$\mu = 2.28$ B.M.	(*115*)
$\mathrm{[TcCl_2(dPe)_2]Cl}$	Red-orange		$\mu = 2.74$ B.M.	(*115*)
$\mathrm{[TcBr_2(dPe)_2]Br}$	Red-orange		$\mu = 3.04$ B.M.	(*115*)

[a] Vis., visible.

Two arylimido complexes, [Re(NPh)(dPe)Cl_3] and [Re(NPh)(dee)Cl_3], are formed from [ReOCl_3(diphos)] and aniline, or by displacing PPh_3 from [ReCl_3(NPh)(PPh_3)$_2$] (*63*, *95*). Violet-blue [Re(NMe)(dPe)Cl_3] has recently been obtained (*60*).

Technetium complexes have only recently been prepared (*113*, *115*). $Tc^{(III)}$ complexes, [Tc(dPe)$_2X_2$]X (X = Cl, Br), are produced by reaction of TcX_4 with dPe. They are 1 : 1 electrolytes. The reaction of these with $NaBH_4$ produces [Tc(dPe)$_2X_2$], which are presumably octahedral (see Table VI).

F. GROUP VIII (Fe, Ru, AND Os)

Brown, diamagnetic [Fe(dme)$_2$] was obtained by reduction of *trans*-[Fe(dme)$_2Cl_2$] with sodium naphthalenide. It reacts normally with iodine to produce *trans*-[Fe(dme)$_2I_2$] (*82*).

Several hydrido complexes are known. Iron powder reacts with PEE in the presence of hydrogen to form [FeH_2(PEE)$_2$] in low yield (*66*). A much higher yield is obtained from the reduction of [Fe(PEE)$_2Cl_2$] with $LiAlH_4$ (*70*). The aliphatic diphosphine complexes [Fe(diphos)$_2Cl_2$] (diphos = dme, dee) are only reduced to [FeHCl(diphos)$_2$] by $LiAlH_4$. Attempted further reduction produced yellow oils (*70*). *trans*-[FeHCl(PEE)$_2$] can be prepared by the reaction between *trans*-[FeH_2(PEE)$_2$] and one equivalent of hydrogen chloride in ether. The chlorine in *trans*-[FeHCl(dee)$_2$] is labile; reaction with NaI in acetone yielding *trans*-[FeHI(dee)$_2$] (*70*). [FeHCl(dee)$_2$], in the presence of sodium tetraphenylborate in acetone solution, forms a number of complexes containing cationic hydrides, *trans*-[FeH(L)(dee)$_2$]BPh_4 [L = N_2, CO, PhCN, MeCN, *p*-$MeOC_6H_4NC$, Me_3CNC, P(OPh)$_3$, P(OMe)$_3$] (*16*). Analogous Ru and Os complexes are known, and structures were assigned on the basis of IR and ^1H NMR studies. In the phosphite complexes the NMR pattern shows a further doublet splitting due to the *trans*-phosphite, in addition to the quintet due to the four equivalent ^{31}P in the diphosphine ligands (*16*).

An interesting reaction occurs between Fe(acac)$_3$, dPe, and ethoxydiethylaluminum (*143*). [Fe(dPe)$_2 \cdot C_2H_4$] is formed, and on irradiation with UV light the hydride [HFe($C_6H_4PPhCH_2CH_2PPh_2$)(dPe)] is produced. Hydrogen at atmospheric pressure produced [FeH_2(dPe)$_2$]. The complex formed between iron and dPe is the first example in iron chemistry of the transfer of a proton from the ligand to the metal. A similar effect was observed in the Ru–dme complex, but not in the Fe–dme system. The hydrogen in the Fe–H bond in [HFe($C_6H_4PPhCH_2CH_2PPh_2$)(dPe)] is labile and returns to the ligand with ease (see Fig. 2).

An investigation of the closely analogous system, $Fe(acac)_3 + 2dPe + 3Et_3Al$, by Bowden and Johnson has yielded a yellow solid, $[Fe(acac)_2(dPe)]$, which has a high-spin configuration, and is an intermediate in the reduction process (*33*). These workers have also isolated a series of complexes, $[Fe(dPe)_2(olefin)]$ (olefin = propene, pent-1-ene, styrene) and $[Fe(dPp)_2(C_2H_4)]$.

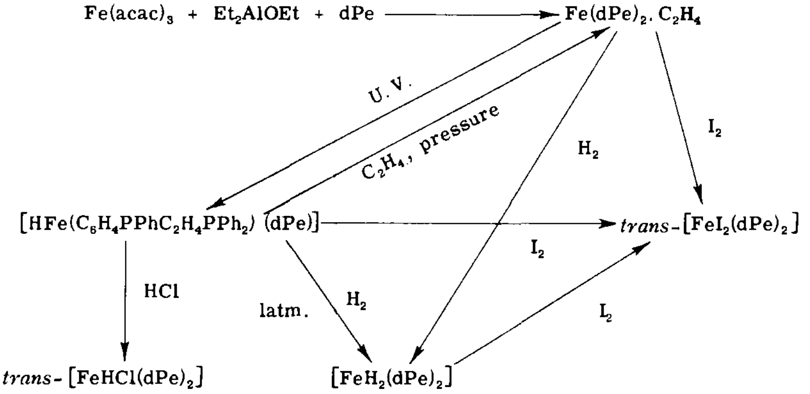
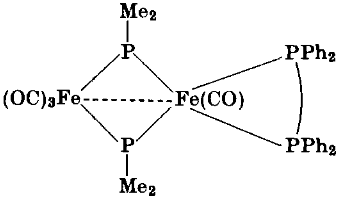
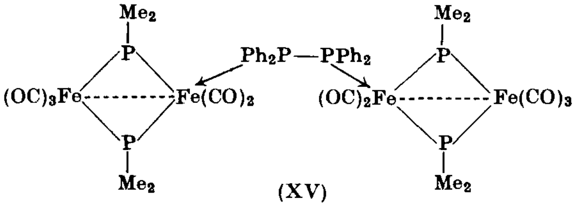


FIG. 2. Reactions of Fe–dPe complexes (*143*).

Diphosphines containing a P–P bond react with iron pentacarbonyl to produce phosphido- and diphosphine-bridged complexes [cf. Cr, Mo, and W (*79, 146, 147, 157, 178*)]. The nature of the product can be controlled to a great extent by varying the conditions. The reaction of dPe with the phosphido-bridged $[Fe_2(PMe_2)_2(CO)_6]$ produces (XIV) and (XV) (*255*). The structure of $[(OC)_4Fe(MP–P)Fe(CO)_4]$ has been determined;

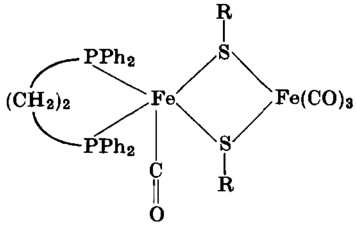


(XIV)



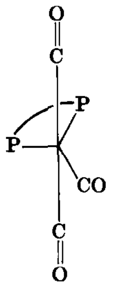
(XV)

there is a staggered configuration about the P–P and Fe–P bonds (*187*). An interesting complex related to (X) is the S-bridged complex (XVI) (*162*). $Fe(CO)_5$ and dPe produce $[Fe(CO)_4)_2]$dPe (*198*). Manuel obtained

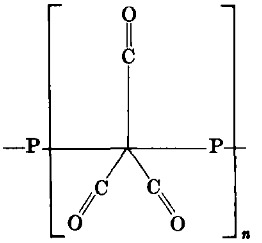


(XVI)

two forms of $[Fe(CO)_3(dPe)]$ from $Fe(CO)_5$, $Fe_3(CO)_{12}$, or [(cyclooctatetraene) $Fe(CO)_3$] and dPe (*208*). Zingales *et al.* obtained $[Fe(CO)_3(dne)]$ (*268*). Ferrous chloride, CO, and dPe in benzene or THF produce $[Fe(CO)_2(dPe)Cl_2]$ (various isomers) (*208*). Cullen and Harbourne have recently reinvestigated the reactions of the iron carbonyls with dPe. In each case $[Fe(CO)_3(dPe)]$ and $[Fe(CO)_4]_2$dPe were obtained in varying amounts (*101*). All these complexes are yellow or orange and are very air-sensitive. On the basis of IR measurements Manuel suggested the following structures:



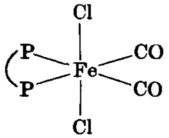
$[Fe(CO)_3(dPe)]$

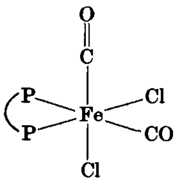


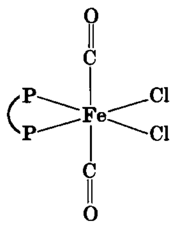
$[Fe(CO)_3(dPe)]_n$

$(OC)_4Fe \longleftarrow P{-}P \longrightarrow Fe(CO)_4$

$[Fe(CO)_4]_2dPe$

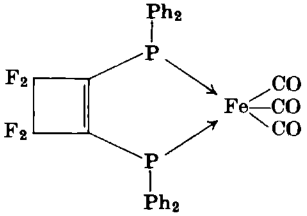




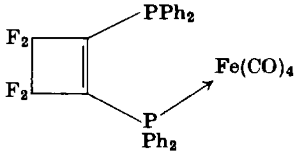


Cullen *et al.* have prepared a number of carbonyl complexes with ffos, $f_6$fos, and $f_8$fos (*100*, *103–105*). Only $[(f_8fos)Fe(CO)_3]$ is obtained with

$f_8$fos, and the $>C=C<$ is not involved in the bonding. The complexes [(ffos)$Fe(CO)_3$], [(ffos)$Fe_2(CO)_6$], [($f_6$fos)$Fe(CO)_3$], [($f_6$fos)$Fe_2(CO)_6$], [($f_6$fos)$Fe_2(CO)_7$], and [(ffos)$Fe(CO)_4$] were obtained. On the basis of IR, NMR, mass spectroscopic, and Mössbauer data, the structures (VI), (VII), (XVII), and (XVIII) were suggested. [$Fe(CO)_3$(VPP)] has been obtained by irradiation of $Fe_2(CO)_9$ and VPP in hexane (*194*).

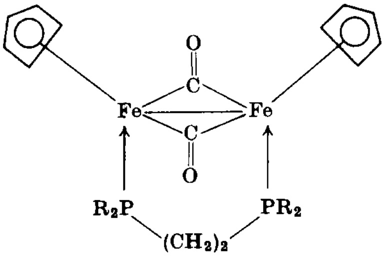


(XVII)



(XVIII)

A large number of other derivatives of iron carbonyls are known which contain π-C_5H_5, etc., as well as diphosphines (*1*). [(π-C_5H_5)Fe-$(CO)_2]_2$(diphos) (diphos = dPm, dPe, dPp) has a structure containing both carbonyl and diphosphine bridges (XIX) (*137*). The complex formed by DPPA, $[(C_5H_5)_2Fe_2(CO)_3]_2$(DPPA), has structure (VIII) (*50, 52*).



(XIX)

A number of substituted iron nitrosyl compounds are known. [$Fe(NO)_2$(dPe)] and $[Fe(NO)_2(CO)]_2$·dPe are formed from [$Fe(NO)_2$-$(CO)_2$] and dPe (*210, 213*). The complexes $[Fe(PMe_2)(NO)_2]_2$, [$Fe_2(CO)_2$-(MP–P)$(NO)_4$], and [Fe_2(MP–P)$_2(NO)_4$] are formed from MP–P and [$Fe(CO)_2(NO)_2$] (*149*). The reduction of $[Fe(NO)_2I]_2$ with sodium amalgam in the presence of dPe produces [$Fe(NO)_2$(dPe)] (*160*). However, the reaction with PP–P is more complex; $[Fe(NO)_2Br]_2$ reacted with PP–P in THF to form [$Fe(NO)_2$(PP–P)$_2$], [$Fe(NO)_2$(PP–P)], and other products (*158*).

Compared with the other Group VIII metals, iron does not form a large number of diphosphine complexes. The yellow-green *trans*-[Fe(diphos)$_2$X$_2$] (X = Cl, Br, I; diphos = dme, dee, PEE) compounds were obtained by Chatt and Hayter from FeX$_2$ and the appropriate diphosphine (*70*). When dPm and dPe were used unstable, not well-defined complexes resulted. The chlorine in *trans*-[Fe(dee)$_2$Cl$_2$] is readily replaced on treatment with LiX to form *trans*-[Fe(dee)$_2$X$_2$] (X = NCO, NCS, N$_3$, Br, I); with SnCl$_2$ the blue *trans*-[Fe(dee)$_2$(SnCl$_3$)Cl] was obtained (*15*). A series of these octahedral [FeX$_2$(dee)$_2$] complexes have been studied by Mössbauer spectroscopy (*15*). Isslieb and Hohlfeld have prepared [Fe(diphos)$_2$Br$_2$] (diphos = dCyp, dCyf) (*176*).

The ferric complexes [Fe(diphos)$_2$Cl$_2$][FeCl$_4$] (diphos = dme, dee, PEE) are stable, dark red or green solids, readily soluble in polar organic solvents, but insoluble in water (*70*) (see Table VII).

The carbonyl Ru$_3$(CO)$_{12}$ reacts with ffos and f$_6$fos under a variety of conditions to give red [Ru$_3$(CO)$_8$(ffos)$_2$], white [Ru$_2$(CO)$_6$(ffos)], white [Ru$_2$(CO)$_6$(f$_6$fos)], and brown [Ru(CO)$_3$(f$_6$fos)]. The products were characterized by IR and ^{19}F NMR (*102*). [Ru(CO)$_2$(dPe)]I$_2$ has been obtained from Ru(CO)$_2$(p-MeC$_6$H$_4$NH$_2$)$_2$I$_2$ and dPe, and IR and NMR data indicate that the product has a cis structure (*156*, *189*).

Chatt and Hayter prepared an extensive series of octahedral complexes of ruthenium and osmium, [M(diphos)$_2$XY] (M = Ru, Os; X, Y = halogen; diphos = dme, dee, dPe, PEE, dPm) (*68*, *70*, *72*). The *trans*-[M(diphos)$_2$Cl$_2$] complexes are obtained by refluxing a slight excess of the diphosphine in aqueous ethanol with RuCl$_3$ or (NH$_4$)$_2$OsCl$_6$. The cis isomers are obtained on heating [M$_2$Cl$_3$(PR$_3$)$_6$]Cl with the diphosphine in the absence of a solvent. In the case of dPe a good yield of *trans*-[Ru(dPe)$_2$Cl$_2$] was obtained, probably due to steric interaction between the phenyl groups in the cis isomer. The corresponding *cis*- or *trans*-[M(diphos)$_2$X$_2$] are obtained from the chloro-complex and M$^{\text{I}}$X (X = Br, I, SCN, CN, OAc); isomerization does not occur. Only the *cis*-[Os(diphos)$_2$X$_2$] are appreciably air-sensitive. *cis*- and *trans*-[Ru(dee)$_2$Cl$_2$]ClO$_4$ form on treating *cis*- or *trans*-[RuCl$_2$(diphos)$_2$] with HClO$_4$ in ethanol (*68*). The formation of various isomers from the reaction of 1,2-bis(methylphenylphosphino)ethane with RuCl$_3$ has been studied by Bercz *et al.* (*24a*).

trans-Hydrido complexes, [MHX(diphos)$_2$] (M = Ru, Os; X = Cl, Br, I, SCN, CN, NO$_2$), were obtained by reduction of the *cis*-[MX$_2$(diphos)$_2$] with LiAlH$_4$ (X = Cl, Br, I) or by metathesis from *trans*-[MHCl(diphos)$_2$] (X = SCN, CN, NO$_2$). The *trans*-[MX$_2$(diphos)$_2$] complexes are not reduced by LiAlH$_4$. The structures of *trans*-[MHX(diphos)$_2$] were established by ^{1}H NMR and dipole moment studies.

TABLE VII

Diphosphine Complexes of Iron

Compound	Color	M.p.(°C)	Properties	Ref.
$[Fe(dme)_2]$	Brown	205	$\mu = 0$	*(82)*
trans-$[FeH_2(PEE)_2]$	Orange	248	IR, NMR, M, $\mu = 1.80$	*(15, 66, 70)*
trans-$[FeH_2(dPe)_2]C_6H_6$	Yellow	219	IR	*(143)*
$[HFe(C_6H_4PPhC_2H_4PPh_2)(dPe)]$	Orange-brown	179	IR, NMR	*(143)*
trans-$[FeHCl(dme)_2]$	Red	180(d)	IR	*(70)*
trans-$[FeHCl(dee)_2]$	Red	155	IR, NMR, M, D.M. = 4.23	*(15, 70)*
trans-$[FeHCl(PEE)_2]$	Red	231	IR, NMR	*(70)*
trans-$[FeHI(dee)_2]$	Red-brown	173(d)	IR, NMR, M	*(15, 70)*
trans-$[FeH(N_2)(dee)_2]BPh_4$	Yellow-red	—	IR, NMR, M	*(16)*
trans-$[FeH(CO)(dee)_2]BPh_4$	Yellow-red	—	IR, NMR, M	*(16)*
$\{Fe(CO)_4\}_2(MP\text{-}P)$	Orange-yellow	147(d)	IR, NMR	*(79, 146)*
$[Fe(CO)_3(dPe)]$	Yellow	143	IR, mass spec.	*(101, 208)*
$[Fe_2(CO)_8(dPe)]$	Yellow	186	IR, mass spec.	*(101)*
$[Fe(CO)_3(dPe)]_n$	Red-brown	203(d)	IR	*(208)*
$\{Fe(CO)_4\}_2(dPe)$	Yellow	171	IR	*(198, 208)*
$[Fe(CO)_3(VPP)]$	Yellow-orange	139	IR, NMR	*(194)*
$[Fe_2(CO)_6(ffos)]$	Orange	220(d)	IR, NMR, M, mass spec.	*(103–105)*
$[Fe_2(CO)_6(f_6fos)]$	Orange	226		
$[Fe_2(CO)_7(f_6fos)]$	—	—		
$[Fe(CO)_3(ffos)]$	Brown	179		
$[Fe(CO)_4(ffos)]$	Yellow	130		
$[Fe_2(CO)_3(f_6fos)]$	Brown	211		
$[Fe(CO)_3f_8fos]$	—	—	—	*(100)*
$[Fe(NO)_2(dPe)]$	Red-brown	148(d)	IR	*(210, 213)*
$\{Fe(NO)_2(CO)\}_2(dPe)$	Deep red	140	IR	*(210)*

[a] M is Mössbauer.

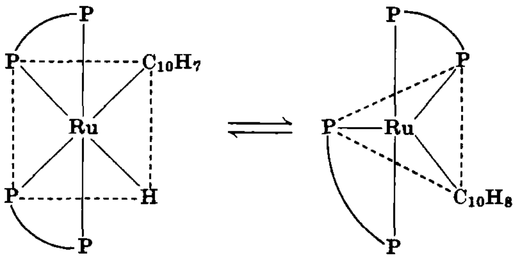
(continued)

TABLE VII—*continued*

Compound	Color	M.p.(°C)	Properties	Ref.
trans-[FeI$_2$(dPe)$_2$]	Yellow-green	376	—	(*82*)
trans-[FeCl$_2$(dee)$_2$]	Green	170	M, D.M. = 1.3	(*15, 70*)
trans-[FeCl$_2$(dme)$_2$]	Green	258	M	(*15, 70*)
trans-[FeCl$_2$(PEE)$_2$]	Green	192	M	(*15, 70*)
trans-[FeBr$_2$(dee)$_2$]	Yellow-green	—	M	(*15*)
trans-[FeCl(SnCl$_3$)(dee)$_2$]	Blue	—	M	(*15*)
trans-[FeBr$_2$(PEE)$_2$]	Yellow	—	M	(*15*)
trans-[Fe(NCO)$_2$(dee)$_2$]	Purple	—	M	(*15*)
trans-[Fe(NCS)$_2$(dee)$_2$]	—	—	M	(*15*)
trans-[Fe(N$_3$)$_2$(dee)$_2$]	—	—	M	(*15*)
trans-[FeI$_2$(dee)$_2$]	Orange-yellow	—	M	(*15*)
trans-[FeI$_2$(dPe)$_2$]	Yellow	143	M	(*143*)
trans-[FeCl$_2$(dee)$_2$][FeCl$_4$]	Dark red	149	—	(*70*)
trans-[FeCl$_2$(dme)$_2$][FeCl$_4$]	Purple	236	—	(*70*)
trans-[FeCl$_2$(PEE)$_2$][FeCl$_4$]	Dark green	150	—	(*70*)

The dPm and dPe complexes tend to crystallize as solvates from benzene. In air the hydridohalides tend to decompose slowly in the order $[o\text{-}C_6H_4(AsMe_2)_2] > \text{dPe} > \text{dee} > \text{PEE} = \text{dPm}$. Excess of $LiAlH_4$ reduces the *trans*-[MHX(diphos)$_2$] complex to the dihydrides, *trans*-[MH$_2$(diphos)$_2$] (*72*). *cis*-[RuH$_2$(dme)$_2$] was obtained from *trans*-[RuHBr(dme)$_2$] and sodium naphthalenide. A series of σ-bonded alkyl and aryl derivatives, *cis*-[MR$_2$(diphos)$_2$] and *cis*- and *trans*-[MRX(diphos)$_2$] (M = Ru, Os) were synthesized from alkyl- or aryllithium reagents or trialkylaluminums (*72*). These compounds vary in stability from [MMe$_2$(dme)$_2$] and [M(Aryl)X(dme)$_2$], which decompose slowly in air and hydrolyze immediately in water, to the [M(alkyl)X(dPm)$_2$] and [M(alkyl)X(dPe)$_2$], which have high resistance to oxidation and hydrolysis. The [MRX(diphos)$_2$] compounds are reduced to [MRH(diphos)$_2$] by $LiAlH_4$. The metal–carbon bond is cleaved by HCl or halogens, usually with retention of configuration. *trans*-[MHCl(dee)$_2$] reacts with $NaBPh_4$ and various ligands in acetone (or with N_2 in $CHCl_3$) to form colorless [MH(L)(dee)$_2$]BPh$_4$, analogous to the iron complexes (*16*) (see Table VIII).

Chatt and Davidson observed (*58*) that, unlike iron, the ruthenium and osmium complexes, [M(dme)$_2$Cl$_2$], reduced with sodium naphthalenide, retained naphthalene in the product. *cis*- or *trans*-[Ru(dme)$_2$Cl$_2$] reacted with sodium arenes (arene = naphthalene, anthracene, phenanthrene, or benzene) in THF to produce [Ru(arene)(dme)$_2$]. Physical measurements indicate that they are *cis*-[RuH(aryl)(dme)$_2$], but chemically they behave as [Ru(arene)(dme)$_2$]. The naphthalene compound has ν(Ru–H) at 1820 cm^{-1}, and τ(Ru–H) at 17.6 and 19.8. On heating *in vacuo* naphthalene is lost, and with iodine no HI was detected—both of which are consistent with [Ru(naphthalene)(dme)$_2$]. The fact that one of the hydrogens on the naphthalene becomes attached to the metal was confirmed by the preparation of deuterium analogs. Clearly the system is tautomeric. The X-ray structure shows that in the solid state



(XX)

TABLE VIII

RUTHENIUM AND OSMIUM COMPLEXES (*68*, *69*, *72*)

Compound	Color	M.p.(°C)	Properties
trans-[RuCl$_2$(dee)$_2$]	Yellow	241^d	D.M. = 0.85
trans-[RuCl$_2$(dme)$_2$]	Yellow	294^d	D.M. = 0.75
trans-[RuCl$_2$(dPe)$_2$]	Pale Yellow	284(d)	—
trans-[RuCl$_2$(dPm)$_2$]	Orange	277(d)	—
trans-[RuCl$_2$(PEE)$_2$]	Yellow	241(d)	D.M. = 0.7
trans-[RuI$_2$(dee)$_2$]	Orange-brown	269(d)^d	—
trans-[RuBr$_2$(dme)$_2$]	Orange	288(d)^d	—
trans-[RuI$_2$(dme)$_2$]	Red	303(d)^d	—
trans-[RuBr$_2$(dee)$_2$]	Pale orange	265^d	—
trans-[Ru(CN)$_2$(dme)$_2$]·H$_2$O	Colorless	>350	—
trans-[Ru(OAc)$_2$(dme)$_2$]·H$_2$O	Colorless	247^d	—
cis-[RuCl$_2$(dee)$_2$]	Lemon yellow	214	D.M. = 9.75
cis-[RuCl$_2$(dme)$_2$]	Yellow	263^d	—
cis-[RuCl$_2$(dPm)$_2$]	Canary yellow	273(d)	D.M. = 9.5
cis-[RuCl$_2$(PEE)$_2$]	Yellow	233(d)	—
cis-[RuBr$_2$(dee)$_2$]	Yellow	191(d)	—
cis-[RuI$_2$(dee)$_2$]	Orange-brown	263^d	D.M. = 10.35
cis-[Ru(SCN)$_2$(dee)$_2$]	Colorless	325(d)^d	—
cis-[RuBr$_2$(dme)$_2$]	Yellow	242(d)	—
cis-[RuI$_2$(dme)$_2$]	Golden yellow	290(d)	—
cis-[Ru(SCN)$_2$(dme)$_2$]	Colorless	328(d)	—
cis-[RuI$_2$(PEE)$_2$]	Yellow	247(d)	—
trans-[RuCl$_2$(dee)$_2$]ClO$_4$	Dark green	173(d)	—
cis-[RuCl$_2$(dee)$_2$]ClO$_4$	Dark green	168(d)	—
trans-[RuHCl(dee)$_2$]	Colorless	175	IR, NMR, D.M. = 4.91
trans-[RuHBr(dee)$_2$]	Yellow	189(d)	IR, NMR, D.M. = 5.65
trans-[RuHI(dee)$_2$]	Yellow	220(d)	IR, NMR, D.M. = 5.8
trans-[RuH(SCN)(dee)$_2$]	Colorless	247(d)	IR
trans-[RuH(CN)(dee)$_2$]	Colorless	—	IR
trans-[RuH$_2$(dee)$_2$]	Colorless	149	IR, D.M. = 2.1
trans-[RuHCl(dme)$_2$]	Colorless	219	IR, D.M. = 4.8
trans-[RuHBr(dme)$_2$]	Yellow	217(d)	IR
trans-[RuHI(dme)$_2$]	Yellow	322(d)	IR
trans-[RuH(SCN)(dme)$_2$]	Colorless	240(d)	IR
trans-[RuH(CN)(dme)$_2$]	Yellow	230(d)	IR
trans-[RuH(NO$_2$)(dme)$_2$]	Yellow	240(d)	IR
trans-[RuHCl(PEE)$_2$]	Yellow	253(d)	IR, D.M. = 4.45
trans-[RuHI(PEE)$_2$)	Brown	280(d)	IR
trans-[RuH$_2$(PEE)$_2$]	Yellow	277(d)	IR, D.M. = 1.2
trans-[RuHCl(dPm)$_2$]·$\frac{1}{2}$C$_6$H$_6$	Yellow	284	IR, D.M. = 4.95
cis-[RuMe$_2$(dme)$_2$]	Colorless	285	D.M. = 4.35
trans-[RuMe$_2$(dme)$_2$]	Yellow	315	D.M. = 3.7
cis-[RuMe$_2$(dPe)$_2$]	Yellow	253	D.M. = 3.45
cis-[RuIMe(dPe)$_2$]·$\frac{1}{2}$C$_6$H$_6$	Orange	329	D.M. = 7.8

TABLE VIII—*continued*

Compound	Color	M.p.(°C)	Properties
trans-[RuClEt(dPe)$_2$]	Lemon yellow	230	D.M. = 4.7
[RuClPr(dPe)$_2$]	Yellow	333	D.M. = 4.85
[RuClPh(dme)$_2$]	Colorless	295	D.M. = 1.75
[RuPh$_2$(dPm)$_2$]	Yellow	177	—
cis-[RuHMe(dPe)$_2$]	Colorless	249	IR, NMR, D.M. = 3.25
trans-[RuHMe(dPe)$_2$]	Colorless	292	IR, NMR, D.M. = 2.95
cis-[RuHEt(dPe)$_2$]	Colorless	291	IR, D.M. = 3.25
cis-[RuHPr(dPe)$_2$]	Colorless	279	IR, D.M. = 3.15
trans-[RuHPh(dme)$_2$]	Colorless	160	IR, D.M. = 3.90
[RuH(p-tolyl)(dme)$_2$]	Colorless	148	IR
trans-[RuH(N$_2$)(dee)$_2$]BPh$_4$[a]	Colorless	—	NMR
[Ru(CO)$_2$(dPe)Br$_2$][b]	Yellow	>170	—
[Ru(CO)$_2$(dPe)I$_2$][b]	Orange	150	IR, NMR
trans-[OsCl$_2$(dee)$_2$]	Yellow	248	—
trans-[OsCl$_2$(dme)$_2$]	Yellow	299(d)[d]	—
trans-[OsCl$_2$(dPe)$_2$]	Orange	294(d)	—
trans-[OsCl$_2$(dPm)$_2$]	Gold-yellow	>350	—
cis-[OsCl$_2$(dee)$_2$]	Colorless	210	D.M. = 9.3
cis-[OsCl$_2$(dme)$_2$]	Colorless	300(d)	—
cis-[OsCl$_2$(dPe)$_2$]	Pale yellow	290(d)	D.M. = 8.3
cis-[OsCl$_2$(PEE)$_2$]	Pale yellow	265(d)	—
trans-[OsI$_2$(dee)$_2$]	Orange	273[d]	—
cis-[OsI$_2$(dee)$_2$]	Pale yellow	223(d)	—
OsCl$_3$(PMe$_2$Ph)(dPe)[c]	Orange	140(d)	—
trans-[OsHCl(dee)$_2$]	Colorless	171	IR, NMR, D.M. = 4.6
trans-[OsHI(dee)$_2$]	Yellow	227	IR, NMR
trans-[OsH(SCN)(dee)$_2$]	Colorless	200(d)	IR
trans-[OsH$_2$(dee)$_2$]	Colorless	152	IR
trans-[OsHCl(dme)$_2$]	Colorless	198(d)	IR D.M. = 5.05
trans-[OsHCl(dPe)$_2$]·C$_6$H$_6$	Yellow	316(d)	IR
trans-[OsHCl(dPm)$_2$]·C$_6$H$_6$	Yellow	296(d)	IR, D.M. = 3.85
trans-[OsH$_2$(PEE)$_2$]	Lemon	295	IR
[OsMe$_2$(dPm)$_2$]	Pale yellow	254	—
cis-[OsClMe(dPm)$_2$]	Orange	196	D.M. = 6.6
trans-[OsClMe(dPm)$_2$]·$\frac{1}{2}$C$_6$H$_6$	Pale yellow	286	D.M. = 5.5
trans-[OsClEt(dPm)$_2$]·$\frac{1}{2}$C$_6$H$_6$	Gold-yellow	296	D.M. = 4.95
cis-[OsPh$_2$(dPm)$_2$]·$\frac{1}{2}$C$_6$H$_6$	Pale yellow	237	D.M. = 6.1
cis-[OsClMe(dPe)$_2$]·$\frac{1}{2}$C$_6$H$_6$	Pale yellow	295	D.M. = 6.6
[OsClEt(dPe)$_2$]	Pale yellow	312	—
[OsHMe(dPe)$_2$]·C$_6$H$_6$	Pale yellow	150	IR
[OsHEt(dPe)$_2$]·$\frac{1}{2}$C$_6$H$_6$	Pale yellow	313	IR
trans-[OsH(N$_2$)(dPe)$_2$]BPh$_4$[a]	Colorless		NMR

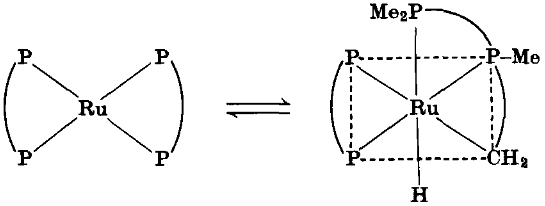
[a] Bancroft *et al.* (*16*).

[b] Hieber and John (*156*) and John (*189*).

[c] Johnson *et al.* (*190*).

[d] Sublimed before melting.

it exists as *cis*-[$RuH(C_{10}H_7)(dme)_2$]. The $C_{10}H_7(dme)_2$ forms a square-pyramid, and although location of the proton was difficult, it is thought to be trans to the phosphorus with Ru–H = 1.7 Å. [$Ru(dme)_2$], formed on heating [$RuH(C_{10}H_7)(dme)_2$] *in vacuo* also exhibits tautomerism. It has an infrared absorption at 1791 cm^{-1} [ν(Ru–H)], but was not sufficiently soluble for NMR studies. Chemically, it behaves as [$Ru(dme)_2$] (*58*). The tautomerism is

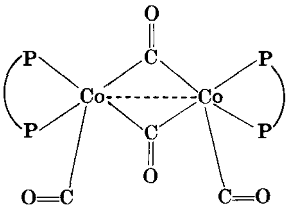


[$Fe(dme)_2$] does not exhibit tautomerism (*82*), but [$Fe(dPe)_2$] does (*143*).

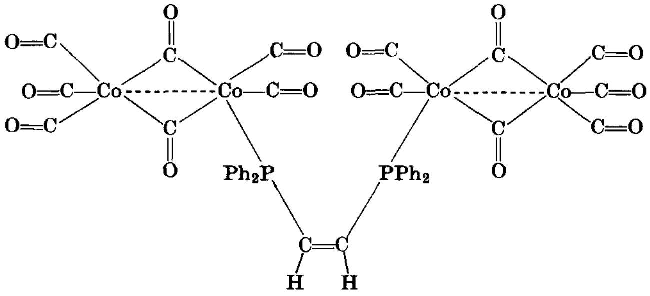
G. Group VIII (Co, Rh, and Ir)

The compound [$Co(dme)_2$] was reported (*82*) as orange needles resulting from the reduction of $CoCl_2$ with sodium naphthalenide in the presence of dme. There were no IR bands attributable to ν(Co–H). Finely powdered cobalt reacts with PEE on heating in nitrogen or hydrogen to give [$Co(PEE)_2$] (*66*). Heating [$Co(dPe)_2Br_2$] with KOH in aqueous ethanol under nitrogen produced [$Co(dPe)_2$] (*234*). By reduction of [$CoBr_2(dPe)_2$] with $NaBH_4$ in aqueous ethanol, Chatt *et al.* obtained red crystals which they formulated as [$Co(dPe)_2$] (*66*); no ν(Co–H) was present in the IR spectrum. Zingales *et al.* examined the reaction using $LiAlH_4$ in place of $NaBH_4$, and obtained a compound of almost identical properties, but which contained a band at 1884 cm^{-1} which was assigned to ν(Co–H) (*267*). An investigation of the reaction by Sacco and Ugo using $NaBH_4$ led to a product characterized as [$CoH(dPe)_2$]. This compound was diamagnetic if great care was taken in the preparation (*236*). In $HClO_4$ solution [$CoH_2(dPe)_2$]ClO_4 was formed [ν(Co–H) = 1940, 1985 cm^{-1}], and this reaction was reversed by alkalis. Reduction of $Co(acac)_3$ with $Al(OEt)Et_2$ in the presence of dPe also produced [$CoH(dPe)_2$] (*143*). Both the Co(0) compounds and the hydrides are readily decomposed by air.

A number of carbonyls and nitrosyls are known. $Co_2(CO)_8$ reacts with dPe to produce yellow [$Co_2(CO)_4(dPe)_3$][$Co(CO)_4$]$_2$. The cation has also been isolated as the iodide, perchlorate, and tetraphenylborate (*232*). Diamagnetic [$Co_2(CO)_4(dPe)_2$] was obtained from [(norbornadiene)$_2Co_2(CO)_4$] and dPe (*19*). The solid has structure (XXI). It adds iodine to produce $[Co_2(CO)_4(dPe)I]$. The anion $[Co(CO)_2(dPe)]^-$ is also known (*19*). VPP reacts with $Co_2(CO)_8$ in benzene to produce the red-brown diphosphine-bridged complex (XXII) (*49*). As with the other metal carbonyls there have been many studies on organometallic derivatives, e.g., $[C_5H_5Co(dme)I]PF_6$ (*195*). A ligand-bridged complex, $[(OC)_3Co(PP{-}P)Co(CO)_3]$, is formed from PP–P (*242*).

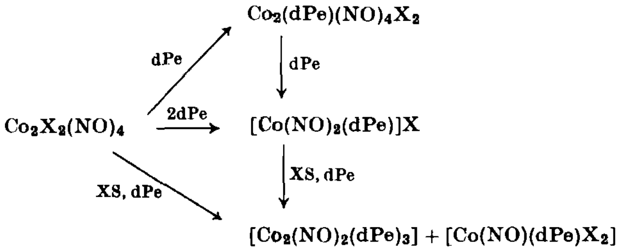


(XXI)



(XXII)

$[Co(NO)(CO)_3]$ and dPe form two orange solids, $[Co(NO)(CO)_2]_2dPe$ and $[Co(NO)(CO)(dPe)]$ (*210*). The orange $[Co(NO)(CO)(dPm)]$ and red $[Co(NO)(CO)(dPp)]$ were obtained similarly (*150*). PP–P reacts with $[Co(NO)_2X]_2$ (X = halogen) to produce $[X(NO)_2Co(PP{-}P)Co(NO)_2X]$ and phosphido-bridged derivatives (*158*). Nitrosyl complexes containing dPe have also been prepared (*25, 160*). Bianco *et al.* reported (*25*) the following reactions:



$[Co_2(NO)_2(dPe)_3]$ has also been obtained by reduction of $[Co_2(NO)_4(dPe)Cl_2]$ with Zn/EtOH in the presence of dPe (*160*). $Co_2X_2(NO)_4(dPe)$ are believed to exist in two forms due to the equilibrium (*25*).

$$[Co_2(dPe)X_2(NO)_4] \rightleftharpoons [Co(NO)_2(dPe)]^+ + [Co(NO)_2X_2]^-$$

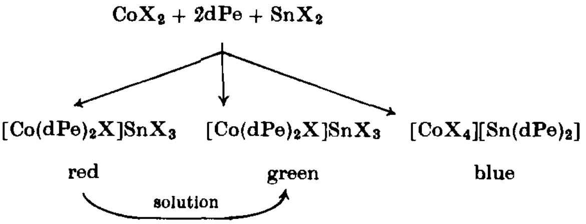
Four- and five-coordinate Co(I) complexes are known (*235*). On heating $[Co(dPe)_2]$ with $Co(dPe)_2Br_2$ in a 1:1 ratio under nitrogen, brown $[Co(dPe)_2Br]$ is formed. By metathesis with $NaClO_4$ or $NaBPh_4$ in ethanol, green four-coordinate $[Co(dPe)_2]X$ ($X = ClO_4$, BPh_4) can be prepared. Co(I) complexes add hydrogen to give $[CoHX(dPe)_2]X$ and $[CoH_2(dPe)_2]X$. $[Co(CO)(dPe)_2]X$ (X = Cl, Br, I) was also obtained (*235*).

The diphosphine complexes of Co(II) have recently been the subject of a great deal of interest. Co(II) combines with diphosphines in the ratios 1:1, 1:2, and, occasionally, 1:1.5. The first investigation was by Wymore and Bailar on dee complexes, published in 1960 (*264*). Complexes having empirical formulas $Co(dee)_2Br_2$ (green) and $Co(dee)_2I_2$ (brown) were isolated. The iodide is probably six-coordinate in the solid state, but behaves as a 1:1 electrolyte in nitrobenzene, suggesting pentacoordination in solution, $[Co(dee)_2I]I$. On heating over P_2O_5 it turns green, with loss of some dee, and its physical properties then become more like the bromide. The bromide was formulated as $[Co(dee)_2][CoBr_4]$ containing planar $[Co(dee)_2]^{2+}$.

The complexes with dCyp, dCyb, and dCyf are tetrahedral $[CoX_2(diphos)]$ (*176*), with magnetic moments in the range 3.5–4.7 B.M. Isslieb and Schwager studied the CyP–P and PP–P complexes (*181, 182*). The latter gives rise to $Co(PP\text{–}P)_2X_2$, in which the bromide has $\mu_{eff} = 2.28$ B.M. and a dipole moment of 6.66 D; it was assigned a square planar structure in which the ligands are monodentate. The iodide has $\mu_{eff} = 4.16$ B.M. and appears to be tetrahedral. $CoCl_2$ did not yield a crystalline product. CyP–P forms complexes of type $[Co(CyP\text{–}P)X_2]$ (X = Cl, Br, I) (*182*); all are monomeric and nonelectrolytes. The blue chloride, $\mu_{eff} = 4.48$ B.M., is tetrahedral; the very dark brown iodide, $\mu_{eff} = 2.25$ B.M., has a dipole moment of 8.7 D, consistent with a square-planar structure. Two isomers of the bromide exist, a green square-planar, and a blue tetrahedral form. Unlike PP–P, CyP–P behaves as a chelating ligand towards cobalt(II).

The dPe complexes of cobalt(II) have been most studied; 1:1 complexes, $[Co(dPe)X_2]$, are difficult to obtain. They crystallize on long standing from solutions of $[Co(dPe)_2X_2]$ in CH_2Cl_2, $CHCl_3$, or acetone. Pseudotetrahedral structures are indicated by the magnetic moments and electronic spectra (*167*). dPp, dPb, and dPf form only 1:1 complexes, obtained by refluxing alcoholic solutions of the diphosphine and CoX_2 (*167*, *237*). Like the dPe complexes they are pseudotetrahedral. Similar 1 : 1 complexes can be obtained with the ligand POPO, which behaves as a chelating diphosphine, and the oxygen atom does not coordinate (*237*).

Complexes of type $Co(dPe)_2X_2$ are well known, and the structures depend on the nature of X. When X = ClO_4, the cobalt is four-coordinate and square-planar, $[Co(dPe)_2](ClO_4)_2$, and related $[Co(dPe)_2][CoX_4]$ complexes are also known. When X is an anion capable of coordinating to the cobalt, pentacoordinate $[Co(dPe)_2X]^+$ complexes are formed. Sacco and Gorieri assigned five-coordinate structures, on the basis of conductivity and magnetic measurements, to the complexes $[Co(dPe)_2X]^+$, $[Co(dPe)_2Cl]_2[CoCl_4]$, and $[Co(dPe)_2(NCS)]_2[Co(NCS)_4]$ (*233*). Horrocks *et al.* obtained electronic and ESR spectra which were consistent with a five-coordinate structure (*167*). It was also noted that the electronic spectrum of $[Co(dPe)_2I]BPh_4$ differed slightly from that of $Co(dPe)_2I_2$, and it was suggested that there were two coordinated iodides in the latter complex. Dyer *et al.* (*111*) have discovered the interesting system



X = Cl, Br

The red isomer becomes green in solution and has the same electronic spectrum as the green isomer in solution, which is indicative of the same pentacoordinate structure in solution. In the solid state the electronic spectral bands differ in relative intensity, but not in energy, and again pentacoordination is observed. It is likely that the red and green isomers are either square-pyramidal and trigonal-bipyramidal isomers, or that some subtle chelate carbon–chain conformation makes the isomers crystallize in the red and green forms. The blue isomer, $[CoX_4][Sn(dPe)_2]$, is a rare example of $[SnP_4]$ coordination. Interestingly, Dyer and coworkers could only obtain the green $[CoL_2X]^+$ (X = Cl, Br, I, NCS) and $[CoL_2(NCS)]_2[Co(NCS)_4]$ when L = VPP (*111*). Ramaswamy *et al.* have obtained the square planar $[Co(VPP)_2]Y_2$ (Y = ClO_4, NO_3) (*225*) (see Table IX).

TABLE IX

DIPHOSPHINE COMPLEXES OF COBALT

Compound	Color	M.p.(°C)	Properties	Ref.
$[Co(dme)_2]$	Pale orange	101	—	*(82)*
$[Co(dPe)_2]$	Red	228	D.M. = 1.2	*(234)*
$[Co(PEE)_2]$	Deep purple	—	—	*(66)*
$[CoH(dPe)_2]$	Red	265	$\mu = 0$	*(66, 143)* *(236, 267)*
$[Co_2(CO)_4(dPe)_2]$	Light brown	—	$\mu = 0$	*(49)*
$[\{Co_2(CO)_7\}_2(VPP)]$	Red-brown	221	—	*(247)*
$[\{Co(CO)_3\}_2(PP\text{–}P)]$	—	140	—	*(242)*
$[\{Co(CO)_2(NO)\}_2(dPe)]$	Orange	146	—	*(210)*
$[Co(CO)(NO)(dPe)]$	Orange	166	—	*(210)*
$Co_2Cl_2(NO)_4(dPe)$	Brown	188(d)	IR	*(25, 160)*
$Co_2I_2(NO)_4(dPe)$	Brown	169(d)	IR	*(25)*
$[Co(NO)_2(dPe)]Cl$	Red	117(d)	IR	*(25)*
$[Co(NO)_2(dPe)]BPh_4$	Red	188(d)	IR	*(25)*
$[Co_2(NO)_2(dPe)_3]$	Brown-red	314(d)	IR	*(25)*
$[Co(dPe)_2Cl]Cl$	Green	—	$\mu = 2.212$, ESR, vis.	*(166, 233)*
$[Co(dPe)_2Br]Br$	Green	118	$\mu = 1.86$, ESR, vis.	*(166, 233)*
$[Co(dPe)_2I]I$	Dark brown	148	$\mu = 1.92$, ESR, vis.	*(166, 233)*
$[Co(dPe)_2][CoI_4]$	Light green	—	—	*(166, 233)*
$[Co(dPe)Cl_2]$	Blue	—	$\mu = 4.41$, ESR, vis.	*(166, 233)*
$[Co(dPe)Br_2]$	Blue	—	$\mu = 4.66$, ESR, vis.	*(166, 233)*
$[Co(dPe)I_2]$	Blue	—	$\mu = 4.63$	*(166, 233)*
$[Co(dPe)_2I]BPh_4$	Red	192	$\mu = 2.31$	*(233)*
$[Co(dPe)_2](ClO_4)_2$	Yellow	237	$\mu = 2.50$	*(233)*
$[Co(dPe)_2(NO_3)]NO_3$	Red	139	$\mu = 2.30$	*(233)*
$[Co(dPe)_2(NO_3)]BPh_4$	Orange	—	—	*(233)*

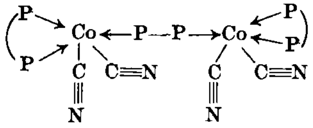
$[Co(dPe)_2I]NO_3$	Maroon	133		—	(*233*)
$[Co(dPe)_2Br]ClO_4$	Green	190		$\mu = 2.22$	(*233*)
$[Co(dPe)_2(NCS)]NCS$	Maroon	152		$\mu = 2.30$	(*233*)
$[Co(dPe)_2(NCS)]_2[Co(NCS)_4]$	Green	154		—	(*233*)
$[Co(dPe)_2][CoCl_4]$	Green	173		$\mu = 3.35$/Co atom	(*233*)
$[Co(dPe)_2Cl]_2[CoCl_4]$	Green	179		—	(*233*)
$[Co(dPe)_2Cl]ClO_4$	Green		—	$\mu = 1.97$, vis.	(*111*)
$[Co(dPe)_2Cl]SnCl_3$	Green		—	$\mu = 1.97$, vis.	(*111*)
$[Co(dPe)_2Cl]SnCl_3$	Red		—	$\mu = 2.36$, vis.	(*111*)
$[Co(dPe)_2Br]SnBr_3$	Green		—	$\mu = 1.96$, vis.	(*111*)
$[Co(dPe)_2Br]SnBr_3$	Dark red		—	$\mu = 2.37$, vis.	(*111*)
$Co(dee)_2I_2$	Brown		—	$\mu = 2.2$	(*264*)
$Co(dee)_2I_2$	Green		—	$\mu = 3.9$	(*264*)
$[Co(dee)_2][CoBr_4]$	Green		—	$\mu = 3.7$	(*264*)
$[Co(VPP)_2Cl]BPh_4$	Green		—	$\mu = 1.91$, vis.	(*111*)
$[Co(VPP)_2Cl]SnCl_3$	Green		—	$\mu = 1.94$, vis.	(*111*)
$[Co(VPP)_2Br]BPh_4$	Green		—	$\mu = 1.90$, vis.	(*111*)
$[Co(VPP)_2I]BPh_4$	Green-black		—	$\mu = 1.98$, vis.	(*111*)
$[Co(VPP)_2(NCS)]BPh_4$	Green		—	$\mu = 1.97$, vis, IR	(*111*)
$[Co(VPP)_2(NCS)]_2[Co(NCS)_4]$	Green		—	$\mu = 2.33$/Co atom	(*111*)
$[Co(POPO)Cl_2]$	Blue		—	$\mu = 4.5$	(*237*)
$[Co(POPO)Br_2]$	Blue		—	$\mu = 4.55$	(*237*)
$[Co(POPO)I_2]$	Green		—	$\mu = 4.61$	(*237*)
$[Co(POPO)(NCS)_2]$	Green		—	$\mu = 4.41$	(*237*)
$[Co(dPp)Cl_2]$	Blue		—	$\mu = 4.43$, vis.	(*167*)
$[Co(dPp)Br_2]$	Blue-green		—	$\mu = 4.47$, vis.	(*167*)
$[Co(dPp)I_2]$	Brown		—	$\mu = 4.56$, vis.	(*167*)
$[Co(dPp)_{1.5}(CN)_2]$	Pink		—	$\mu = 2.30$	(*228*)
$[Co(dPp)_{1.5}(CNS)_2]$	Brown		—	$\mu = 2.7$	(*228*)
$[Co(dPb)Br_2]$	Blue		—	$\mu = 4.5$	(*237, 238*)
$[Co(dPb)(NCS)_2]$	Green	160	—	$\mu = 4.56$	(*237*)
$[Co(dPb)_{1.5}(CN)_2]$	Pink		—	$\mu = 2.40$	(*228*)

(*continued*)

TABLE IX—*continued*

Compound	Color	M.p.(°C)	Properties	Ref.
$[Co(dPb)_{1.5}(CNS)_2]$	Brown	—	$\mu = 2.2$	(*228*)
$[Co(dPf)Br_2]$	Turquoise	—	$\mu = 4.49$	(*237*)
$[Co(dCyp)Br_2]$	Blue	210	$\mu = 4.41$	(*176*)
$[Co(dCyp)I_2]$	Dark brown	194	$\mu = 4.40$, D.M. = 10.11	(*176*)
$[Co(dCyb)Br_2]$	Blue	—	$\mu = 4.59$	(*176*)
$[Co(dCyb)I_2]$	Yellow-green	290	$\mu = 3.52$	(*176*)
$[Co(dCyf)Cl_2]$	Blue	—	$\mu = 4.72$	(*176*)
$[Co(dCyf)Br_2]$	Blue	215	$\mu = 4.38$	(*176*)
$[Co(dCyf)I_2]$	—	175	D.M. = 7.95	(*176*)
$Co(dP_se)_2Cl_2$	Green	172	—	(*185*)
$Co(dP_se)_2Br_2$	Green	178	—	(*185*)
$Co(dP_se)_2I_2$	Green	175(d)	—	(*185*)
$Co(de_se)_2Br_2$	Blue-violet	157(d)	—	(*185*)
$[Co(CyP\text{–}P)Cl_2]$	Blue	129	$\mu = 4.48$	(*182*)
$[Co(CyP\text{–}P)Br_2]$	Green	214	$\mu = 3.52$, D.M. = 4.67	(*182*)
$[Co(CyP\text{–}P)Br_2]$	Blue	158	$\mu = 3.90$, D.M. = 7.52	(*182*)
$[Co(CyP\text{–}P)I_2]$	Dark brown	220	$\mu = 2.25$, D.M. = 8.7	(*182*)
$Co(PP\text{–}P)_2Br_2$	Black	162	$\mu = 2.28$, D.M. = 6.66	(*181*)
$Co(PP\text{–}P)_2I_2$	Dark brown	—	$\mu = 4.16$	(*181*)
$[Co(dee)_2Cl_2]_2Cl$	Green	—	$\mu = 0$	(*264*)
$[Co(dee)_2Br_2]Br$	Green	—	$\mu = 0$	(*264*)
$[Co(dee)_2I_2]I$	Brown	—	$\mu = 0$	(*264*)
$[CoH_2(dPe)_2]ClO_4$	Yellow	185(d)	$\mu = 0$	(*236*)
$[Co(dP_se)_2Br_2]Br$	Dark red	187(d)	—	(*185*)

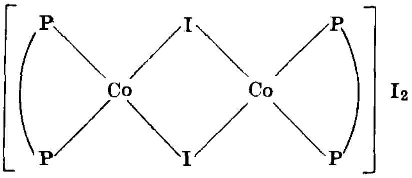
The unusual Co(diphos)$_{1.5}$X$_2$ complexes (diphos = dPp, dPb; X = CN, NCS) were prepared by Rigo *et al.* (*228*). The isothiocyanato complexes were prepared directly from Co(NCS)$_2$ and diphos, but the cyano derivatives were obtained by passing a solution of CoBr$_2$ and diphos through an anionic resin in the CN$^-$ form. Infrared spectra rule out the presence of bridging CN$^-$ or NCS$^-$, and the molecular weights of the cyanides indicate a dimeric formula.



Diphosphinocarborane derivatives are known. Smith *et al.* isolated [Co(dPC)(B$_{10}$H$_{10}$C$_2$S$_2$)] and [Co(dPe)(B$_{10}$H$_{10}$C$_2$S$_2$)], but said they were unable to isolate simple dPC complexes (*251*). However, Hill and McAuliffe have isolated the green, pentacoordinate [Co(dPC)$_2$X]$^+$ (X = Br, I, NCS) (*163*); these compounds were very difficult to isolate, and would not form at all in most solvents.

Chow and McAuliffe have isolated a complex of empirical formula Co(PPPhen)(NCS)$_2$, but no structural data are yet available (*84*).

Isslieb and Weichmann found (*185*) that the disecondary phosphines, de$_s$e and dP$_s$e, are strong chelating agents toward Co(II). The hexacoordinate [Co(diphos)$_2$X$_2$] complexes (X = Cl, Br, I) have magnetic moments in the range 1.77–1.99 B.M. A complex [Co$_2$(diphos)$_2$I$_2$]I$_2$ was obtained, which has the probable structure



Air oxidation of Co(II) salts in the presence of dee produced Co(III) complexes, [CoX$_2$(dee)$_2$]X (X = Cl, Br, I). The iodide is insoluble but the green chloro and bromo complexes dissolve in water and undergo slow hydrolysis to produce yellow solutions. The brown iodo complex turns green on long heating over P$_2$O$_5$ *in vacuo* (*264*). [Co(dP$_s$e)$_2$Br$_2$]Br is formed by bromination of the Co(II) complex (*185*).

The compound $Rh_4(CO)_{10}(dPe)$ has been obtained from $Rh_4(CO)_{12}$ (*262*), while $Rh_6(CO)_{16}$ adds three equivalents of dPe to give $Rh_6(CO)_{10}(dPe)_3$, which almost certainly retains the Rh_6 cluster (*190*).

The diphosphines dPm and dPe react with $[Rh(CO)_2Cl]_2$ to form $[Rh(CO)_2Cl]_2$(diphos), [Rh(CO)Cl(diphos)], $[Rh(CO)Cl(dPm)]_n$, and $[Rh(dPe)_2]Cl$ (*159*). Mague and Mitchener reported that dPm also formed $[Rh(CO)(dPm)Cl]_2$ (*200*). They also found that TVPP and DPPA, which cannot chelate, formed polymers, $[Rh(CO)Cl(diphos)]_n$, whereas a 2:1 ratio of VPP:$[Rh(CO)_2Cl]_2$ produced $[Rh(VPP)_2][Rh(CO)_2Cl_2]$. Excess VPP or POP gave $[Rh(diphos)_2]Cl$. The $[Rh(CO)_2X_2]^-$ complexes are approximately 1:1 electrolytes in CH_3CN, and the infrared spectra are essentially identical with that of n-$Bu_4N[Rh(CO)_2Cl_2]$ (*200*). PP–P and $[Rh(CO)_2Cl]_2$ form both phosphido and diphosphine complexes (*159*). Cullen and Thompson found (*106*) that $[Rh(CO)_2X]_2$ (X = Cl, Br) reacted with ffos or $f_6$fos to form $[Rh(diphos)_2][cis\text{-}Rh(CO)_2X_2]$, whereas a fourfold excess of ffos, $f_6$fos, or $f_8$fos formed $[Rh(diphos)_2]Cl$. $[Rh(ffos)_2]Cl$ reacted with hydrogen chloride in CH_2Cl_2 to form $[RhHCl(ffos)_2]Cl$, which exhibited ν(Rh–H) at 2080 cm^{-1}. All the complexes are 1:1 electrolytes and ^{19}F NMR data were also reported (*106*).

Heating rhodium with PEE in hydrogen led to very small yields of an orange-yellow compound, $Rh_2H_n(PEE)_3$ ($n \geqslant 0$) (*66*). $[RhH(dPe)_2]$ was obtained on reducing $[Rh(dPe)_2]Cl$ with $NaBH_4$ or $LiAlH_4$ (*200, 236*). Unlike the cobalt analog, it decomposes in perchloric acid to form $[Rh(dPe)_2]ClO_4$ and hydrogen. Upon reaction of $[RhH(dPe)_2]$ with hydrogen chloride in ether, $[RhHCl(dPe)_2]Cl$ results. $[Rh(dPe)_2]Cl$ can be converted to $[Rh(dPe)_2]ClO_4$ by $HClO_4$, and the latter complex has been shown to be square-planar by X-ray analysis (*138*).

When $RhCl_3 \cdot 3H_2O$ reacts with dme under nitrogen a mixture of *cis*- and *trans*-$[Rh(dme)Cl_2]Cl$ is formed (*41*). The pure trans isomer can be obtained from *mer*-$[RhCl_3(n\text{-}Bu_3P)_3]$ and dme, but *mer*-$[RhBr_3(n\text{-}Bu_3P)_3]$ gives the cis isomer. *cis*-$[Rh(dme)_2Cl_2]Cl$ is formed from $[Rh(dme)_2]Cl$ and chlorine, or by reaction with CCl_4 or $CHCl_3$; *trans*-$[Rh(dme)_2Br_2]Cl$ results from treating $[Rh(CO)(dme)_2]Cl$ with bromine in CCl_4. *trans*-$[Rh(dme)_2Cl_2]Cl$ is reduced to the metal by $LiAlH_4$, but the milder reductant $NaBH_4$ forms *trans*-$[RhHCl(dme)_2]Cl$, which can also be obtained from $[Rh(CO)(dme)_2]Cl$ and HCl (*41*). $[Rh(dme)_2]Cl$ forms from $[RhCl(PPh_3)_3]$ and dme in benzene (*41, 56*). It is a 1:1 electrolyte and takes up hydrogen chloride reversibly to form $[RhH_2(dme)_2]Cl$, ν(Rh–H) at 1900 and 1870 cm^{-1}. $RhCl_3$ and ffos react to form $[RhCl_3(ffos)_2]$ (*99*).

In contrast to $[Rh(dPe)_2]Cl$, which does not react with CO, $[Rh(dme)_2]Cl$ takes up CO reversibly to give $[Rh(CO)(dme)_2]Cl$ (*56*). Solid

$[Rh(dme)_2]Cl$ takes up oxygen, apparently to form $[Rh(O_2)(dme)_2Cl]$ containing O_2^{2-} (*56*). $[Rh(O_2)(dPe)_2]PF_6$ was obtained from $[Rh(dPe)_2]Cl$, NH_4PF_6, and O_2 in anhydrous methanol (*215*). The oxygen is lost on boiling in CH_2Cl_2 or CH_3OH solution.

Interaction of $[Ir(CO)_2Cl(py)]$ and PP–P gives yellow $Ir(PP–P)_2(CO)_2Cl$ and a phosphido complex (*159*). From the reaction between dPm and $[Ir(CO)_2Cl(py)]$ were obtained $[Ir(CO)_2Cl]_2(dPm)$ and $[Ir(CO)(dPm)_2]Cl$, whereas dPe gave $[Ir(CO)_2Cl(dPe)]$, $[Ir(CO)(dPe)_2]Cl$, and $[Ir(dPe)_2]Cl$ (*154, 159*). $[Ir(CO)(dPe)_2]Cl$, which reversibly loses CO, has a distorted trigonal-bipyramidal structure (*186*). *In vacuo* CO is lost and the red, diamagnetic four-coordinate $[Ir(dPe)_2]Cl$ is formed (*235*).

trans-$[Ir(CO)Cl(PPh_3)_2]$ reacts readily with dme in THF to form hygroscopic *trans*-$[Ir(CO)(dme)_2]Cl$ (*170*). With methanol or ethanol unusual hydridoalkoxycarbonyl complexes of Ir(III) are formed, $[IrH(CO_2R)(dme)_2]^+$ ($R = Me$, Et), which have been isolated as the tetraphenylborates. These are stable in alkalis, but lose an alkoxide group in dilute acids to form $[IrH(CO)(dme)_2]^+$. On refluxing *trans*-$[Ir(CO)(dme)_2]Cl$ in wet ethanol, CO is lost to form $[IrHCl(dme)_2]^+$, isolated as the tetraphenylborate, $\nu(Ir–H) = 2162\ cm^{-1}$. The complex $[Ir(CO)(dPe)_2]Cl$ does not form a hydride under similar conditions (*170*).

Vaska and Catone found (*257*) that $[Ir(dPe)_2]Cl$, which they obtained from $[Ir(CO)Cl(PPh_3)_2]$ and dPe, readily adds a number of small molecules to give 5- and 6-coordinated complexes. Among the reactions studied were those with HCl and HBr to give the hexacoordinate $[IrHX(dPe)_2]Cl$, and with CO, O_2, and PF_3 to form the pentacoordinate $[Ir(L)(dPe)_2]Cl$. $[Ir(dPe)_2Cl]$ adds carbon subsulfide at $-70°$ to form yellow $[Ir(dPe)_2(C_3S_2)]Cl$, a 1 : 1 electrolyte, whereas in refluxing CH_2Cl_2, purple $[Ir(dPe)_2(C_3S_2)_2Cl]_n$ results (*124a*). Molecular hydrogen forms $[IrH_2(dPe)_2]BPh_4$, which, on the basis of IR evidence, probably has the cis structure. It also appears to be possible to add NO, probably to produce $[Ir(NO)_2(dPe)_2]Cl$, since in air $[Ir(NO_2)_2(dPe)_2]Cl$ is formed (*257*). The X-ray structure of $[Ir(O_2)(dPe)_2]PF_6$ has been reported, and the Ir atom is in a trigonal-bipyramidal environment (*214, 215*). *trans*-$[Ir(CO)(PPh_3)_2X]$ and excess dPe give $[Ir(dPe)_2]X$ on heating in benzene under nitrogen, but at room temperature in the presence of carbon monoxide $[Ir(CO)(dPe)_2]X$ is formed, in contrast to $[Rh(dPe)_2]^+$ which does not take up CO. The CO can be removed by passing nitrogen through the solution. $[Ir(CO)(dPm)_2]X$ is obtained similarly, but it does not lose CO to form $[Ir(dPm)_2]X$ (*253*) (see Table X).

The compound $[IrH_2(PPh_3)(dPe)]ClO_4$ (*11a*) and the germyl complex $[IrH_2(CO)(dPe)(GeEt_3)]$ (*127*) have been prepared.

TABLE X

DIPHOSPHINE COMPLEXES OF RHODIUM AND IRIDIUM

Compound	Color	M.p.(°C)	Properties	Ref.
$[Rh(ffos)_2][Rh(CO)_2Cl_2]$	Yellow	200(d)	^{19}F NMR	(*106*)
$[Rh(f_6fos)_2][Rh(CO)_2Cl_2]$	Yellow	170(d)	^{19}F NMR	(*106*)
$[Rh(ffos)_2]Cl$	Yellow	200(d)	^{19}F NMR	(*106*)
$[Rh(f_8fos)_2]Cl$	Light orange	187	^{19}F NMR	(*106*)
$[RhHCl(ffos)_2]Cl$	Yellow	192	^{19}F NMR, IR	(*106*)
$[Rh(VPP)(CO)Cl]$	Yellow	184(d)	IR	(*200*)
$[Rh(VPP)_2]BPh_4$	Yellow	—	—	(*200*)
$[Rh(POP)_2]BF_4$	Yellow	225(d)	—	(*200*)
$[Rh(TVPP)(CO)Cl]$	Yellow	246(d)	IR	(*200*)
$[Rh(dPm)(CO)Cl]_2$	Orange	221(d)	IR	(*159, 200*)
$[Rh(VPP)_2][Rh(CO)_2Cl_2]$	Yellow	238(d)	IR	(*200*)
$[RhH(dPe)_2]$	Orange	280(d)	D.M. = 4.35	(*236*)
$[RhHCl(dPe)_2]Cl$	Yellow	181	—	(*236*)
$[Rh(dPe)(CO)Cl]$	Yellow	135	$\mu = 0$, IR	(*159*)
$[Rh(dPe)_2]Cl$	Yellow	215	—	(*236*)
$[Rh(dPe)_2]ClO_4$	Yellow	282	—	(*236*)
$Rh(ffos)_2Cl_3$	Yellow	231	—	(*99*)
$[Rh(CO)(dme)_2]Cl$	Yellow	110(d)	IR	(*41*)
$[Rh(dme)_2]Cl$	Yellow	245(d)	—	(*41*)
cis-$[RhH_2(dme)_2]Cl$	White	—	IR	(*41*)
trans-$[RhHCl(dme)_2]Cl$	White	185	IR	(*41*)

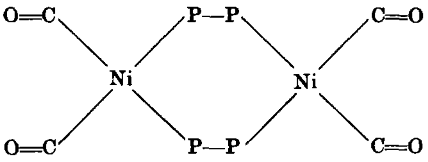
trans-[Rh(dme)$_2$Cl$_2$]Cl	Yellow	189(d)	—	(*41*)
cis-[Rh(dme)$_2$Cl$_2$]Cl	Yellow	295(d)	—	(*41*)
cis-[Rh(dme)$_2$Br$_2$]Br	Yellow	334	—	(*41*)
trans-[Rh(dme)$_2$Cl$_2$]Br	Yellow	186(d)	—	(*41*)
trans-[Rh(dme)$_2$Br$_2$]Cl	Yellow	335(d)	—	(*41*)
trans-[Rh(dme)$_2$Cl$_2$]BPh$_4$	Pale yellow	181	—	(*41*)
[Ir(CO)$_2$Cl]$_2$dPm	Yellow	180	IR	(*159*)
[Ir(CO)(dPm)$_2$]Cl	Yellow	195	IR	(*159*)
[Ir(CO)$_2$(dPe)]Cl	Yellow	162	IR	(*154*)
[Ir(CO)(dPe)$_2$]Cl	Yellow	320	IR	(*170*)
trans-[Ir(CO)(dme)$_2$]Cl	Cream	105	NMR	(*170*)
trans-[IrH(CO)(dme)$_2$](BPh$_4$)$_2$	White	237	IR, NMR	(*170*)
trans-[IrHCl(dme)$_2$]BPh$_4$	White	225	IR, NMR	(*170*)
[Ir(dPe)$_2$]Cl	Orange	225	—	(*257*)
[Ir(dPe)$_2$]BF$_4$	Orange	270	IR	(*257*)
[Ir(CO)(dPe)$_2$]Cl	White	260	IR	(*257*)
[Ir(dPe)$_2$(PF$_3$)]Cl	White	270	IR	(*257*)
[Ir(dPe)$_2$(O$_2$)]Cl	Cream	185	ν(Ir–O$_2$) 845 cm^{-1}	(*257*)
[Ir(dPe)$_2$(O$_2$)]BPh$_4$	Cream	175	ν(Ir–O$_2$) 844 cm^{-1}	(*257*)
[IrH$_2$(dPe)$_2$]BPh$_4$	White	220	IR	(*257*)
[IrHCl(dPe)$_2$]Cl	White	270	IR	(*257*)
[Ir(dPe)$_2$(NO$_2$)$_2$]Cl	Cream	163	IR	(*257*)
[IrH$_2$(dPe)PPh$_3$]ClO$_4$	Colorless	183(d)	IR	(*11a*)
IrH$_2$(CO)(dPe)GeEt$_3$	White	196	IR, NMR	(*127*)

H. GROUP VIII (Ni, Pd, AND Pt)

Nickel(0) complexes, [Ni(diphos)$_2$], were obtained by Chatt *et al.* by reduction [Ni(diphos)$_2$X$_2$] with NaBH$_4$ or sodium naphthalenide (*67*). Aromatic, but not aliphatic, diphosphines can replace all the CO from Ni(CO)$_4$, while [Ni(PEE)$_2$] and [Ni(dPe)$_2$] can also be obtained by heating Raney nickel with the diphosphine at 160° (*64*). Van Hecke and Horrocks used the reaction of nickelocene with the diphosphine to prepare [Ni(dPe)$_2$] and [Ni(dPp)$_2$], a method which avoids using the highly toxic Ni(CO)$_4$ (*150*). The Ni(0) complex K$_4$Ni(CN)$_4$ reacts with dPm and dPe in liquid ammonia to form the [Ni(diphos)$_2$] compounds (*21*).

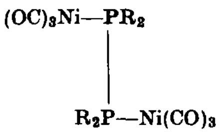
The reaction of Ni(CO)$_4$ with most diphosphines produces [Ni(CO)$_2$(diphos)] complexes, although aromatic diphosphines (dPe, PEE, PPP) can react further (*64*). Among the diphosphines which produce [Ni(CO)$_2$(diphos)] are dee (*64*, *210*, *217*), dPe, dPp, dPm (*166*, *210*), dne (*217*), PMM, PEE, PPP (*64*), ffos (*217*), and VPP (*251*). In general, all these complexes have good thermal stability, but oxidize readily in air. The ligands dm$_f$e (*39*) and dm$_f$e$_f$ (*40*) have also been used, the complex with the former being volatile without decomposition in contrast to most of the [Ni(CO)$_2$(diphos)] complexes.

The bridged derivatives of type (XXIII) have also been obtained as biproducts of the reaction of Ni(CO)$_4$ and diphosphines (*64*, *217*).

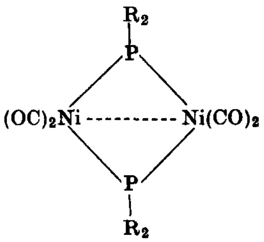


(XXIII)

With MP–P, EP–P, PP–P (*146*), CyP–P (*178*), and M$_f$P–P (*38*, *201*) both diphosphine (XXIV) and phosphido (XXV) complexes are formed

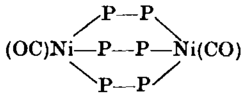


(XXIV)



(XXV)

(*188*, *206*). From $Ni(CO)_4$ or $[\pi\text{-}C_5H_5Ni(CO)]_2$ and DPPA and DPPB, bridged complexes were obtained, the triply bridged $[Ni_2(CO)_2(DPPA)_3]$, (XXVI), and $[Ni(CO)_3]_2DPPA$ were also isolated (*51*, *193*). Orange or yellow $[Ni(CO)_2(diphos)]$ (diphos = deC, dPC) complexes react with a further mole of ligand to form $[Ni(diphos)_2]$ compounds (*230*). The halogenated *o*-carboranediphosphines were investigated. With $B_{10}H_{10-n}X_n(PPh_2)_2$ ($n = 1$, 2, or 3) $[Ni(CO)_2L]$ formed which, on reaction with halogens, gave $[Ni(L)X_2]$ and $[NiL_2]X_2$ (*265*). The unusual $[Ni(diphos)_{1.5}(CN)_2]$ (diphos = dPp, dPb) complexes are reduced by $NaBH_4$ in ethanol to the yellow $Ni(diphos)_{1.5}(CN)$, $\mu_{eff} = 2.0\text{–}2.3$ B.M. (*94*). These complexes are dimeric, [(diphos)(CN)Ni(diphos)Ni(CN)-(diphos)]. Hieber *et al.* (*18*, *158*, *160*) have prepared several nitrosyl complexes, e.g., the red-violet [Ni(NO)(dPe)I] and $[Ni(NO)C(CN)_3(dPe)]$, as well as the more unusual $[X(PPh_3)(NO)Ni(dPe)Ni(NO)(PPh_3)X]$, obtained from $[Ni(NO)(PPh_3)X]_2$ and dPe. PP–P reacts with $[Ni(NO)X]_4$ to form the halogen-bridged $[Ni_2(NO)_2(PP\text{–}P)_2X_2]$ and phosphido complexes.



(XXVI)

Nickel(II) complexes are of four main types: $[Ni(L)X_2]$, $[Ni(L)_2X_2]$, $[Ni(L)_2X]Y$, and $[Ni(L)_2]X_2$. The general methods of preparation include the reaction of NiX_2 with the diphosphine in aqueous ethanol, acetone, dichloromethane, etc.; the action of halogens on $[Ni(diphos)(CO)_2]$ (*64*); or from the chloride by metathesis with LiX. Aqueous acids convert $[Ni(diphos)_2]$ to the nickel(II) complexes (*46*). $Ni(dme)_2X_2$ are readily obtained as alcohol-soluble complexes; reaction with NiX_2 converts them to the insoluble $Ni(dme)X_2$ (*31*). Wymore and Bailar (*264*) obtained diamagnetic $[Ni(dee)X_2]$ (X = Cl, Br) and $[Ni(dee)_2](ClO_4)_2$. Booth and Chatt found that $Ni(dee)_2X_2$ were formed initially, but only when X = I was the product stable (*31*). $Ni(PEE)_2Br_2$ was obtained as a dark red complex from the action of bromine on $[Ni(PEE)_2]$; the solid is diamagnetic, and is a 1 : 1 electrolyte in nitrobenzene (*64*). The same compound is formed from $NiCl_2$ and PEE in aqueous ethanol, and then treatment of the product with NaBr. It crystallizes from solution as the octahydrate. In $[Ni(dPm)_2X_2]$ the ligand appears to function as a monodentate (*31*, *150*). Because dPm is bidentate in $[Ni(CO)_2(dPm)]$, it was suggested (*150*) that halogenation of this complex might produce the bidentate nickel(II) halide derivatives, but this suggestion has not yet been carried out. However, dPm is bidentate in $[Ni(dPm)_2]Y_2$ ($Y = NO_3, ClO_4, BF_4$) (*118*).

The ligand dPe forms 1:1 complexes, $[NiX_2(dPe)]$, readily and 2:1 complexes, $Ni(dPe)_2X_2$ ($X = Br, I$), under forcing conditions (*31*). Booth and Chatt assigned hexacoordinate structures to the latter complexes in the solid state (*31*), but no magnetic or spectral evidence was produced in confirmation; moreover, these complexes are almost 1:1 conductors in nitrobenzene, and so their octahedral structural assignment is questionable. Van Hecke and Horrocks concluded (*150*) on the basis of the difference in optical spectra of the solids and the solutions that in CH_2Cl_2 solution the reaction

$$Ni(dPe)_2X_2 \rightleftharpoons Ni(dPe)X_2 + dPe$$

occurs. Optical spectra rule out the presence of a five-coordinate species, which have never been observed with dPe (*150*, *212*). Hudson *et al.* obtained $[Ni(dPe)_2]Y_2$ ($Y = NO_3, ClO_4$) complexes, which are square-planar ($\mu_{eff} = 0$–0.4 B.M.) 1:2 electrolytes (*168*). Small magnetic moments in the range 0–0.4 B.M. have been reported for several apparently square-planar Ni(II) complexes, but no satisfactory explanation has been forthcoming. The isolation of two forms of $Ni(dPe)Cl_2$ has been claimed (*31*): a yellow-brown diamagnetic plates form and a paramagnetic ($\mu_{eff} = 1.34$ B.M.) dull orange crystalline form, but other workers have only isolated the diamagnetic compound.

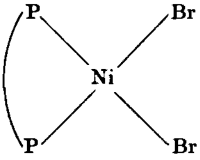
Solid $[Ni(dPp)X_2$ complexes are planar, diamagnetic compounds. On dissolution in CH_2Cl_2, $PhNO_2$, or $CHCl_3$ magnetic moments in the range 2.12–2.73 B.M. were reported. The difference in optical spectra between solid $Ni(dPp)I_2$ and solutions of $Ni(dPp)X_2$ ($X = Cl, Br, I$) were studied, and it was concluded that in the solution the equilibrium

$$\underset{\substack{\text{square planar}\\ \text{diamagnetic}}}{Ni(dPp)X_2} \rightleftharpoons \underset{\substack{\text{tetrahedral}\\ \text{paramagnetic}}}{Ni(dPp)X_2}$$

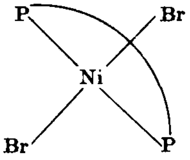
exists (*150*). On the basis of spectral evidence the proportion of tetrahedral isomer present decreases in the order I > Br > Cl. Solid tetrahedral complexes have not been obtained. The thermodynamic parameters for the equilibrium were determined by NMR (*150*). Sacconi and Gelsomini found that dPb and dPf formed pseudotetrahedral 1:1 complexes with nickel halides (*237*). The isolation of these paramagnetic ($\mu_{eff} = 3.3$ B.M.) complexes is not unexpected; since an increase in chelate chain length from dPe → dPp produced complexes which exhibited square-planar $\rightleftharpoons$ tetrahedral equilibrium in solution, then further increase in chain length to dPb and dPf leads to tetrahedral compound formation.

McAuliffe and Meek obtained the planar $[Ni(VPP)X_2]$ (X = Cl, Br, I, NCS) and the diamagnetic, pentacoordinate $[Ni(VPP)_2X]BPh_4$ (X = Cl, Br, I), which were assigned square-pyramidal structures on the basis of electronic spectra (*212*). $[Ni(VPP)_2(NCS)]BPh_4$ is paramagnetic ($\mu_{eff} = 1.86$ B.M.) in the solid state, and in solution the electronic spectrum resembled the other pentacoordinate $[Ni(VPP)_2X]^+$ complexes, but the solid spectrum was different. Six-coordinate VPP complexes could not be obtained (*212*). $[Ni(VPP)_2](ClO_4)_2$ and $[Ni(VPP)_2](NO_3)_2$ show interesting differences (*225*). The former exhibits normal magnetic behavior and follows the Curie–Weiss Law. The latter, however, is an example of the so-called "anomalous behavior of nickel." It does not obey the Curie–Weiss Law, and magnetic susceptibility measurements indicate an equilibrium between the spin-free and spin-paired electronic ground states. The differences between these two complexes has been explained in terms of the greater coordinating ability of the nitrate ions, which produce axial perturbation along the *z* axis. The poorer coordinating perchlorate ions do not produce this effect. This explanation is supported by the observation that in concentrated solutions of the complexes, ion-pairing occurs in the nitrate, but not in the perchlorate, complex (*225*). This difference has been observed in other nickel complexes (*128*). $[Ni(VPP)(NCS)_2]$ (*226*) and also $[Ni(diphos)(NCS)_2]$ [diphos = dPp (*229*), dPb (*237*)] are planar, diamagnetic complexes (see Table XI).

Nickel(II) bromide reacts with dCyp to form $[Ni(dCyp)Br_2]$, a planar complex with a dipole moment of 11.13 D, indicating a cis structure (XXVII). The complex with dCyb is probably analogous, but with dCyf a trans planar structure (XXVIII) is indicated, D.M. = 2.37 D (*176*).



(XXVII)



(XXVIII)

CyP–P reacts with NiX_2 (X = Cl, Br) to form $[Ni(CyP\text{–}P)X_2]$ in which the ligand is bidentate (*182*), but PP–P forms $[Ni(PP\text{–}P)_2X_2]$, a diamagnetic nonelectrolyte with a dipole moment of 5.97 D, indicating a cis square-planar structure with monodentate PP–P ligands (*176*).

TABLE XI

DIPHOSPHINE COMPLEXES OF NICKEL

Compound	Color	M.p.(°C)	Properties	Ref.
$[\mathrm{Ni(PPP)_2}]$	Red-orange	—	—	(*64*)
$[\mathrm{Ni(dme)_2}]$	White	120	D.M. = 1.65	(*67*)
$[\mathrm{Ni(dPe)_2}]$	Orange	253(d)	D.M. = 1.5	(*67*)
$[\mathrm{Ni(PEE)_2}]$	Red-orange	241	—	(*67*)
$[\mathrm{Ni(dPp)_2}]$	Red-orange	—	—	(*150*)
$[\mathrm{Ni(CO)_2(PMM)}]$	White	123	IR, D.M. = 5.40	(*64, 150*)
$[\mathrm{Ni(CO)_2(PPP)}]$	Yellow	226	IR, D.M. = 5.39	(*64*)
$[\mathrm{Ni(CO)_2(dPe)}]$	White	139	IR, D.M. = 4.81	(*64*)
$[\mathrm{Ni(CO)_2(PEE)}]$	White	65	IR, D.M. = 5.48	(*64*)
$[\mathrm{Ni(CO)_2(dee)}]$	White	13	IR	(*64, 217*)
$[\mathrm{Ni(CO)_2(dm_fe)}]$	Colorless	5	IR	(*39*)
$[\mathrm{Ni(CO)_2(dme)}]$	Cream	71	IR	(*31*)
$[\mathrm{Ni_2(CO)_4(dee)_2}]$	White	116	IR, D.M. = 1.6	(*64*)
$[\mathrm{Ni_2(CO)_6(m_fP{-}P)}]$	Red-black	105	IR	(*38*)
$[\mathrm{Ni(CO)_2(ffos)}]$	Yellow	—	IR	(*99*)
$[\mathrm{Ni(CO)_2(dne)}]$	Cream	132	IR, ^{31}P NMR	(*217*)
$[\mathrm{Ni_2(CO)_6(PP{-}P)}]$	Yellow	195	IR, NMR	(*146*)
$[\mathrm{Ni_2(CO)_6(MP{-}P)}]$	Yellow	12	IR	(*146*)
$[\mathrm{Ni(CO)_2(VPP)}]$	Yellow	156	IR	(*251*)
$[\mathrm{Ni_2(CO)_4(DPPA)_2}]$	White	190	IR	(*51*)
$[\mathrm{Ni_2(CO)_2(DPPA)_3}]$	Yellow	264(d)	IR	(*51*)
$[\mathrm{Ni(CO)_2(dm_fe_f)}]$	Colorless	30	IR	(*40*)
$[\mathrm{Ni_2(CO)_4(DPPB)_2}]$	Yellow	80	IR	(*193*)
$[\mathrm{Ni(CO)_2(dPC)}]$	Yellow	119	IR	(*230*)
$[\mathrm{Ni(CO)_2(deC)}]$	Yellow	206(d)	IR	(*230*)
$[\mathrm{Ni(dPC)_2}]$	Orange	268(d)	—	(*230*)

$[Ni(deC)_2]$	Yellow	288(d)	—	*(230)*
$[Ni(CO)_2(dPp)]$	White	—	IR	*(166)*
$[Ni(CO)_2(dPm)]$	Yellow-white	—	IR	*(166)*
$[Ni(dme)Cl_2]$	Yellow	—	$\mu = 1.23$	*(31)*
$Ni(dme)_2Cl_2$	Orange	—	—	*(31)*
$[Ni(dPm)_2Cl_2]$	Dark brown	—	$\mu = 0$, vis.	*(31, 150)*
$[Ni(dPm)_2Br_2]$	Red	116	$\mu = 0$, vis.	*(150)*
$[Ni(dPm)_2I_2]$	Purple	—	$\mu = 0$, vis.	*(150)*
$[Ni(dPm)_2](NO_3)_2$	Yellow	286	—	*(118)*
$[Ni(dPm)_2](ClO_4)_2$	Yellow	178	—	*(118)*
$[Ni(dPm)_2](BF_4)_2$	Yellow	280(d)	—	*(118)*
$[Ni(dee)Cl_2]$	Yellow-brown	—	$\mu = 0$	*(264)*
$[Ni(dee)Br_2]$	Red-brown	—	$\mu = 0$	*(264)*
$Ni(dee)_2I_2$	Dark red	—	—	*(64)*
$[Ni(dee)_2](ClO_4)_2$	Yellow	—	—	*(264)*
$[Ni(dPe)Cl_2]$	Orange	—	$\mu = 0.3$, IR	*(31, 168)*
$[Ni(dPe)Br_2]$	Red	—	$\mu = 0.4$, IR	*(31, 167, 168, 212)*
$[Ni(dPe)I_2]$	Mauve	—	$\mu = 0.3$	*(166, 168, 212)*
$[Ni(dPe)(NCS)_2]$	Yellow	276	$\mu = 0.4$, IR, vis.	*(168, 226)*
$[Ni(dPe)(CN)_2]$	Yellow	—	Vis.	*(229)*
$[Ni(dPe)_2](ClO_4)_2$	Yellow	248	$\mu = 0.3$	*(67, 168)*
$[Ni(dPe)_2](NO_3)_2$	Yellow	218	$\mu = 0.4$	*(31, 168)*
$[Ni(dPe)_2]Br_2$	Yellow	—	$\mu = 0.3$	*(31, 168)*
$[Ni(dPe)_2]I_2$	Yellow	—	$\mu = 0.3$	*(31, 168)*
$[Ni(PEE)Cl_2]$	Brown	339(d)	$\mu = 0$	*(64)*
$[Ni(PEE)Br_2]$	Brown	333(d)	—	*(64)*
$[Ni(PEE)I_2]$	Red-black	279	—	*(64)*
$[Ni(PEE)_2]Br_2$	Dark red	—	$\mu = 0$	*(64)*
$[Ni(PEE)_2](NO_3)_2$	Yellow	210	—	*(67)*
$[Ni(VPP)Cl_2]$	Light brown	—	$\mu = 0$, vis.	*(212)*
$[Ni(VPP)Br_2]$	Red-brown	—	$\mu = 0$, vis.	*(212)*
$[Ni(VPP)I_2]$	Black	—	$\mu = 0$, vis.	*(212)*

(continued)

TABLE XI—*continued*

Compound	Color	M.p.(°C)	Properties	Ref.
[Ni(VPP)(NCS)$_2$]	Yellow	—	$\mu = 0$, IR, vis.	*(212, 226)*
[Ni(VPP)$_2$Cl]BPh$_4$	Purple	—	$\mu = 0$, vis.	*(212)*
[Ni(VPP)$_2$Br]BPh$_4$	Purple	—	$\mu = 0$, vis.	*(212)*
[Ni(VPP)$_2$I]BPh$_4$	Black	—	$\mu = 0$, vis.	*(212)*
[Ni(VPP)$_2$(NCS)]BPh$_4$	Light brown	—	$\mu = 1.66$, IR, vis.	*(212)*
[Ni(VPP)$_2$](ClO$_4$)$_2$	Yellow	286	$\mu = 1.50$, IR, vis	*(225)*
[Ni(VPP)$_2$](NO$_3$)$_2$	Yellow	200	$\mu = 1.67$, IR, vis.	*(225)*
[Ni(BPEP)Cl$_2$]	Purple	167	D.M. = 9.3, vis., NMR	*(9)*
[Ni(BPEP)Br$_2$]	Deep blue	149	$\mu = 2.8$ B.M., vis. NMR	*(9)*
[Ni(BPEP)I$_2$]	Dark brown	176	$\mu = 3.08$ B.M., D.M. = 9.4, NMR	*(9)*
[Ni(BPEP)(NCS)$_2$]	Red-brown	183	vis.	*(9)*
Ni(PP–P)$_2$Br$_2$	Red-brown	155	$\mu = 0$, D.M. = 5.97	*(181)*
Ni(CyP–P)Cl$_2$	Red	203	$\mu = 0$, D.M. = 3.72	*(182)*
Ni(CyP–P)Br$_2$	Red	193	$\mu = 0$, D.M. = 2.24	*(182)*
[Ni(dCyp)Br$_2$]	Red	235	$\mu = 0$, D.M. = 11.13	*(176)*
[Ni(dCyf)Cl$_2$]	Red	164	$\mu = 0$, D.M. = 2.37	*(176)*
[Ni(de$_s$e)$_2$Cl]Cl	Yellow	138	—	*(185)*
[Ni(de$_s$e)$_2$Br]Br	Red	157	—	*(185)*
[Ni(de$_s$e)$_2$I]I	Red	161	—	*(185)*
[Ni(de$_s$e)$_2$Br]$_2$NiBr$_4$	Dark brown	136	—	*(185)*
[Ni(dP$_s$e)$_2$Cl]Cl	Orange-red	150	—	*(185)*
[Ni(dP$_s$e)$_2$Br]Br	Orange-red	159	—	*(185)*
[Ni(dP$_s$e)$_2$I]I	Dark red	177	—	*(185)*

$[Ni(dP_{s}e)_2Br]_2NiBr_4$	Brown	184	—	(*185*)
$[Ni(dPp)Cl_2]$	Red	—	Vis.	(*150*)
$[Ni(dPp)Br_2]$	Red	—	Vis.	(*150*)
$[Ni(dPp)I_2]$	Purple	—	Vis.	(*150*)
$[Ni(dPp)(NCS)_2]$	Yellow	276	IR, vis.	(*226, 229*)
$Ni(dPb)_{1.5}(CN)_2$	Red	—	IR, vis.	(*229*)
$Ni(dPp)(PBu_3)(CN)_2$	Red	143	IR, vis.	(*229*)
$[Ni(dPb)Br_2]$	Dark green	—	$\mu = 3.30$, vis.	(*237, 238*)
$[Ni(dPb)(NCS)_2]$	Brick red	212	$\mu = 0$, IR, vis.	(*226, 237*)
$[Ni(dPb)(CN)_2]$	Yellow	—	—	(*229*)
$Ni(dPp)_{1.5}(CN)_2]$	Red	—	IR, vis.	(*229*)
$[Ni(dPf)Br_2]$	Dark green	—	$\mu = 3.28$, vis.	(*237*)
$[Ni(dPf)I_2]$	Maroon	—	$\mu = 3.24$, vis.	(*237*)
$[Ni(POPO)Cl_2]$	Amethyst	—	$\mu = 3.26$, vis.	(*237*)
$[Ni(POPO)Br_2]$	Brown	—	$\mu = 3.23$, vis.	(*237*)
$[Ni(POPO)I_2]$	Brown	—	$\mu = 3.24$, vis.	(*237*)
$[Ni(POPO)(NCS)_2]$	Brown	—	$\mu = 0$, IR, vis.	(*251*)
$[Ni(dPC)Cl_2]$	Red	310(d)	—	(*251*)
$[Ni(dPC)(B_{10}H_{10}C_2S_2)]$	Brown	380(d)	—	(*251*)
$[Ni(dPe)(B_{10}H_{10}C_2S_2)]$	Yellow	375(d)	—	(*251*)
$[Ni(dme)Br_3]$	Black	—	$\mu = 2.12$	(*31*)
$[Ni(dee)Br_3]$	Green-black	—	$\mu = 2.0$	(*264*)
$[Ni(dme)_2Br_2]Br$	Dark brown	—	$\mu = 2.05$	(*31*)
$[Ni(dme)_2Br_2]Br_3$	Light brown	—	$\mu = 2.02$	(*31*)
$[Ni(dPe)Br_3]$	Dark brown	—	$\mu = 2.02$, ESR, vis.	(*150*)
$[Ni(dPp)Br_3]$	Black	—	$\mu = 1.93$, ESR, vis.	(*150*)

PPPhen reacts with nickel(II) halides to form the planar [Ni(PPPhen)X_2] (X = Cl, Br, I, NCS) and the planar [Ni(PPPhen)$_2$](ClO_4)$_2$ compounds (*84*).

The unusual diphosphine BPEP forms complexes [Ni(BPEP)X_2] (X = Cl, Br, I, NCS). The *N*-bonded isothiocyanate is planar, the dark brown iodide ($\mu_{eff} = 2.80$–3.08 B.M.) is pseudotetrahedral, while the bromide and chloride exhibit planar-tetrahedral isomerism. The magnetic moments appear to depend on previous physical treatment of the complex, are roughly temperature independent, and follow the Curie–Weiss law, which rules out the type of anomalous behavior found for [Ni(VPP)$_2$](NO_3)$_2$. The electronic and NMR spectra support the presence of both planar and tetrahedral species in samples of the chloride and bromide (*9*).

Some dPC complexes have been prepared by Smith and co-workers. They include [Ni(dPC)$_2$]X_2 (X = Cl, Br), [Ni(dPC)Cl_2], [Ni(dPC)(*o*-$B_{10}H_{10}C_2S_2$)], and [Ni(dPe)(*o*-$B_{10}H_{10}C_2S_2$)] (*250*, *251*, *265*).

The [Ni(POPO)X_2] complexes are similar to those of dPb and dPf and were assigned pseudotetrahedral structures (*237*). The crystal structure of the chloride has been determined, and shows that the oxygen atom is not coordinated and an eight-membered ring is present (*132*). This contrasts with the nitrogen and sulfur analogs ($Ph_2PCH_2CH_2NHCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2SCH_2CH_2PPh_2$) which behave as terdentate ligands forming square-pyramidal complexes.

Unlike cobalt(II), nickel(II) is reluctant to form pentacoordinate complexes with the bis(diphenylphosphino)alkanes. Five-coordination has, however, been obtained with the cyanide (*229*). Only the four-coordinate [Ni(dPe)(CN)$_2$] has been isolated, but the complex [Ni(dPe)$_2$(CN)$_2$] has been studied by continuous variation spectrophotometry in CH_2Cl_2 solution and shown to be pentacoordinate with one dPe acting as a monodentate ligand. The presence of [Ni(dPe)$_2$(CN)]$^+$ is ruled out by the negligible conductance of the solution. With dPp and dPb the Ni(diphos)$_{1.5}$(CN)$_2$ complexes are obtained, which are probably dimeric and contain chelating and bridging diphosphines, (NC)$_2$(diphos)Ni(diphos)Ni(diphos)(CN)$_2$. Five-coordinate [Ni(dPp)(*n*-Bu_3P)(CN)$_2$] is also known. [Ni(dPb)(CN)$_2$] is dimeric in CH_2Cl_2, and the IR spectrum indicates *trans*-CN^- groups, and thus bridging diphosphines are indicated (*229*).

The only hydrido complex reported is [NiH(dPe)$_2$]$AlCl_4$, prepared from Ni(dPe)$_2$, $AlCl_3$, and dry HCl in toluene. These orange crystals exhibit ν(Ni–H) = 1950 cm^{-1} and τ(Ni–H) = 23 (*241*).

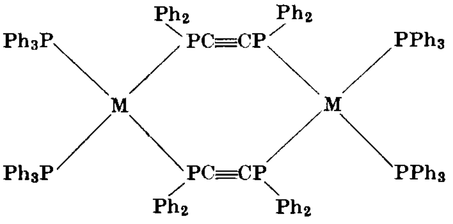
The disecondary phosphines de$_s$e and dP$_s$e form pentacoordinate, trigonal-bipyramidal [Ni(diphos)$_2$X]Y (X = Cl, Br, I; Y = Cl, Br, I,

BPh_4) complexes when reacted in a 2 : 1 ratio. A 1 : 1 diphosphine : $NiBr_2$ ratio produced [Ni(diphos)$_2$Br]$_2$[$NiBr_4$] (*185*).

Green-black Ni(dee)Br_3 was formed on oxidizing the Ni(II) complex with bromine in benzene (*264*). It is insoluble in water and a polymeric octahedral structure has been proposed. [Ni(dme)Br_2] reacts with bromine to form [Ni(dme)Br_3], whereas the oxidation in HBr of [Ni(dme)$_2$-Br_2] produced the very stable [Ni(dme)$_2Br_2$]Br (*31*). The latter adds bromine to form [Ni(dme)$_2Br_2$](Br_3). Booth and Chatt reported that Ni(dPe)$_2Br_2$ was not oxidized (*31*), but Van Hecke and Horrocks obtained Ni(III) complexes from the 1 : 1 complexes [Ni(diphos)Br_2] (diphos = dPe, dPp) (*150*). These complexes have been studied by ESR and electronic spectroscopy. The magnetic moments are in good agreement with theory for a low-spin d^7 complex, but the spectra have not been unambiguously assigned. McAuliffe oxidized [Ni(VPP)Br_2] to [Ni(VPP)Br_3], and found that the latter complex is reduced to the nickel(II) complex upon standing in air (*211*).

Palladium(0) and platinum(0) form [M(diphos)$_2$], thermally stable, air-sensitive complexes. Palladium also forms Pd(diphos)(diphos′) and Pd(diphos)(diars) (diars = chelating diarsine). [Pd(PEE)$_2$] forms on heating palladium black with PEE under nitrogen (*66*). Reduction of M(diphos)$_2X_2$ with $NaBH_4$ produced [M(diphos)$_2$], while [M(dme)$_2$] was obtained from [M(dme)Cl_2], dme, and sodium naphthalenide in THF (*67*, *74*). The [Pd(diphos)(diphos′)] and [Pd(diphos)(diars)] were obtained by reduction of [Pd(diphos)Cl_2] in the presence of an equimolar quantity of diphos′ or diars. Reduction of [Pd(PEE)Cl_2] in the presence of PPh_3 gave only [Pd(PPh_3)$_3$], and not [Pd(PEE)(PPh_3)$_2$] (*67*). [Pd(PEE)MeC(CH_2PPh_3)$_3$] has been obtained in an analogous manner to [Pd(diphos)(diphos′)]. It has been suggested that the former complex is pentacoordinate, probably square-pyramidal. $K_2Pt(CN)_4$ reacts with dPe in liquid ammonia to form [Pt(dPe)$_2$] (*219*).

The carbonyl complexes [$Pt_3(CO)_4(PEt_3)_4$] and $Pt(CO)_2Cl_2$ are decomposed by dPe to [Pt(dPe)$_2$] (*54*). [M(PPh_3)$_4$] reacts with DPPA to form [$M_2(PPh_3)_4(DPPA)_2$] (XXIX) (*261*). Oxidative addition

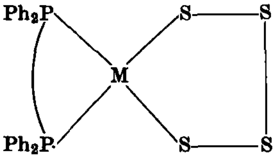


(XXIX)

M = Pd, Pt

reactions of perfluoroalkyl iodides to Pd(0) and Pt(0) complexes have been reported (*231*).

The [M(diphos)$_2$] complexes react with $HClO_4$ to form M(II) compounds. On heating with sulfur in benzene solution the [M(dPe)$_2$] complexes take up sulfur to form tetrasulfido complexes, of probable structure (XXX) (*73*).



(XXX)

M = Pd, Pt

Palladium(II) and platinum(II) readily form diphosphine complexes, usually resulting in the planar configuration. Palladium(II), especially, has been complexed with many of the more unusual diphosphines (see Table XII).

Complexes [Pd(diphos)$_2$]X$_2$ (diphos = dPm, dPe, PEE: X = Br, NO_3) were obtained by Chatt *et al.* by reaction of $PdCl_2$ or Na_2PdCl_4 with two equivalents of diphosphine and excess of NaBr, or with $Pd(NO_3)_2$ (*67*). Westland prepared [Pd(dPe)Cl$_2$] and found that it would react with a further molecule of dPe to form [Pd(dPe)$_2$]Cl$_2$, from which other halide derivatives could be obtained by metathesis (*259*). Platinum complexes were similarly isolated. The conductivity of the halides in nitromethane is less than that of the perchlorates, but the tendency toward association to form pentacoordinate cations is much less than with the corresponding diarsine complexes. In methanol the [Pd(dPe)$_2$]X$_2$ complexes are 1 : 2 electrolytes.

The 1 : 1 complexes [M(diphos)X$_2$] have been prepared from [M(PhCN)$_2$Cl$_2$], dPe, and excess LiX (*168*), or by reaction of the diphosphine (dme, dee, dPe) with Na_2MX_4 in ethanol to produce [M(diphos)$_2$][MX$_4$] complexes, which are decomposed to [M(diphos)X$_2$] on refluxing in DMF (*54*). These complexes are diamagnetic nonelectrolytes, and, when soluble, are monomeric in CH_2Cl_2 (*168*). dPm behaves as a normal chelating agent toward Pd(II) and Pt(II), in contrast to its preferred monodentate behavior with Ni(II) (*55*, *67*).

The palladium compound [Pd(dee)Cl$_2$] was obtained from $PdCl_4^{2-}$ and dee, but the platinum analog was isolated by displacement of Me_2S from *trans*-[Pt(SMe$_2$)$_2$Cl$_2$] in chloroform (*76*). Similar reactions produce [Pd(PP–P)$_2$Cl$_2$] and [Pd(diphos)X$_2$] (diphos = CyP–P, V_fPP, X = Cl;

TABLE XII

DIPHOSPHINE COMPLEXES OF PALLADIUM AND PLATINUM

Compound	Color	M.p.(°C)	Properties	Ref.
[Pd(dme)$_2$]	White	182	D.M. = 1.6	*(67)*
[Pd(dPm)$_2$]	Scarlet	203(d)	—	*(67)*
[Pd(dPe)$_2$]	Yellow	234	D.M. = 1.6	*(67)*
[Pd(PEE)$_2$]	Orange	229	D.M. = 0	*(66, 67)*
[Pd(PEE)(dPe)]	Yellow	207	D.M. = 2.1	*(67)*
[Pd(PEE)MeC(CH$_2$PPh$_2$)$_3$]	Yellow	200	D.M. = 3.1	*(67)*
[Pd(PEE)C$_6$H$_4$(AsMe$_2$)$_2$]	Orange	141	—	*(67)*
[Pd(PEE)C$_6$H$_4$(AsEt$_2$)$_2$]	Yellow	185	D.M. = 0.95	*(67)*
[Pd$_2$(DPPA)$_2$(PPh$_3$)$_4$]	Yellow	267(d)	IR, vis., NMR	*(261)*
[Pd(dPe)$_2$S$_4$]	Brown	234	—	*(73)*
[Pd(dPm)$_2$]Br$_2$	Yellow	314(d)	—	*(67, 259)*
[Pd(dPm)$_2$]Br$_2$·2H$_2$O	Orange	105	—	*(67, 259)*
[Pd(PEE)Cl$_2$]	White	350	—	*(67, 259)*
[Pd(PEE)$_2$]Br$_2$	White	240	—	*(67, 259)*
[Pd(dPe)Cl$_2$]	Yellow	>360	μ = 0.1, IR	*(168, 259)*
[Pd(dPe)Br$_2$]	Yellow	—	μ = 0.2, IR	*(168, 259)*
[Pd(dPe)I$_2$]	Brown	—	μ = 0.3	*(168, 259)*
[Pd(dPe)(SCN)$_2$]	White	—	μ = 0.3, IR	*(168, 259)*
[Pd(dPe)$_2$]Cl$_2$	White	291	—	*(259)*
[Pd(dPe)$_2$]Br$_2$	White	248	—	*(67, 259)*
[Pd(dPe)$_2$]I$_2$	Yellow	283	—	*(259)*
[Pd(dPe)$_2$](NO$_3$)$_2$	White	283(d)	—	*(67, 259)*
[Pd(dPe)$_2$](ClO$_4$)$_2$	White	330(d)	—	*(259)*
[Pd(VPP)Cl$_2$]	Cream	280	Vis.	*(84)*
[Pd(VPP)Br$_2$]	Yellow	300	Vis.	*(84)*

(continued)

TABLE XII—*continued*

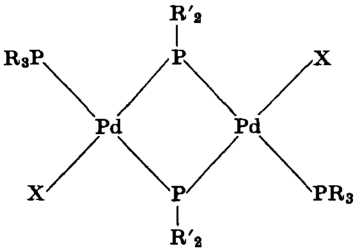
Compound	Color	M.p.(°C)	Properties	Ref.
$[Pd(VPP)I_2]$	Orange-yellow	300	Vis.	*(84)*
$[Pd(VPP)(CNS)_2]$	Pink	260	IR, vis.	*(84)*
$[Pd(dme)Me_2]$	Colorless	125(d)	—	*(32)*
$[Pd(dPe)MeBr]$	Cream	142(d)	—	*(32)*
$[Pd(dPe)Me_2]$	—	167	—	*(42)*
$[Pd_2(DPPA)_2Cl_4]$	—	264	—	*(47)*
$[Pd_2(DPPA)_2(SCN)_4]$	Orange	>300	IR	*(47)*
$[Pd(CyP{-}P)Cl_2]$	Yellow	>330	—	*(182)*
$[Pd(PP{-}P)_2Cl_2]$	Yellow	270	$\mu = 0$	*(182)*
$[Pd(BPEP)Br_2]$	Yellow	246	—	*(9)*
$[Pd(ffos)Cl_2]$	Yellow	320	—	*(99)*
$[Pd(DMBP)_2][PdBr_4]$	Buff	200–300	—	*(164)*
$[Pd(DMBP)Br_2]$	Orange-brown	148	—	*(164)*
$[Pd(4MePEE)Br_2]$	Cream	>300	—	*(141)*
$[(dPe)Pd(PPh_2)_2Pd(dPe)]Cl_2$	Orange	174	—	*(144)*
$[(dPe)Pd(PPh_2)_2Pd(dPe)]I_2$	Red	182	—	*(144)*
$[(dPe)Pd(PPh_2)_2Pd(dPe)](NO_3)_2$	Orange	203	—	*(144)*
$[(dPe)Pd(PPh_2)_2Pd(dPe)](ClO_4)_2$	Orange	281	—	*(144)*
$[(dPe)Pd(PPh_2)_2Pd(dPe)](BPh_4)_2$	Red	167	—	*(144)*
$[(dPe)Pd(PEt_2)_2Pd(dPe)](ClO_4)_2$	Yellow	332	—	*(148)*
$[(dPe)Pd(PEt_2)_2Pd(dPe)](BPh_4)_2$	Yellow	168	—	*(148)*
$[Pt(dPm)_2]$	Yellow	>300	—	*(74)*
$[Pt(PEE)_2]$	Red-orange	248(d)	—	*(74)*
$[Pt(dPe)_2]$	Yellow	253	—	*(74)*
$[Pt_2(DPPA)_2(PPh_3)_4]$	Yellow	226(d)	IR, vis., NMR	*(261)*
$[Pt(dPe)_2S_4]$	Orange	282	—	*(73)*

[Pt(dPm)Cl_2]	Colorless	340(d)	—	(*32*)
[Pt(dme)Me_2]	Colorless	143	—	(*32*)
[Pt(dee)Cl_2]	Colorless	289	—	(*32*, *76*)
[Pt(dee)Me_2]	Colorless	75	D.M. = 6.7	(*76*, *77*)
[Pt(dee)Ph_2]	Colorless	212(d)	D.M. = 8.4	(*77*)
[Pt(dPe)Cl_2]	Light yellow	360(d)	$\mu = 0.3$, IR	(*32*, *168*, *259*)
[Pt(dPe)Br_2]	Light yellow	—	$\mu = 0.4$, IR	(*32*, *168*, *259*)
[Pt(dPe)I_2]	Brown	—	$\mu = 0.3$	(*32*, *168*, *259*)
[Pt(dPe)Me_2]	Colorless	219	D.M. = 6.7, IR	(*32*)
[Pt$(dPe)_2$]Cl_2	—	270	—	(*259*)
[Pt$(dPe)_2$]Br_2	—	308	—	(*259*)
[Pt$(dPe)_2$]$(NO_3)_2$	—	310(d)	—	(*259*)
[Pt$(dPe)_2$]$(ClO_4)_2$	—	367	—	(*259*)
cis-[PtHCl(dPe)]	—	143	IR	(*89*)
[Pt(dPe)(PEt_3)Me]Cl·C_6H_6	—	174	IR, NMR	(*165*)
[Pt(dPe)(PEt_3)Et]Cl	—	140	IR, NMR	(*165*)
[Pt(dPe)(PEt_3)Ph]Cl·C_6H_6	—	145	IR, NMR	(*165*)
[PtH(dPe)($SiCl_3$)]	—	>330	IR	(*61*)
[Pt(dPe)$(SiCl_3)_2$]	—	>330	—	(*61*)
[Pt(dPe)$(SiHPh_2)_2$]	—	223(d)	IR	(*61*)
[Pt(dPe)$(SiMePh_2)_2$]	White	206	IR	(*61*)
[Pt(dPe)($GeMe_3$)Cl]	Yellow	224(d)	IR, NMR	(*165*)
[Pt(dPe)$(GeMe_3)_2$]	—	—	D.M. = 8.85	(*35*)
[PtH(dPe)($GeMe_3$)]	—	222(d)	IR	(*35*)
[Pt(ffos)Cl_2]	Light brown	335	—	(*99*)
[$Pt_2(DPPB)_2Cl_4$]	White	208	—	(*193*)
[$Pt_2(DPPA)_2Cl_4$]	White	312	—	(*47*)
[$Pt_2(DPPA)_2Br_4$]	Yellow	298(d)	—	(*47*)
[$Pt_2(DPPA)_2I_4$]	—	277(d)	—	(*47*)

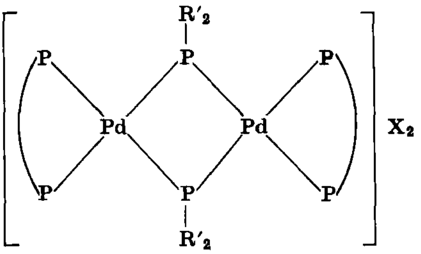
diphos = VPP, PPPhen, X = Cl, Br, I, NCS) (*84*, *182*). Infrared results indicate that in [Pd(VPP)(CNS)$_2$] there is an *N*- and an *S*-bonded thiocyanate group (*84*), and an X-ray structure has also confirmed this type of isomerism in [Pd(dPe)(NCS)(SCN)] (*24*).

The unusual diphosphine dne reacts with K_2PdBr_4 to form [Pd(dne)-Br$_2$] in ethanol, and from solutions of DMBP and K_2PdBr_4, is precipitated [Pd(DMBP)$_2$][PdBr$_4$]; [Pd(DMBP)Br$_2$] can be obtained from the filtrate (*164*). [Pd(BPEP)Br$_2$] is a normal planar complex, unlike the nickel(II) analog (*q.v.*) (*9*).

Hayter (*144*) and Hayter and Humiec (*148*), found that the phosphido-bridged complexes (XXXI) reacted with dPe to form the unusual



(XXXI)



(XXXII)

R = Et, Ph

complexes (XXXII). The structure (XXXII) was shown to be present by conductivity measurements which indicated a 1:2 electrolyte, and hence ruled out larger cations such as [Pd$_3$(dPe)$_3$(PPh$_2$)$_3$]$^{3+}$. Clark *et al.* isolated the chloro-bridged complex [M$_2$(dPe)$_2$Cl$_2$](BF$_4$)$_2$ (M = Pd, Pt) (*85*).

The ligands DPPA and DPPB form complexes [X$_2$M(diphos)$_2$MX$_2$] with two bridging diphosphines (*47*, *193*). It was suggested that Pd$_2$-(DPPA)$_2$(SCN)$_4$, obtained from KNCS and the chloro complex, contained both *N*- and *S*-bonded thiocyanate groups (*47*).

Platinum and palladium alkyls and aryls have been obtained by reaction of [M(diphos)Cl$_2$] with alkyl- or aryllithiums or Grignard reagents (*32*, *42*, *76*, *77*).

Hooton obtained [Pt(dPe)(PEt$_3$)R]Cl (R = Me, Et, Ph). On heating the ethyl compound loses ethylene, but the other two lose PEt$_3$. The Pt–C bonds are cleaved by iodine and HCl to [Pt(dPe)I$_2$] and [Pt(dPe)-(PEt$_3$)Cl]Cl, respectively (*165*). Interesting compounds are those formed by $C_{10}H_{12}OMe$-(dicyclopentadienemethoxide)-[M($C_{10}H_{12}OMe$)(dPe)]X (M = Pd, Pt, X = Cl, Br). The organic ligand is bonded to the metal by a σ and a π bond (*256*).

Several hydrido complexes of platinum are known. *cis*-[PtHCl(dPe)], the first *cis*-hydridohalide of platinum, is formed by the hydrogenolysis of [Pt(dPe)($SiMe_3$)Cl]. The IR spectrum exhibits a band at 2002 cm^{-1}, ν(Pt–H) (*89*). [PtH(dPe)(PEt_3)]Cl is formed by the hydrogenolysis of [Pt(dPe)(PEt_3)($GeMe_3$)]Cl (*126*), or from *trans*-[PtHCl$(PEt_3)_2$] and dPe (*135*). In the latter reaction [H$(PEt_3)_2$Pt(dPe)Pt$(PEt_3)_2$H] is also obtained. Related complexes are [Pt(dPe)(PEt_3)Cl]Y (Y = Cl, $SnCl_3$) (*135*).

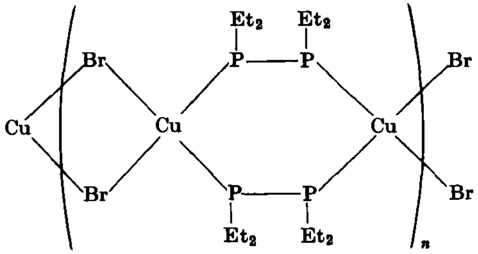
Platinum–silicon complexes have been obtained by Chatt *et al.* (*61*, *62*). [Pt$(dPe)_2$] reacts with $SiHCl_3$, SiH_2Ph_2, and $(XC_6H_4)_3SiH$ to form complexes such as [PtH($SiCl_3$)(dPe)], [Pt$(SiCl_3)_2$(dPe)], and [Pt$(HSiPh_2)_2$(dPe)]. One equivalent of bromine reacts with [Pt$(SiHPh_2)_2$(dPe)] to form [Pt$(SiBrPh_2)_2$(dPe)], but excess bromine cleaves the Pt–Si bond. $MePh_2SiLi$ reacts with [Pt(dPe)Cl_2] to form [Pt$(MePh_2Si)_2$(dPe)].

Some platinum–germanium complexes have been studied by Glockling *et al.* (*35*, *126*). For example, [Pt(dPe)(PEt_3)($GeMe_3$)]Cl is formed from [Pt$(Et_3P)_2$($GeMe_3$)Cl] and dPe, and [Pt(dPe)$(GeMe_3)_2$] from [Pt$(PEt_3)_2(GeMe_3)_2$]. [Pt(dPe)($GeMe_3$)Cl] is formed on heating [Pt(dPe)(PEt_3)($GeMe_3$)]Cl (*165*). The platinum–germyl complexes have recently been reviewed (*125*).

I. Group IB (Cu, Ag, and Au)

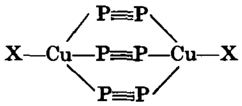
The reaction of CuI in saturated KI solution with dee, under nitrogen, produced colorless [Cu$(dee)_2$][Cu(dee)I_2], a 1:1 electrolyte in nitrobenzene (*264*). $[Cu(dPe)Cl]_3$, $[Cu(dPe)I]_3$, and Cu(dPe)BH_4 have been isolated (*44*). Isslieb and Hohlfeld obtained [Cu(dCyp)Br] from CuBr and dCyp in toluene. dCyf forms $(CuBr)_2$dCyf under similar conditions, while the intermediate ligand dCyb produces both [Cu(dCyb)Br] and $(CuBr)_2$dCyb (*176*). The 1:1 complexes contain three-coordinate copper, but the structure of the 2:1 complexes is uncertain. Colorless, diamagnetic compounds [Cu(PP–P)Cl] (*182*), [Cu(EP–P)Br] (*139*), $(CuCl)_2$(CyP–P), and $(CuBr)_2$(CyP–P) (*182*) have been reported. CuBr(EP–P) has structure (XXXIII), which contains alternate halogen and diphosphine bridges (*139*). The piperidinodiphosphine complexes of Cu(I) are reasonably stable—[Cu(diphos)Br] and $(CuBr)_2$(diphos) when diphos is NP–P (*245*) and NNP–P (*243*), respectively—but $(CuBr)_2$(NNPP–P) (*244*) is less stable.

A series of complexes $(CuX)_2(DPPA)_3$ (X = Cl, Br, I, NO_3, NCS, BH_4) has been prepared by reaction of the copper(II) salts with DPPA in ethanol (*48*) or by metathesis from $\{Cu(NO_3)\}_2$(DPPA) (X = I, BH_4).



(XXXIII)

All are colorless or white and melt with decomposition. A binuclear diphosphine-bridged structure (XXXIV) has been proposed. A number



(XXXIV)

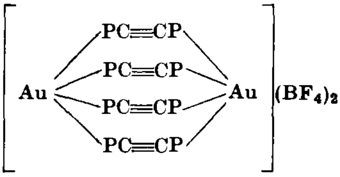
of organocopper complexes containing dPm and dPe have been prepared (*43*).

With chelating diphosphines silver forms complexes of the type $[Ag(diphos)_2][AgX_2]$ and, less frequently, $[Ag(diphos)_2]X$. Davis and Mann obtained a mixture on shaking 4Me-PEE with AgI and aqueous KI. Ethanol extraction and subsequent evaporation yielded Ag(4Me–PEE)$_2$I as colorless crystals (*108*). The ethanol-insoluble residue, recrystallized from DMF, gave [Ag(4Me–PEE)$_2$][AgI$_2$]. With dee, only the diiodoargentate(I) was obtained, [Ag(dee)$_2$][AgI$_2$] (*264*).

The ligand DPPA, which cannot chelate, gave rise to three types of complex. The complexes [AgX(DPPA)] (X = Cl, Br, I, SCN, NO_3) are obtained from $AgNO_3$ and DPPA in ethanol, and the subsequent metathesis yields halo and pseudohalo complexes (*10*). Two polymeric structures have been proposed: either three-coordinate silver with monodentate nitrate groups or four-coordinate silver with bridging bidentate nitrate groups. The compounds AgX(DPPA)$_2$ have been prepared for X = BF_4 or PF_6. The only representative of the third type of complex is (AgCl)$_2$(DPPA)$_3$, produced by reaction of (AgNO$_3$)(DPPA), NaCl, and DPPA in ethanol.

The diphosphines NP–P and NNP–P formed (AgI)$_2$(diphos); these are much more stable complexes than those of these same ligands with Cd and Zn, and resemble those of Cu(I) (*243*, *245*). Colorless (AgI)$_2$(NNPP–P) forms from NNPP–P and AgI in benzene (*244*).

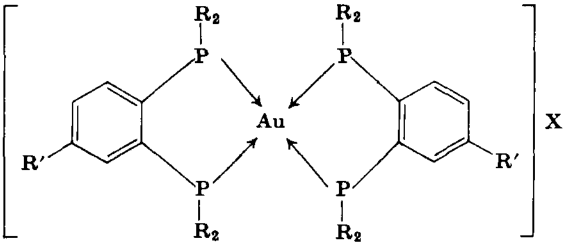
Carty and Efraty (*48*) isolated three types of gold(I) complexes with DPPA: (*a*) $(AuX)_2(DPPA)$ (X = Cl, Br, I, SCN); (*b*) $(AuX)_2(DPPA)_3$ (X = I, SCN); and (*c*) $(AuX)_2(DPPA)_4$ ($X = BF_4$, PF_6). Type (*a*) was obtained from AuX_4^- and DPPA in ethanol (X = Cl, Br) or by metathesis from the chloride (X = I, SCN) and they are thought to have a linear structure with a bridging DPPA ligand. In the case of the iodide and thiocyanate it is possible to add a further two ligands to produce type (*b*) complexes. Reaction of $(AuX)_2(DPPA)$, DPPA, and the appropriate anion in ethanol produced type (*c*) complexes. The structure suggested was (XXXV), although a polymeric structure is also possible.



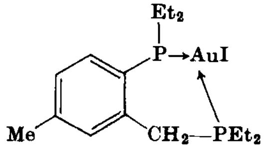
(XXXV)

In none of the complexes was there any evidence for coordination of the triple bond. A compound $(AuCl)_2(DPPB)$ has recently been obtained as yellow crystals (*193*).

Davis and Mann obtained a number of gold(I) complexes with unsymmetrically substituted, chelating diphosphines, and attempted to resolve them into optically active forms using optically active anions (*108*). In no case was any resolution observed. The complexes were obtained by reacting $HAuCl_4$ with the diphosphine in ethanol to form the chloride, from which other complexes could be obtained by metathesis.



(XXXVI)



(XXXVII)

Mostly, complexes $[Au(diphos)_2]X$ (XXXVI) were obtained (see Table XIII), but (2-diethylphosphino-4-methylbenzyl)diethylphosphine, even in excess, gave only the 1:1 adducts (XXXVII) (*108*).

The complexes $[ClAu(HMP)AuCl]$ and $[Au(4\text{-}MePEE)_2]I$ decompose on heating *in vacuo* to give the pure diphosphine (*141*, *164*).

TABLE XIII

DIPHOSPHINE COMPLEXES OF GOLD

Compound	Color	M.p.(°C)	Properties	Ref.
$[(AuCl)_2DPPA]$	White	266(d)	IR, Raman	(*48*)
$[(AuI)_2DPPA]$	White	267(d)	IR, Raman	(*48*)
$[(AuI)_2(DPPA)_3]$	White	218	IR, Raman	(*48*)
$(AuBF_4)_2(DPPA)_4$	White	246	IR, Raman	(*48*)
$[(AuCl)_2HMP]$	Yellow	—	—	(*164*)
$[(AuCl)_2BPPP]$	White	287(d)	—	(*83*)
$[(AuCl)_2BPEP]$	Yellow	292	—	(*9*)
$[(AuCl)_2dPe]$	White	291	IR	(*44*)
$[Au(dPe)_2]Cl$	—	245	—	(*44*)
$[Au_6(dPe)_2Cl]Cl \cdot 2H_2O$	Brown	202	IR	(*44*)
$[Au_6(dPe)_2Cl]ClO_4$	Red-brown	218	IR	(*44*)
$[Au_6(dPe)_2Cl_2 \cdot 2H_2O]_n$	Red-violet	210	IR	(*44*)
$[Au_6(dPe)_3]Cl_2 \cdot H_2O$	Green	210	IR	(*44*)
$[Au_6(dPe)_3](ClO_4)_2$	Green	245	IR	(*44*)
$[Au(PEP)_2]I$	Yellow	278	—	(*108*)
$[Au(PEE)_2]Cl$	Colorless	317	—	(*108*)
$[Au(PEE)_2]Br$	Colorless	251	—	(*108*)
$[Au(PEE)_2]I$	Colorless	266	—	(*108*)
$[Au(4Me\text{–}PEE)_2]I$	Colorless	240	—	(*48*, *108*)
$[Au(4P\text{–}PEE)_2]I$	Yellow	314(d)	—	(*107*)
$[Au(4Me\text{–}PEE)_2]NO_3 \cdot 2H_2O$	Colorless	244	—	(*108*)
$[Au(PEE)_2]Cl_3 \cdot 3H_2O$	Colorless	162	—	(*108*)
$Au(PEE)_2Br_3 \cdot 2H_2O$	Green-yellow	154	—	(*108*)
$Au(PEE)_2I_3$	Yellow-orange	180	—	(*108*)
$[Au(PEE)_2I](ClO_4)_2$	Yellow	191	—	(*108*)
$[Au(4Me\text{–}PEE)_2]I_3$	—	110	—	(*108*)

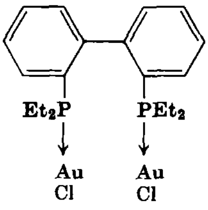
Davis and Mann also prepared a number of Au(III) complexes of PEE. $HAuCl_4$ reacts with two equivalents of PEE to form $[Au(PEE)_2]Cl_3$ (*108*). Boiling this complex in ethanol for 30 minutes the Au(I) complex is formed. The bromo and iodo complexes can be obtained from the Au(III) chloro complex and LiX, or from the Au(I) complex and free halogen. The compound $Au(PEE)_2I_3$ is especially interesting. In hot, 60% perchloric acid, yellow $[Au(PEE)_2I](ClO_4)_2$ is produced, whereas with sodium picrate in ethanol $[Au(PEE)_2](pic)_3$ is obtained. The $[Au(PEE)_2I](ClO_4)_2$ complex is a 1:2 electrolyte in nitrobenzene, but

$Au(PEE)_2I_3$ is intermediate between a 1 : 1 and 1 : 2 electrolyte, which suggests an equilibrium of the kind

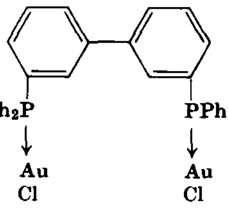
$$[Au(PEE)_2I_2]I \rightleftharpoons [Au(PEE)_2I]I_2$$

The triodide probably exists as $[Au(PEE)_2]I_3$ in ethanol, since the tripicrate can be obtained.

With dPe Malatesta obtained some cluster complexes of gold. These were of three types: ionic, brown $[Au_6(dPe)_2X]Y$; polymeric, red $[Au_6(dPe)_2X_2]_n$; and ionic, green $[Au_6(dPe)_3]X_2$ ($X = Cl$, Br, I, SCN; $Y = Cl$, Br, I, SCN, ClO_4, PF_6) (*45*). $(AuCl)_2(dPe)$ was obtained as white crystals from $HAuCl_4$ and dPe in ethanol, and contains a bridging diphosphine. It is possible to prepare $[Au(dPe)_2]Cl$ by varying the conditions. Reaction of $[Au(dPe)_2]Cl$ with $NaBH_4$ produced the red-brown cluster $Au_6(dPe)_2Cl_2 \cdot 2H_2O$ compound, in which the gold has an average oxidation number of one-third. Strongly nucleophilic ions replace both chlorides, but anions of low nucleophilicity replace only one, e.g., with perchlorate the 1 : 1 electrolyte $[Au_6(dPe)_2Cl]ClO_4$ is obtained. The compounds $Au_6(dPe)_2X_2 \cdot 2H_2O$ ($X = Cl$, Br, I, SCN) isomerize in CH_2Cl_2 solution to form red-brown polymers, which will react with dPe to yield green complexes $[Au_6(dPe)_3]X_2 \cdot H_2O$. The fact that $Au_6(dPe)_2Cl_2$ only loses one Cl^- with ClO_4^- indicates the nonequivalence of these chlorines. There is IR evidence for a bridging chlorine, and thus the structures of $[Au_6(dPe)_2Cl]Y$ appear to be two clusters of three gold atoms, bridged by two dPe ligands and one chlorine. In the polymeric compounds $[Au_6(dPe)_2X_2]_n$ both X groups are probably involved in bridging.



(XXXVIII)



(XXXIX)

The compound [IAu(dee)AuI] was obtained from AuI, NaI, and dee in ethanol. The white product is oxidized to black $I_3Au(dee)AuI_3$ by iodine in chloroform (*264*). Two interesting complexes containing bridging diphosphines are (XXXVIII) (*164*) and (XXXIX) (*83*).

J. GROUP IIB (Zn, Cd, AND Hg)

Few diphosphine complexes of zinc and cadmium have been reported. $M(dPe)X_2$ (M = Zn, Cd) crystallized on mixing the appropriate halide with dPe in ethanol or ethanol/propanol. Apart from melting point and $\nu(M\text{–}X)$ nothing is known about them. Presumably they have a pseudotetrahedral structure (*90*). Wymore and Bailar obtained $Zn(dee)Br_2$ and $(CdBr_2)_3(dee)_2$ from MBr_2 and dee (*264*). The latter complex dissolves in DMF and $Cd(dee)Br_2$ is precipitated by addition of water. $Cd(dee)Br_2$ reacts with $CdBr_2$ in DMF to reform $(CdBr_2)_3(dee)_2$. Zinc did not form an analogous complex (*264*). Seidel obtained 1 : 1 complexes from MI_2 (M = Zn, Cd) and NNP–P and from CdI_2 and NP–P, but these are rather unstable complexes (*243*, *245*). With NNPP–P and MI_2 even less stable complexes are formed (*244*). Unlike mercury, zinc and cadmium do not react with DPPA (*10*).

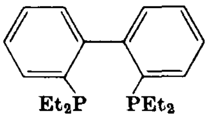
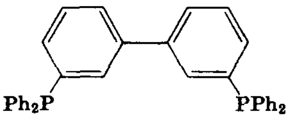
Mercuric halides HgX_2 (X = Cl, Br, I) form colorless, insoluble complexes with DPPA (*10*). The triple bond is not coordinated. Seidel obtained cream $Hg(NNP\text{–}P)I_2$, but with NP–P the HgI_2 cleaved the P–P bond (*243*). Yellow $Hg(ffos)Cl_2$ has been prepared (*99*).

Wymore and Bailar found that $HgBr_2$ reacted with dee to form $Hg(dee)Br_2$ (*264*). The reactions of mercury(II) halides with dPe were studied by Coates and Ridley (*90*), and have also been investigated by Sandhu *et al.* (*239*). The latter workers also prepared dPb complexes. Complexes isolated were $Hg(diphos)X_2$ and $(HgX_2)_2(diphos)$; $(HgI_2)_2(dPe)$ could not be obtained (*239*). All are white, are insoluble in all common solvents, and are nonelectrolytes in a nitrobenzene suspension. White $(C_6F_5)_2Hg(dPe)$ forms from $(C_6F_5)_2Hg$ and dPe in benzene/hexane (*53*).

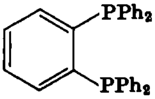
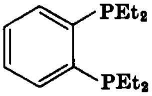
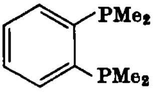
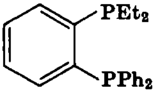
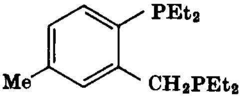
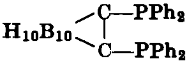
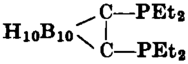
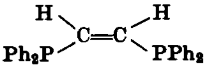
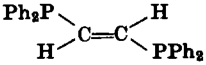
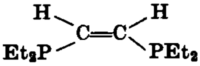
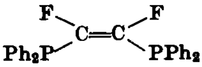
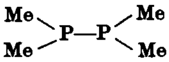
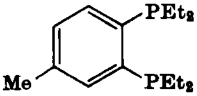
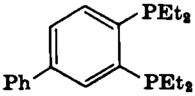
VII. Appendix: Ligand Abbreviations

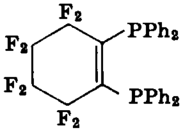
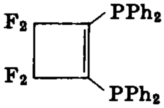
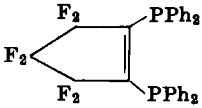
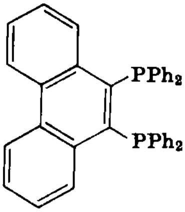
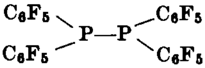
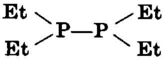
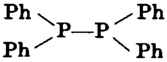
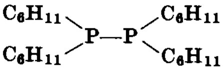
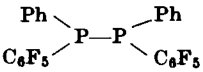
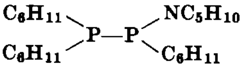
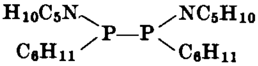
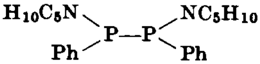
A. DITERTIARY PHOSPHINES

The system of abbreviations is a simple one, name y, *di*(*substituent*-phosphino)*backbone*. For example, bis(diphenylphosphino)ethane is dPe. Aryl substituents on the phosphorus atom are represented by capital letters (e.g., phenyl = P), alkyl substituents by lower-case letters (e.g., methyl = m). The references refer to the preparations of the ligands.

Compound	Abbrev.	Ref.
$(C_6H_{11})_2PCH_2P(C_6H_{11})_2$	dCym	(*180*)
$Ph_2PCH_2PPh_2$	dPm	(*152*, *180*)
$Me_2PC_2H_4PMe_2$	dme	(*68*)
$Et_2PC_2H_4PEt_2$	dee	(*64*, *152*, *263*)
$Ph_2PC_2H_4PPh_2$	dPe	(*64*, *180*)
$(C_6H_{11})_2PC_2H_4P(C_6H_{11})_2$	dCye	(*180*)
$(PhCH_2)_2PC_2H_4P(CH_2Ph)_2$	dBze	(*164*)
$(NCC_2H_4)_2PC_2H_4P(C_2H_4CN)_2$	dne	(*130*)
$(F_3C)_2PC_2H_4P(CF_3)_2$	dm_fe	(*37*, *129*)
$(F_3C)_2PC_2F_4P(CF_3)_2$	dm_fe_f	(*129*)
$Et_2PC_4H_8PEt_2$	deb	(*180*)
$Ph_2PC_4H_8PPh_2$	dPb	(*166*, *180*, *237*)
$(C_6H_{11})_2PC_4H_8P(C_6H_{11})_2$	dCyb	(*180*)
$Et_2PC_5H_{10}PEt_2$	def	(*180*)
$Ph_2PC_5H_{10}PPh_2$	dPf	(*166*, *180*, *237*)
$(C_6H_{11})_2PC_5H_{10}P(C_6H_{11})_2$	dCyf	(*180*)
$Et_2PC_6H_{12}PEt_2$	deh	(*180*)
$Ph_2PC_6H_{12}PPh_2$	dPh	(*166*, *180*, *237*)
$(C_6H_{11})_2PC_6H_{12}P(C_6H_{11})_2$	dCyh	(*180*)
$Et_2PC_3H_6PEt_2$	dep	(*180*)
$Ph_2PC_3H_6PPh_2$	dPp	(*166*, *180*, *237*)
$(C_6H_{11})_2PC_3H_6P(C_6H_{11})_2$	dCyp	(*180*)
$(NCC_2H_4)_2PC_3H_6P(C_2H_4CN)_2$	dnp	(*130*)
	HMP	(*164*)
	DMPP	(*164*)
	DMBP	(*164*)
	BPEP	(*8*)
	BPPP	(*83*)
$Ph_2PC{\equiv}CPPh_2$	DPPA	(*142*)
$Ph_2PCH_2C{\equiv}CCH_2PPh_2$	DPPB	(*193*)
$Et_2PC{\equiv}CPEt_2$	DEEA	(*64*)
$Ph_2PCH_2OCH_2PPh_2$	POP	(*6*)
$Ph_2PC_2H_4OC_2H_4PPh_2$	POPO	(*237*)

(*continued*)

Compound	Abbrev.	Ref.
	PPP	(*140*)
	PEE	(*140*)
	PMM	(*140*)
	PEP	(*140*)
	BzEE	(*107*)
	dPC	(*7*)
	deC	(*230*)
	VPP	(*5*)
	TVPP	(*5*)
	VPE	(*65*)
	V_fPP	(*84*)
	MP-P	(*37, 202, 223*)
	4-MePEE	(*107, 141*)
	4-PPEE	(*107, 141*)

Compound	Abbrev.	Ref.
	f$_8$fos	(*100*)
	ffos	(*98*)
	f$_6$fos	(*103*)
	PPPhen	(*84*)
	P$_f$P–P	(*11*)
	EP–P	(*152, 202*)
	PP–P	(*79, 249*)
	CyP–P	(*183*)
	P$_f$PP–P	(*117*)
	NP–P	(*243–245*)
	NNP–P	(*243–245*)
	NNPP–P	(*243–245*)

B. DISECONDARY PHOSPHINES

Quite a number of these have been prepared, but very few have been used in complexation reactions. The following examples serve to illustrate the type of abbreviation used in the text.

Compound	Abbrev.	Ref.
$PhP(H)C_2H_4P(H)Ph$	dP_se	(*172–174, 177, 179, 184*)
$EtP(H)C_2H_4P(H)Et$	de_se	
$(C_6H_{11})P(H)C_4H_8P(H)(C_6H_{11})$	dCy_sb	

C. DIPRIMARY PHOSPHINES

Compound	Abbrev.	Ref.
$H_2PC_2H_4PH_2$	dHe	(*204*)

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