COMPLEXES OF THE TRANSITION METALS WITH PHOSPHINES, ARSINES, AND STIBINES

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I. *Introduction**

Just over a century ago Hofmann (*263*) prepared complexes of platinum and gold containing triethyl-phosphine, -arsine, and -stibine. In 1870

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* Abbreviations used: X = Cl, Br, I (or sometimes other anions); M = metal; E = P, As, or Sb; R = alkyl or aryl; L = neutral ligand; dias = *o*-phenylenebisdimethyl-arsine; diphosphine = ditertiary phosphine; am = amine; en = ethylenediamine; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; All = allyl; Am = amyl; Cy = cyclohexyl; Bz = benzyl; Ph = phenyl.

Cahours and Gal (*60–62*) reported complexes of palladium, platinum, and gold with tertiary phosphines and arsines, which may be correctly formulated from their analyses. This was the start of a field of chemistry which has since expanded enormously, especially during the last decade. Complexes have now been prepared from salts of most transition metals and many other types of complex (e.g., derivatives of metal carbonyls) have also been obtained.

Tertiary phosphines, arsines, and stibines show many properties as ligands which distinguish them from amines. They have a marked tendency to form nonionic complexes readily soluble in organic solvents, in contrast to the saltlike complexes formed by ammonia and amines. The relative coordinating affinities of ligand atoms from Group V have been considered by Ahrland and associates (*9*). A modified form of their classification of the transition elements is given in Fig. 1. To the right of the dividing line we have elements of class (b), which in their normal oxidation states form complexes in which the coordinating affinities of the donor atom lie in the sequence $N < P > As > Sb > Bi$. All these metals form stable phosphine complexes, and some form somewhat less stable arsine complexes and much less stable stibine complexes. To the left are the elements of class (a) character, where the sequence tends to change to $N > P > As > Sb > Bi$. The boundary is, however, not a sharp one and this classification is necessarily approximate. More definite is the tendency to form the most stable phosphine complexes along the diagonal toward platinum and gold.

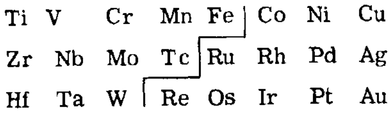


FIG. 1. Classification of the transition elements.

Quantitative work in support of the above classification is difficult but nevertheless requires extension. One comparison shows the affinities of a set of ligands toward Ag(I) ions to be in the order phosphine > arsine > amine (*10*). It is relevant also that the ligand field strength of tripropylphosphine is higher than that of tripropylamine or piperidine in a series of Pt(II) complexes (*80*).

The fact that stable phosphine complexes are derived mainly from salts of elements to the right of the transition series is due to the character of the ligand. Phosphines act as σ-bond donors and π-bond acceptors, the vacant $3d$ orbitals of the phosphorus being capable of interaction with filled nonbonding d orbitals of a transition metal. In many cases the acceptor character may be at least as important as the donor character. For example, stable complexes may be obtained from PF_3, where much reduced donor properties are more than compensated by the increased electron affinity of the vacant *d* orbitals of the phosphorus. Because of the extent of the π-bonding, PF_3 shows even greater similarity to carbon monoxide than the tertiary phosphines as ligands (*131*). The high ligand-field strength of tertiary phosphines ensures a large energy difference between the low energy and high energy *d* orbitals of the metal. Generally the most stable complexes are those in which the metal has its low energy orbitals completely occupied by electrons, and its high energy orbitals vacant. Further, the energy difference should be sufficient to prohibit promotion of electrons from the low energy to the high energy orbitals.

Group IV (d^0) and Group V (d^1) elements can have little or no ligand-field stabilization energy, and the ligand-metal bonds have almost entirely σ character. Coordination with elements such as these, having empty non-bonding *d* orbitals, will therefore depend more upon the basicity of the ligand, and until recently it was thought that ligands more electronegative than those with Group VB ligand atoms were necessary. It has now been found that in many instances complex formation takes place, provided that a reaction medium with minimum donor capacity is used. This is an important observation to be remembered in any attempted preparation of complexes.

The stabilizing effect of phosphine ligands has been utilized in the preparation of a wide range of stable hydrido- and organometallic compounds where, due to the high ligand-field strengths of hydrogen and organic groups (*93*), the ligand-field stabilization energy is even further enhanced. Another application, particularly marked when using chelating diphosphine or diarsine ligands, lies in the stabilization of a large number of oxidation states for many transition metals. With the lower oxidation states the reducing properties of the ligands are an advantage, but in higher oxidation states of the metals any tendency toward dissociation will result in decomposition, since such complexes contain both an oxidizing and a reducing agent. Stable phosphine complexes have been used in kinetic studies (*36*), which are required to test current theories on reaction mechanisms of metal complexes and on metal-ligand bonding. This important question of the nature of the metal-ligand bond has also been studied in various other ways involving the examination of complexes having phosphine or arsine ligands.

All the above functions of the ligands will be evident from the present survey in which the transition metals are considered according to their position in the Periodic Table.

II. Group IV

A. Titanium

Titanous salts do not readily form complexes with phosphines and arsines due to the high polarizing power of Ti(III). The complexes [$TiCl_3(Et_2PC_2H_4PEt_2)$] (*97*) and [TiX_3 · dias · H_2O] (X = Cl, Br; dias = *o*-phenylenebisdimethyl-arsine) (*421*) have been described, although it has been suggested (*138*) that the last are in fact complexes of Ti(IV).

Complexes of Ti(IV) are somewhat more stable, but nevertheless are decomposed by air or water. With monodentate ligands, the red complexes [$TiCl_4(PR_3)_2$] (R = Et or Ph) (*97*) and [$TiCl_3MePPh_3$] (*38*) have been prepared. Investigation of further complexes of the latter type, with determination of their configuration, would be of considerable interest. Using the bidentate ligands tertiary diarsine or diphosphine, the complexes [TiX_4dias] (*138*, *139*) and [$TiCl_4$(diphosphine)] (*97*) are readily prepared in an inert solvent. The 1:1 dias complexes react with further ligand to form [TiX_4(dias)$_2$]. A preliminary report on the crystal structure of [$TiCl_4$(dias)$_2$] shows it to be an eight-coordinate dodecahedral complex with the atoms forming two interpenetrating tetrahedra (*138*). This is the first example of a coordination number eight for a first-row transition element.

Attempted preparation of a complex of Ti(0) by reduction of [$TiCl_4$-($Me_2PC_2H_4PMe_2$)] in the presence of excess of the diphosphine was unsuccessful (*125*).

B. Zirconium and Hafnium

$ZrCl_4$ and $HfCl_4$ complex with dias in acetone medium to give [$ZrCl_4$-(dias)$_2$] and [$HfCl_4$(dias)$_2$], both isostructural with the titanium analogue (*138*, *139*).

The scarcity of complexes of Group IV metals with monophosphine or monoarsine ligands may not be significant, since preparative conditions, particularly in respect to reaction medium, are obviously extremely critical.

III. Group V

Very little work has been published on vanadium halide complexes, presumably due to difficulties in preparing characterizable products. Issleib and Bohn (*275*) report that triphenyl-phosphine coordinates with VCl_3 to give compounds of varying atomic ratios, possibly including the dimeric [VCl_3PPh_3]$_2$. Triethyl- and tripropyl-phosphines, on the other hand, form the red complexes [$VCl_3(PR_3)_2$], which have a magnetic moment corresponding to two unpaired spins. In carbon tetrachloride solution, dias coordinates with VCl_4 to give the orange complex $[VCl_4(dias)_2]$. A magnetic moment of 1.8 B.M. is in keeping with this formulation, and the complex has been shown to be isostructural with the analogous complexes of Group IV metals (*138, 139*).

Several interesting complexes of V(0) have recently been reported. Vanadium hexacarbonyl reacts with triphenyl-phosphine to give the orange complex $[V(CO)_4(PPh_3)_2]$, which like the parent carbonyl is paramagnetic (μ = 1.78 B.M.) (*253, 442*). This complex is unstable in air; the analogous arsine and stibine complexes are even less stable and are pyrophoric. When the reaction of triphenyl-phosphine is carried out in ether the product is $[V(Et_2O)_6][V(CO)_5PPh_3]_2$ (*253*). Reduction of $[V(CO)_4(PPh_3)_2]$ with sodium amalgam gives not the expected $[V(CO)_4(PPh_3)_2]^-$, but the $[V(CO)_5PPh_3]^-$ anion. This redistribution of ligands is assumed to be due to steric factors. Nitric oxide displaces one triphenyl-phosphine molecule from $[V(CO)_4(PPh_3)_2]$ to give the diamagnetic $[V(CO)_4(NO)PPh_3]$ (*443*). This reaction suggests that the four carbonyls exist as a stable planar entity with the other two ligands in *trans* positions. The simplicity of the infrared spectra of the two complexes also supports this configuration.

The complex $[V(Me_2PC_2H_4PMe_2)_3]$ is prepared by reduction of VCl_3 in the presence of the diphosphine (*123, 125*). A magnetic moment corresponding to one unpaired electron confirms the analogy to $[V(CO)_6]$.

No complexes of niobium and tantalum are known.

IV. Group VI

A. CHROMIUM

1. *Halide Complexes*

Chromous chloride with trialkyl-phosphines gives complexes of the type $[CrCl_2PR_3]$. Issleib and Fröhlich (*279*) suggest that the triethyl-phosphine complex is polymeric and that the unstable complex $[CrCl_2(PEt_3)_2]$ is first formed in solution. Complexes of methyl-phosphine and dimethyl-phosphine are less stable than those of trimethyl-phosphine (*44*).

Chromic chloride with trialkyl-phosphines forms the dimeric chloro-bridged complexes $[CrCl_3(PR_3)_2]_2$. Triphenyl-phosphine or tricyclohexyl-phosphine does not react with chromic chloride in a solvent, but by using the molten phosphine the violet complexes $[CrCl_3PR_3]$ are obtained (*279*). With diethyl-phosphine the monomeric octahedral complex $[CrCl_3(PHEt_2)_3]$ is formed (*278*). Similarly, phenyl-phosphine forms $[CrCl_3(PH_2Ph)_3]$ (*287*) although, in contrast, diphenyl-phosphine gives no complex with chromic chloride (*286*).

Reaction of trialkyl-phosphines with $K_3[Cr(SCN)_6]$ produces $[R_3PH]$-

$[Cr(SCN)_4(PR_3)_2]$, analogous to Reinecke's salt obtained with ammonia (*284*).

With the bidentate ligand dias, no chromous complexes have been isolated (*59, 385*). Chromic halides readily form the complexes $[CrX_2(dias)_2]$-$[CrX_4dias]$ in nonaqueous solvent, and solvated monomeric complexes are also known, e.g., $[CrCl_3(dias)H_2O]$ (*385*).

Chromic chloride is reduced, by sodium naphthalenide in tetrahydrofuran in the presence of tetramethylethane-diphosphine, to give the zero-valent complex $[Cr(Me_2PC_2H_4PMe_2)_3]$ (*123, 125*).

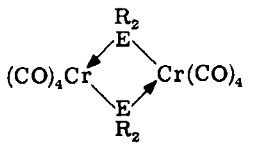
2. Carbonyl Complexes

Chromium hexacarbonyl, on heating at reflux in diglyme with triphenyl-phosphine, -arsine, or-stibine, forms a monosubstituted complex $[Cr(CO)_5(EPh_3)]$ (*339*). Some disubstitution also takes place (*311*), but $[Cr(CO)_4(PPh_3)_2]$ is best formed directly at 140–160° in a sealed tube (*252*) or via $[Cr(CO)_5NH_3]$ under milder conditions (*42*). A single strong carbonyl absorption in the infrared spectrum of the disubstituted derivative suggests the phosphines to be in *trans* positions. The complex $[Cr(CO)_4(PEt_2Ph)_2]$ (*124*), however, has a *cis*-phosphorus configuration as indicated by a dipole moment of ca. 6 Debye units, although there is evidence of some isomerization in solution.

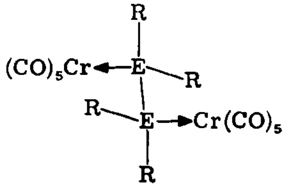
Suitable intermediates for the preparation of trisubstituted derivatives are complexes of the type $[Cr(\pi\text{-toluene})(CO)_3]$, from which $[Cr(CO)_3(AsMe_2Ph)_3]$ is readily obtained (*361*). A mixture of products is obtained by partial displacement of the ammonia from $[Cr(CO)_3(NH_3)_3]$ by triphenylphosphine (*227*).

With the chelating ligands dias (*280, 282*) and ditertiary phosphines (*95*), replacement of two carbonyl groups to give $[Cr(CO)_4(chelate)]$ is effected at ca. 150°. Under more vigorous conditions (200–240°) four carbonyl groups are expelled, resulting in formation of $[Cr(CO)_2(chelate)_2]$. The complexes $[Cr(CO)_2(diphosphine)_2]$ are more readily prepared from π-mesitylene chromium tricarbonyl and exhibit *cis-trans* isomerism. Zingales and Canziani (*459*) report that $[Cr_2(CO)_6(Ph_2PC_2H_4PPh_2)_3]$ is also formed in a reaction of this type.

The diphosphines and diarsines, $R_2E\cdot ER_2$ ($E = P$ or As, $R =$ alkyl or aryl), form two products on reaction with chromium hexacarbonyl. High temperatures (240–260°) favor the formation of highly colored (orange to red) phosphido- and arsenido-bridged carbonyls of structure (I); metal-metal bonding is probable since the complexes are diamagnetic. Less vigorous conditions often result in the formation of complexes of structure (II), which in contrast are weakly colored (*115*).



(I)



(II)

B. Molybdenum and Tungsten

Due to the polymeric and consequently unreactive nature of molybdenum and tungsten halides, halide complexes are not readily prepared. The complexes $[Mo^{II}X_2(dias)_2]$ have been obtained, starting from $[Mo^{III}Cl_6]^{3-}$, and are isomorphous with the corresponding iron, technetium, and rhenium complexes (*304*).

It may be mentioned here that uranium tetrachloride and tetrabromide readily form complexes of the type $[UX_4(PEt_3)_2]$ (*12*).

Carbonyl complexes are formed in a similar way to those of chromium, but they are generally more stable. Examples of mono-, di-, and trisubstituted derivatives have been prepared (see Table I). *Cis*- and *trans*-$[Mo(CO)_4(PEt_3)_2]$ have been isolated and characterized by their infrared spectra (*398*); $[W(CO)_4(PEt_3)_2]$ is more prone to isomerization, but a preliminary crystallographic study of the *trans* complex confirms the octahedral configuration (*265*). Trisubstituted derivatives of the type *cis*-$[Mo(CO)_3(PR_3)_3]$ have been prepared by direct substitution (*399*), and a general method of preparation for the complexes $[Mo(CO)_3L_3]$ is by treatment of $[Mo(CO)_3(cycloheptatriene)]$ with the phosphine, arsine, or stibine ligand (*1*). Another precursor which has been used is $[Mo_2(CO)_6(OH)_3H_3]$ (*234*).

The complexes $[M(CO)_4(chelate)]$ and $[M(CO)_2(chelate)_2]$, where M = Mo or W, and chelate = dias (*362*, *364*), $Ph_2AsC_2H_4AsPh_2$ (*460*), or ditertiary phosphine (*124*), are similar to their chromium analogues, but the bisdiphosphine complexes differ by existing only in the *cis* form. Again as with chromium, phosphido- and arsenido-bridged carbonyls (*115*) and diphosphine and diarsine binuclear derivatives may be obtained (*115*, *459*, *460*). The increasing difficulty found in replacing consecutive pairs of carbonyl groups by bidentate ligands and the tendency to form binuclear complexes under certain conditions are due to the increased strength of the metal-carbonyl bonds in the *trans* positions (*419*).

The action of halogens on the dias-molybdenum carbonyl complexes yields carbonyl halide derivatives (*365*). Of particular interest is the seven-

TABLE I
SUBSTITUTION PRODUCTS OF Cr, Mo, AND W CARBONYLS WITH MONODENTATE LIGANDS

Complex	Reference	Color	M.p. (°C)	Dipole moment (D)
$[Cr(CO)_5PPh_3]$	*339*	Pale yellow	127–128	—
$[Cr(CO)_5AsPh_3]$	*339*	Yellow	135	—
$[Cr(CO)_5SbPh_3]$	*339*	Yellow	147–149	—
$[Cr(CO)_5PBu_3]$	*311*	Chartreuse	Liquid	—
$[Mo(CO)_5PPh_3]$	*339*	White	138–139	—
$[Mo(CO)_5PEt_3]$	*398*	—	Liquid	—
$[Mo(CO)_5AsEt_3]$	*51*	—	Liquid	—
$[W(CO)_5PPh_3]$	*339*	Pale yellow	146–147	—
trans-$[Cr(CO)_4(PPh_3)_2]$	*252, 311*	Yellow	251–252	—
cis-$[Cr(CO)_4(PEt_2Ph)_2]$	*124*	Pale yellow	95	ca. 5.90
trans-$[Mo(CO)_4(PPh_3)_2]$	*252*	Yellow	273–275 d[a]	—
cis-$[Mo(CO)_4(PEt_2Ph)_2]$	*124*	Buff	99	6.95
cis-$[Mo(CO)_4(PEt_3)_2]$	*398*	White	73	—
trans-$[Mo(CO)_4(PEt_3)_2]$	*398*	Yellow	58	—
cis-$[Mo(CO)_4(AsEt_3)_2]$	*51*	Pale yellow	—	—
cis-$[Mo(CO)_4(AsPh_3)_2]$	*51*	Yellow	—	—
cis-$[W(CO)_4(PEt_3)_2]$ *trans*-$[W(CO)_4(PEt_3)_2]$	*265, 398*	—	—	—
cis-$[W(CO)_4(PEt_2Ph)_2]$	*124*	Pale yellow	104	7.25
trans-$[W(CO)_4(PPh_3)_2]$	*252*	Yellow	292–294 d	—
$[Cr(CO)_3(PPh_3)_3]$	*361*	—	175–177	—
$[Cr(CO)_3(AsMe_2Ph)_3]$	*361*	Yellow	98–100	—
cis-$[Mo(CO)_3(PPh_3)_3]$	*1*	Yellow	160 d	—
cis-$[Mo(CO)_3(AsPh_3)_3]$	*1*	Yellow	170 d	—
cis-$[Mo(CO)_3(SbPh_3)_3]$	*1*	Yellow	220 d	—
cis-$[Mo(CO)_3(PR_3)_3]$	*399*	—	—	—

[a] Symbol d = decomposed.

coordinate complex $[MoBr_2(CO)_3dias]$, which may be further oxidized to the Mo(IV) complex $[MoBr_4dias]$.

Although total substitution of Group VI carbonyls by direct action of phosphines or arsines cannot be effected, products of the formula [M(diphosphine)$_3$] have been obtained by other methods. For example, $[Mo(Me_2PC_2H_4PMe_2)_3]$ results from treatment of di-π-benzenemolybdenum with the diphosphine (*122*), and $[W(Me_2PC_2H_4PMe_2)_3]$ is prepared similarly to the chromium analogue (*123*, *125*).

Complexes of the chromium group thus provide excellent exemplification of the general trends of the A subgroups. That is to say: (1) the difference between first and second members is very much greater than between second and third; (2) on descending the series, compounds of the higher valency states are more stable; (3) on descending, the tendency to ionization of compounds of lower valency states is much smaller.

V. Group VII

A. MANGANESE

1. *Halide Complexes*

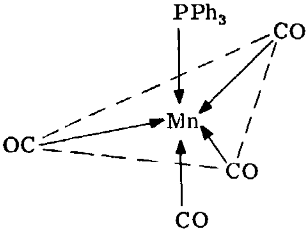
Most known complexes of manganese(II) have a polar metal-ligand bond involving ligands of high electronegativity. Phosphine and arsine complexes are therefore not expected to be very stable, particularly in the presence of donor solvents. There are many recorded examples of unsuccessful attempts to prepare complexes. The manganous ion does not coordinate with dias in water, alcohol, or acetone, although complexes are formed in dioxane (*59*, *386*). The magnetic moments of the octahedral products, $[MnX_2(dias)_2]$, show the presence of five unpaired electrons. Manganous halides complex with triphenyl-phosphine or -arsine in tetrahydrofuran to give $[MnX_2(EPh_3)_2]$, which are spin-free and presumably tetrahedral (*359*); MnI_2 also forms this type of product on reaction with molten triphenyl-phosphine. In acetone solution manganous halides form $[MnX_4][PPh_3H]_2$ and $[MnX_4][AsPh_4]_2$ (*360*).

Manganic salts are readily reduced by phosphines and arsines, but manganic acetate in the presence of perchloric acid and hydrogen chloride has been induced to form the spin-free complex $[MnCl_2(dias)H_2O]ClO_4$ (*386*).

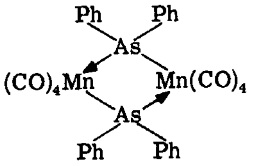
2. *Carbonyl Complexes*

Triphenyl-phosphine and dimanganese decacarbonyl react with expulsion of carbon monoxide and formation of $[Mn(CO)_4PPh_3]$ (*26*, *239*, *259*). This complex is monomeric and paramagnetic ($\mu_{eff} = 1.84$ B.M.) and infrared evidence suggests a trigonal bipyramid structure (III). Triethyl-phosphine and triphenyl-arsine and -stibine give analogous complexes (*239*), but at a slightly higher temperature (139° vs. 120°) triphenyl-arsine gives the very stable diamagnetic complex $[MnAsPh_2(CO)_4]_2$ with the probable bridged structure (IV) (*298*). Tricyclohexyl-phosphine is apparently the only ligand of this type giving the expected dimeric product, $[Mn(CO)_4PCy_3]_2$ (*236*). The phosphorus analogue of (IV) is obtained by reaction of diphenylchloro-phosphine with $Na[Mn(CO)_5]$ (*200*). Another product in the same class is $[Mn_2(CO)_8P(CF_3)_2I]$ (*175*) with phosphorus and iodine bridging atoms.

Dimanganese decacarbonyl and dias form $[Mn(CO)_3dias]_2$ at 130°, which on further heating splits to the monomeric [$Mn(CO)_3$dias] (*177*, *383*). The ditertiary phosphine $Ph_2PCH_2PPh_2$ behaves differently than dias, since the product is [$Mn_2(CO)_8(Ph_2PCH_2PPh_2)$] (*240*). This may mean that the diphosphine is not chelating; a comparison with other diphosphines would be of interest. The carbon monoxide of π-cyclopentadienylmanganese tricarbonyl may be displaced by triphenyl-phosphine (*420*).



(III)



(IV)

The complexes [$Mn(CO)_4PR_3$] are reduced by sodium in tetrahydrofuran to the carbonyl manganates (−1), Na[$Mn(CO)_4PR_3$]. These provide useful intermediates for the preparation of alkyl, acyl, and hydrido derivatives. For example, Na[$Mn(CO)_4PPh_3$] yields [$MnMe(CO)_4PPh_3$], [$Mn(COMe)(CO)_4PPh_3$], [$Mn(SnPh_3)(CO)_4PPh_3$], or [$MnH(CO)_4PPh_3$] on treatment with methyl iodide, acetyl chloride, triphenylstannic chloride, or phosphoric acid, respectively (*197*, *235*, *236*).

3. Carbonyl Halide Complexes

The carbonyl halides [$MnX(CO)_5$] and [$MnX(CO)_4$]$_2$ form complexes of the type [$MnX(CO)_3L_2$] (where L = PPh_3, $AsPh_3$, or $SbPh_3$) (*2*, *254*). Replacement with triphenyl-phosphine is more facile than with triphenylarsine or -stibine, even though there is little difference in double bonding due to the ligands, as judged by carbonyl frequencies (*260*). The monosubstituted products [$MnX(CO)_4L$] may be obtained (*13*, *230*) under different conditions. Complexes of the type [$MnCl(CO)_4PR_3$] are also formed by the action of carbon tetrachloride on [$MnH(CO)_4PR_3$] or by oxidation of [$Mn(CO)_4PR_3$] with chlorine (*236*). The dias-substituted carbonyls, mentioned earlier, are both oxidized with bromine to give [$MnBr_2(CO)_2$dias], but iodine behaves differently and a diamagnetic manganese(I) complex, [$MnI(CO)_3$dias], is produced (*383*). Complexes of the type [$MnX(CO)_3$chelate] (chelate = dias or diphosphine) may also be obtained directly (*390*).

4. Nitrosyl Complexes

Both $[Mn(CO)_4PPh_3]$ and $[MnI(CO)_4PPh_3]$ on treatment with nitric oxide yield the dark green $[Mn(NO)_3PPh_3]$ (*230*). An intermediate product of the reaction, $[Mn(CO)_3(NO)PPh_3]$, can also be isolated (*299*). The trinitrosyl complex may alternatively be prepared by the following scheme (*23*):

$$[MnI(CO)_5] \xrightarrow{NO} [Mn(NO)_3CO] \xrightarrow{PPh_3} [Mn(NO)_3PPh_3] \qquad (1)$$

Reduction of $[MnBr(NO)_2(PPh_3)_2]$ with sodium borohydride produces $[MnH(NO)_2(PPh_3)_2]$ (*257*).

B. TECHNETIUM

Due to the limited availability of compounds of this element, comparatively little complex chemistry has yet been investigated. Fergusson and Nyholm (*180, 181*), using remarkably small quantities of material, have prepared Tc(III) complexes, $[TcX_2(dias)_2]X$, which may be reversibly reduced to the Tc(II) complexes $[TcX_2(dias)_2]$ and oxidized to the Tc(V) complex $[TcCl_4(dias)]Cl$. The Tc(II) complexes differ from their manganese analogues in being spin-paired.

C. RHENIUM

1. Halide Complexes

Some confusion exists in the literature on this subject because of the failure to recognize oxygen in complexes obtained when using a perrhenate or rhenium heptoxide as starting material.

a. Re(II). The complexes formed by reacting together perrhenic acid, triphenyl-phosphine, hydrazine, and a hydrohalic acid were originally formulated $[ReX_2(PPh_3)_2]$ (*187*). They have since been reformulated as $[Re^VO(OEt)X_2(PPh_3)_2]$ (*103, 308*) or $[Re^VNX_2(PPh_3)_2]$ (*81, 82*), the constitution varying according to the precise reaction conditions. The so-called $[ReI_2(PPh_3)_2]$ further coordinates with isocyanides (*186*).

The complexes thought to be $[ReX_2(PPh_3)_2]$ have been reduced with $NaBH_4$ (any oxygen present originally may thus have been removed) to $[ReH_3(PPh_3)_2(EtOH)_2]$, which with triphenyl-phosphine yields $[ReH_3(PPh_3)_4]$ (*188, 320*).

Like their technetium analogues, the complexes $[ReX_2(dias)_2]$ are produced by reduction of $[ReX_2(dias)_2]X$ (*160*). Complexes of Re(II) with diphosphine (*103*) and tri- and tetra-arsine (*340*) ligands have also been described.

b. Re(III). Rhenium trihalides have been reported to coordinate with one, two, and three molecules of tertiary phosphine. $[ReCl_3PPh_3]$ (*147, 148, 187*) and $[ReCl_3(PEt_2Ph)]$ (*103*) are of uncertain structure. The supposed oxidation of $[ReX_2(PPh_3)_2]$ to $[ReX_3(PPh_3)_2]$ (*187*) is really the reaction:

$$[ReOX_2(OEt)(PPh_3)_2] \rightarrow [ReOX_3(PPh_3)_2] \qquad (2)$$

These rhenium(V) oxytrihalide complexes are also readily formed from perrhenic acid (*103, 308*). A further correction in this field lies in the formulation of the product from $[ReCl_3(PPh_3)]$ on treatment with triphenylphosphine and chlorine as $[ReCl_3(OPPh_3)_2]$ (*308*), and not $[ReCl_3(PPh_3)_2]$ (*147*). The complex $[ReCl_3PPh_3]$ reacts with acetylenes and olefins to give products of the type [ReCl(acetylene)$_2$PPh$_3$] (*146*).

The only six-coordinate Re(III) complex with monodentate ligands is $[ReCl_3(PEt_2Ph)_3]$ (*103*). Octahedral complexes of the types [ReCl$_2$(dias)$_2$]Cl (*179*) and [ReX$_2$(dias)$_2$](ClO$_4$) (*160*) are readily obtained and a five-coordinate complex [ReCl$_3$(dias)] has been mentioned (*380*).

c. Re(IV). Rhenium tetraiodide has given the paramagnetic derivative $[ReI_4(PPh_3)_2]$ (*147, 148*). Complexes of the type $[ReX_4(PPh_3)_2]$ (μ = 3.84 B.M.) are also obtained from $[ReH_3(PPh_3)_4]$ by treating with a halogen or a hydrohalide (*188, 320*).

d. Re(V). Complexes of the type $[ReOX_3(PPh_3)_2]$ have already been mentioned; the green isomer of $[ReOCl_3(PEt_2Ph)_2]$ has been shown to have a *trans* octahedral configuration (*174*). The dias-Re(III) complexes may be oxidized to Re(V) complexes (*179*), e.g.,

$$[ReCl_2(dias)_2]Cl \rightarrow [ReCl_4(dias)_2]ClO_4 \qquad (3)$$

Rhenium(V), in combination with tertiary phosphines as ligands, has a strong tendency to form multiple bonds to nitrogen. The formation of $[ReNX_2(PPh_3)_2]$ was described in Section V,C,*1*,*a*; tertiary phosphines containing aliphatic groups show a tendency to form six-coordinate rather than five-coordinate nitrides, e.g., $[ReNCl_2(PEt_2Ph)_3]$ (*81*). Related imido complexes of the type $[ReCl_3(NPh)(PEt_2Ph)_2]$ are obtained by the reaction of an arylamine on the complexes $[ReOX_3(PR_3)_2]$ (*81, 104*).

2. Carbonyl Complexes

Prolonged treatment of $[Re_2(CO)_{10}]$ with triphenyl-phosphine gives $[Re(CO)_4PPh_3]_2$ (*240*). Rhenium carbonyl halides give the complexes $[ReX(CO)_3L_2]$ (L = PPh$_3$, AsPh$_3$) (*2*) in the same way as the manganese compounds. One of these complexes had earlier been formulated as $[Re(CO)_4(PPh_3)_2]Cl$ (*255*), but this seems unlikely to be correct since the reported value of conductivity was very low. Carbonyl halide complexes have also been obtained by treatment of halide complexes with carbon monoxide under pressure. Even where the starting materials are incorrectly formulated, the reducing conditions (especially in the presence of copper) should eliminate any oxygen present, although there are a surprising number of products of different types. With increasingly vigorous conditions the so-called $[ReX_2(PR_3)_2]$ (X = Cl, Br) yields successively products formulated as $[ReX_2(CO)(PR_3)_2]$, $[ReX(CO)_2(PR_3)_2]$, and $[ReX(CO)_3(PR_3)_2]$. In contrast $[ReI_2(PPh_3)_2]$ forms $[ReI(CO)(PPh_3)_2]$ (*185*, *187*).

VI. Group VIIIA

A. IRON

1. *Halide Complexes*

a. Fe(II). Jensen (*291*) showed that ferrous chloride did not complex with PEt_3, in contrast to cobalt(II) and nickel(II) chlorides which readily coordinate, in ethanol solution. Complexes of the type $[FeX_2(PR_3)_2]$ have since been prepared, but they tend to dissociate in solution and are particularly unstable in hydroxylic solvents. The series of colorless complexes $[FeCl_2(phosphine)_2]$, where phosphine = PEt_3, PEt_2Ph, $PEtPh_2$, and PPh_3, prepared in benzene under nitrogen, have a spin-free tetrahedral configuration (μ_{eff} = ca. 5 B.M.), and the complexes containing the last two ligands are the most stable (*49*). A series of yellow complexes $[FeX_2(PPh_3)_2]$, prepared in ether or by fusion, may differ in having an octahedral bridged structure in the solid state (*357*).

The two known complexes of secondary phosphines with ferrous chloride provide an interesting contrast; $[FeCl_2(PHCy_2)_2]$ is colorless and tetrahedral like the tertiary phosphine complexes, but $[FeCl_2(PHEt_2)]$ is red and probably square-planar (*278*). Phenyl-phosphine forms the saltlike complexes $[Fe(PH_2Ph)_4]X_2$ (*287*).

Chelating bidentate ligands form diamagnetic complexes of the type $[FeX_2(dias)_2]$ (*363*, *370*) and $[FeCl_2(diphosphine)_2]$ (*96*) with a *trans* octahedral configuration. The structures of the complexes $[FeBr_2\{Cy_2P(CH_2)_n\text{-}PCy_2\}]$ (*280*) have not been defined.

b. Fe(III). Ferric chloride with methyldiphenyl- or dimethyltolylarsine gives complexes which dissociate so readily in solution that their constitution is not certain (*367*); $2FeCl_3 \cdot 4arsine$ may be formulated $[FeCl_3(arsine)_2]_2$ or $[FeCl_2(arsine)_4][FeCl_4]$. In ethyl acetate, triphenylphosphine and -arsine give complexes of probable formula $[FeCl_3(EPh_3)_2]_2$, but with triphenyl-phosphine and ferric chloride in methanol the solvent is involved in reaction to form $[PMePh_3][FeCl_4]$ (*358*). Tricyclohexylphosphine behaves rather differently in forming $[FeCl_3(PCy_3)]$ (*276*).

Complexes of the type $[FeX_2(chelate)_2][FeX_4]$ have been prepared, where chelate = dias (*370*) or a diphosphine (*96*). Ferric bromide also yields the complex $[FeBr_2(dias)]Br$. Polydentate tertiary arsine ligands give the complexes $[Fe(CNS)_3(triarsine)]$ (*21*) and $[FeCl_2(tetraarsine)][FeCl_4]$ (*20*).

c. Fe(IV). This unusual valency state is exemplified by the complex $[Fe^{IV}Cl_2(dias)_2][Fe^{III}Cl_4]_2$, prepared by oxidation of the ferric chloride-dias complex (*382*).

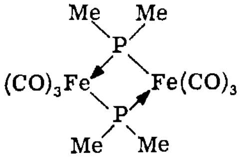
2. Carbonyl Complexes

Products of substitution from iron pentacarbonyl and triphenyl-phosphine and -stibine were first described by Reppe and Schweckendiek (*30, 403*), who mention $[Fe(CO)_4PPh_3]$ and $[Fe(CO)_3(PPh_3)_2]$ as potential catalysts. The infrared spectra of these two complexes are entirely compatible with a trigonal bipyramidal structure (*157*), and both complexes are protonated in sulfuric acid (*162*). Other disubstituted products include $[Fe(CO)_3(SbCl_3)_2]$ (*449*) and $[Fe(CO)_3dias]$ (*362, 363*). Direct substitution of more than two carbon monoxide molecules by monodentate phosphine, arsine, or stibine ligands is not known, although $[Fe(CO)(dias)_2]$ may be prepared by using vigorous conditions. The use of $[Fe_3(CO)_{12}]$ as starting material is preferred for the preparation of certain derivatives (*162*).

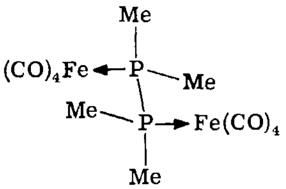
The trisubstituted derivative $[Fe(CO)_2(PPh_3)_3]$ is obtained, together with $[Fe(CO)_3(PPh_3)_2]$, on treatment of $[Fe(CO)_3(cycloheptatriene)]$ with triphenyl-phosphine (*337*). Other substituted carbonyl complexes include $[Fe(CO)_2\ PPh_3(tetracyclone)]$ (*438*), $[FeI(C_3F_7)(CO)_3PPh_3]$ (*397*), and hydrocarbon derivatives (*439*).

Pentaphenyl-phosphole(L) forms the two compounds $[Fe(CO)_4L]$ and $[Fe(CO)_3L]$ in which L behaves, respectively, as a monodentate phosphine or a bidentate diene ligand (*52*). Another diene-carbonyl complex, $[Fe(CO)_2(cyclopentadiene)PPh_3]$, illustrates the stabilizing influence of the phosphine ligand (*161*).

Tetramethyl-diphosphine can be reacted with iron pentacarbonyl to yield either a phosphido-bridged (V) or a diphosphine-bridged (VI) product



(V)



(VI)

(*115*). Tetraphenyl-diphosphine probably behaves similarly (*33*). There is an obvious parallel here with the reactions of Group VI metal carbonyls. The complex $[FeI(CO)_3P(CF_3)_2]_2$ (*175*) may have a structure similar to (V), with iodine occupying the sixth coordination position rather than the metal-metal bonding probable in (V).

3. *Carbonyl Halide Complexes*

The three possible ways of preparing carbonyl halide complexes of Fe(II) have all been effected (*49, 258, 363*):

$$[FeCl_2(CO)_4] \rightarrow [FeCl_2(CO)_2(PPh_3)_2] \tag{4}$$

$$[FeBr_2(CO)_4] \rightarrow [FeBr_2(CO)_2(AsPh_3)_2] \tag{5}$$

$$\begin{tikzcd} {[FeI_2(CO)_4]} \arrow[r] \arrow[dr] & {[FeI_2(CO)_2(SbPh_3)_2]} & (6) \\ {[Fe(CO)_3dias]} \arrow[r] & {[FeI_2(CO)_2dias]} & (7) \end{tikzcd}$$

$$[FeCl_2(PR_3)_2] \rightarrow [FeCl_2(CO)_2(PR_3)_2] \tag{8}$$

Treatment of $[Fe(CO)_3dias]$ with a limited quantity of iodine produces a complex of Fe(I), $[FeI(CO)_2dias]$ (*363*).

4. *Nitrosyl Complexes*

Although triphenyl-phosphine will displace both CO molecules from $[Fe(NO)_2(CO)_2]$ to form $[Fe(NO)_2(PPh_3)_2]$ (*402*), triphenyl-arsine and -stibine may form only monosubstitution products (*318, 341*). Iron nitrosyl halides react with triphenyl-phosphine, giving complexes of the type $[FeX(NO)_2PPh_3]$ (*248*).

5. *Other Complexes*

A study of iron complexes has provided three outstanding examples of the stabilizing effect of phosphine ligands.

The organometallic complex *trans*-$[Fe(C_6Cl_5)_2(PEt_2Ph)_2]$ (*112*) is moderately stable; it dissociates less readily to give the free phosphine than the corresponding halide complex $[FeCl_2(PEt_2Ph)_2]$. The stability of the hydrides *trans*-[FeHX(diphosphine)$_2$] and *trans*-[FeH$_2$(diphosphine)$_2$] (*89, 96*) is attributed to the large ligand-field splitting effects of the phosphine ligands and hydride ion. The only four-coordinate planar Fe(0) compound known is $[Fe(Me_2PC_2H_4PMe_2)_2]$ (*125*), prepared by reduction of *trans*-$[FeCl_2(Me_2PC_2H_4PMe_2)_2]$ with sodium naphthalenide ($NaC_{10}H_8$).

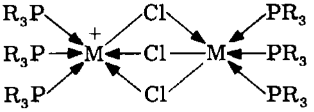
B. RUTHENIUM AND OSMIUM

1. *Complexes Derived from Halides*

Ruthenium(III) halides differ from ferric chloride in forming monomeric complexes with diphenylmethyl-arsine. These complexes, [RuX$_3$-

$(AsMePh_2)_3]$, are reduced with hypophosphorous acid to the Ru(II) complexes $[RuX_2(AsMePh_2)_4]$. Ruthenium(IV) halides are first reduced to Ru(III) by the same tertiary arsine (*166*). Similarly, K_2OsX_6 yields the Os(III) complexes $[OsX_3(arsine)_3]$, which may be reduced, for example, to $[OsCl_2(AsMePh_2)_4]$ (*172*).

From this earlier work with tertiary arsines it might be expected that similar simple octahedral complexes would be formed with tertiary phosphines. However, although products of this type have been prepared, e.g., $[OsCl_3(PEt_2Ph)_3]$ (*111*), complexes of the type $[M^{II}_2Cl_3(phosphine)_6]Cl$ (M = Ru or Os) of cation structure (VII) (*94*) are often obtained directly.



(VII)

Vaska and Sloane treated ruthenium and osmium halides with triphenylphosphine and -arsine in high boiling alcohols to obtain stable products, which were originally incorrectly formulated as $[RuCl(EPh_3)_3]$ (*434*) and $[OsX(EPh_3)_3]$ (*428*) (E = P or As). This proposed univalency for the metals was difficult to reconcile with the properties of the complexes, particularly their diamagnetism. The explanation was found by Chatt and Shaw, who showed that the alcohol was involved in the reactions and that "reductive carbonylation" was taking place with production of $[MHX(CO)(PPh_3)_3]$ (*111*). This has been confirmed by Vaska and Diluzio (*431*). Further examples of the involvement of an alcoholic solvent are provided by the preparation of $[RuHCl(CO)(PEt_2Ph)_3]$ (*110, 269*), $[RuCl_2(CO)(PEt_2Ph)_3]$ (*110*), and $[RuCl_2(CO)_2(PEt_2Ph)_2]$ (*111*) from $[Ru_2Cl_3(PEt_2Ph)_6]Cl$. Participation of alcohols in these reactions is obviously a subject for further work, especially since Vaska has now shown the wide variety of products obtainable from the interaction of ruthenium and osmium halides with triphenyl-phosphine, -arsine, and -stibine, depending upon the reaction conditions and the particular alcohol used (cf. Tables II and III).

No carbonylation has been observed in preparation of complexes containing chelating ligands. $[MX_2(dias)_2]$ where M = Ru (*387*) or Os (*388*) are stable complexes readily oxidized to $[MX_2(dias)_2]X$, having one unpaired spin. Further oxidation of the Os(III) complex yields $[OsX_2(dias)_2](ClO_4)_2$, but the corresponding Ru(IV) complex has not been obtained. α-Picolyldimethyl-arsine forms analogous Ru(II) and Ru(III) complexes (*196*), and the complexes $[RuX_2(tetraarsine)]$ have been described (*214*). The com-

TABLE II
RUTHENIUM COMPLEXES

Complex	Reference	Color	M.p. (°C)	Preparation
$[RuX_2(AsMePh_2)_4]$	*166*	—	—	$[RuX_3(AsMePh_2)_3] + H_3PO_2$
$[RuCl_2(CO)(PEt_2Ph)_3]$	*110*	Colorless	250 d	$[RuHCl(CO)(PEt_2Ph)_3] + HCl$
$[RuCl_2(CO)(AsPh_3)]_3$	*430*	Yellow	178 d	$RuCl_3 + AsPh_3 + MeOC_2H_4OH$ (124°)
$[RuCl_2(CO)_2(PEt_2Ph)_2]$	*111*	—	144–146	$[Ru_2Cl_3(PEt_2Ph)_6]Cl + C_3H_5OH + KOH$
$[RuCl_2(CO)_2(PEt_3)_2]$	*111*	—	104–110	$[Ru_2Cl_3(PEt_3)_6]Cl + C_3H_5OH + KOH$
$[RuI_2(CO)_2(AsMePh_2)_2]$	*272*	Orange-yellow	105	$[Ru(CO)_2I_2]_n + AsMePh_2$
$[RuI_2(CO)_2(PPh_3)_2]$	*246*	—	—	$[Ru(CO)_2I_2]_n + PPh_3$
$[RuHCl(CO)(PEt_2Ph)_3]$	*110*	Colorless	102–103	$[Ru_2Cl_3(PEt_2Ph)_6]Cl + C_2H_4OH + KOH$
$[RuHCl(CO)(PPh_3)_3]$	*111, 431*	—	—	$RuCl_3 + PPh_3 + MeOC_2H_4OH$ (124°)
$[RuX_3(AsMePh_2)_3]$	*166*	—	—	$RuX_3 + AsMePh_2$
$[RuCl_3(PPh_3)_2 \cdot MeOH]$	*430*	Green	140 d	$RuCl_3 + PPh_3 + MeOH$ (25°)
$[RuBr_3(AsPh_3) \cdot MeOH]$	*430*	Dark red	174 d	$(NH_4)_2RuBr_5 + AsPh_3 + MeOH$ (25°)
$[RuBr_3(CO)(PPh_3)_2]$	*430*	Red	204 d	$(NH_4)_2RuBr_5 + PPh_3 + MeOH$ (25°)

TABLE III
OSMIUM COMPLEXES

Complex	Reference	Color	M.p. (°C)	Preparation
$[OsBr_2(PPh_3)_3]$	*430*	Green	232 d	$(NH_4)_2OsBr_6 + PPh_3 + MeOC_2H_4OH$ (25°)
$[OsCl_2(AsMePh_2)_4]$	*172*	Yellow	113	$[OsCl_3(AsMePh_2)_3] + H_3PO_2$
$[OsBr_2(SbPh_3)_4]$	*430*	Orange	248 d	$(NH_4)_2OsBr_6 + SbPh_3 + MeOC_2H_4OH$ (124°)
$[OsHCl(CO)(PEt_2Ph)_3]$	*111*	—	—	$[OsCl_3(PEt_2Ph)_3] + EtOH + KOH$
$[OsHCl(CO)(PPh_3)_3]$	*431*	Colorless	—	$(NH_4)_2OsCl_6 + PPh_3 + MeOC_2H_4OH$ (120°)
$[OsHBr(CO)(PPh_3)_3]$	*430, 431*	White	276 d	$(NH_4)_2OsBr_6 + PPh_3 + MeOC_2H_4OH$ (120°) or EtOH (25°)
$[OsBr_3(AsMe_2Ph)_3]$	*172*	Red	163	$K_2OsBr_6 + AsMe_2Ph + HBr$
$[OsBr_3(AsMePh_2)_3]$	*172*	Red	205	$K_2OsBr_6 + AsMePh_2 + HBr$
$[OsCl_3(PEt_2Ph)_3]$	*111*	Red	210 d	$(NH_4)_2OsCl_6 + PEt_2Ph$
$[OsBr_3(AsPh_3)_3]$	*430*	Purple	270 d	$(NH_4)_2OsBr_6 + AsPh_3 + EtOH$ (25°)
$[OsBr_3(SbPh_3)_3]$	*430*	Purple	215 d	$(NH_4)_2OsBr_6 + SbPh_3 + MeOC_2H_4OH$ (25°)
$[OsCl_3(CO)(PPh_3)_2]$	*430*	Brown	235 d	$(NH_4)_2OsCl_6 + PPh_3 +$ triethylene glycol (270°)
$[OsBr_3(CO)(PPh_3)_2]$	*430*	Purple	230 d	$(NH_4)_2OsBr_6 + PPh_3 +$ triethylene glycol (270°)
$[OsBr_4(AsPh_3)_2]$	*430*	Purple	245 d	$(NH_4)_2OsBr_6 + AsPh_3 + MeOH$ (64°)

plexes [MCl_2(diphosphine)$_2$] have a *trans* configuration when prepared directly. The *cis* isomers (dipole moment = 8–11 D) are obtained by reaction of the diphosphine with the complexes [$M_2Cl_3(PR_3)_6$]Cl (*94*).

Hydrides of the types *trans*-[MHX(diphosphine)$_2$] and *trans*-[MH_2-(diphosphine)$_2$] are prepared by reduction of *cis*-[MX_2(diphosphine)$_2$] with $LiAlH_4$ (*92, 95*). The derivatives *trans*-[RuClR(diphosphine)$_2$] (R = alkyl or aryl) are obtained from the *trans*-dichloro complex by reaction with, for example, aluminum alkyls (*92*). The complexes [MHR(diphosphine)$_2$] are the first examples of compounds with both a hydrogen atom and an organic group attached to a transition metal by σ-bonds (*98*).

A study of the visible and ultraviolet spectra of the compounds *trans*-[RuXY(diphosphine)$_2$] (X = Y = Cl, Br, I, or CN; X = H, Me, Ph, and Y = Cl), thus available, showed that the ligand field strengths of hydrogen and the organic groups are large and of the same order as that of cyanide ion (*93*).

2. Complexes Derived from Carbonyls

Comparatively little work has been done on substitution reactions of ruthenium and osmium carbonyls or carbonyl halides. Polymeric ruthenium carbonyl iodide, [$RuI_2(CO)_2$]$_n$, reacts readily with $AsMePh_2$ (*272*), PCy_3, PPh_3, $AsPh_3$, and $SbPh_3$ (*245, 246*), forming [$RuI_2(CO)_2L_2$].

VII. Group VIIIB

A. COBALT

1. Halide Complexes with Monodentate Ligands

a. Co(II). Jensen (*291*) showed how readily cobalt(II) chloride and triethyl-phosphine, in alcoholic solution, form the blue complex [$CoCl_2(PEt_3)_2$]. A dipole moment of 8.7 D for this complex suggested that it had either a tetrahedral or a *cis*-planar structure, unlike the corresponding nickel complex which has a *trans*-planar structure. Many further complexes of the type [CoX_2(phosphine)$_2$] have since been prepared (see Table IV), and the magnetic moments of a representative selection show this class of compound to be tetrahedral. Square-planar d^7 complexes would have only one unpaired electron compared with three unpaired electrons associated with the metal of a tetrahedral d^7 complex. High actual values of about 4.5 B.M. are due to the considerable orbital contribution to the magnetic moment. Analogous tertiary arsine complexes are much less stable and only a few examples are known. [$CoI_2(AsPh_3)_2$] (*195*) is isomorphous with the corresponding nickel complex, and [$CoCl_2(AsEt_3)_2$] loses arsine to form [$CoCl_2(AsEt_3)$], a halogen-bridged dimer or polymer (*216*).

TABLE IV
Phosphine Complexes of Cobalt(II)

Complex	Reference	Color	M.p. (°C)	Magnetic moment (B.M.)	Dipole moment (D)
$[CoCl_2(PMe_3)_2]$	*50*	Green	(unstable)	—	—
$[CoCl_2(PEt_3)_2]$	*291*	Blue	101–102	4.39	8.7
$[CoBr_2(PEt_3)_2]$	*112*	Blue-green	134–136 d	4.76	—
$[CoI_2(PEt_3)_2]$	*49*	Green	128–135	4.74 (*216*)	—
$[CoCl_2(PPr^n_3)_2]$	*291*	Blue	ca. 80	—	—
$[CoCl_2(PBu^n_3)_2]$	*291*	Blue	oil	—	—
$[CoBr_2(PCy_3)_2]$	*153*	blue	199	4.61	—
$[CoI_2(PCy_3)_2]$	*153, 276*	Green	221–223 d	4.63	—
$[CoCl_2(PPh_3)_2]$	*54, 112*	Blue	247–251 d	4.3	—
$[CoBr_2(PPh_3)_2]$	*112*	Blue-green	234–239	4.57	7.6
$[CoI_2(PPh_3)_2]$	*54, 112*	Dark brown	209–214 d	4.6	9.6
	281	Green	—	4.4	8.08
$[Co(SCN)_2(PPh_3)_2]$	*156, 408*	Green	140	4.46	—
$[CoBr_2(PEt_2Ph)_2]$	*112*	Blue-green	80–82	4.5	—
$[CoI_2(PEt_2Ph)_2]$	*50*	Green	90–94	—	—
$[CoBr_2(PEtPh_2)_2]$	*112*	Green-blue	186–196 d	—	—
$[CoX_2(PMe_2C_6H_4NMe_2)_2]$	*66*	Blue	—	—	—
$[CoCl_2(PHEt_2)_4]$	*278*	Green	78–82 d	—	—
$[CoBr_2(PHEt_2)_4]$	*278*	Green	108–112 d	1.97	5.63
$[CoBr_2(PHCy_2)_2]$	*278*	Light blue	112–114 d	4.85	7.89
$[CoBr_2(PHPh_2)_3]$	*286*	Brown	163–165 d	2.01	—
$[CoCl_2(PH_2Et)_2]$	*215*	—	—	4.3	—
$[CoCl_2(PH_2Ph)_2]$	*287*	Black	—	—	—
$[CoBr_2(PH_2Ph)_2]$	*287*	Black	153–157	2.5	—
$[CoI_2(PH_2Ph)_4]$	*287*	Yellow	—	1.83	6.5

The tetraphenyl-diphosphine in the complex $[CoBr_2(Ph_2PPPh_2)_2]$ (*282*) may be behaving as a monodentate ligand, in which case the properties of the complex suggest a *cis*-planar structure. This unusual configuration could be due to peculiar steric conditions imposed by the ligand.

Tetrahedral anions of the type $[CoX_3PPh_3]^-$ are contained in complexes such as $[NEt_4][CoBr_3PPh_3]$ (*153*).

Primary and secondary phosphines behave differently than tertiary phosphines (as is often the case) and give different types of complex. $[CoX_2(PHEt_2)_4]$ (*278*) and $[CoBr_2(PHPh_2)_3]$ (*286*) both have magnetic moments corresponding to the one unpaired electron expected from their formulation. The black complexes $[CoX_2(PH_2Ph)_2]$ (X = Cl, Br) (*287*) differ considerably in color from the four-coordinate tertiary phosphine complexes, and by virtue of a magnetic moment of 2.5 B.M. have been assigned a planar structure. Phenyl-phosphine behaves differently with

CoI_2 and the product, $[CoI_2(PH_2Ph)_4]$, on further heating in ethanol is transformed into the phosphido compound $[CoI(PHPh)(PH_2Ph)_3]$.

b. Co(III). Although Jensen (cited in *447*) has briefly mentioned the complex $[CoCl_3(PEt_3)_2]$, there is apparently no other record of this type of complex. This is not unexpected, since Co(II) complexes with monodentate ligands are readily oxidized to the phosphine oxide complex rather than the Co(III) complex.

2. Reactions of Co(II) Complexes

Complexes of the type $[CoR_2(PEt_2Ph)_2]$ (R = *o*-substituted aryl, e.g., mesityl), obtained by reaction of the appropriate Grignard reagent with $[CoBr_2(PEt_2Ph)_2]$ (*106, 112*), have a *trans*-planar configuration (*393*) and are members of the series $[MR_2(phosphine)_2]$ where M = Fe, Co, Ni, Pd, or Pt.

Hydrido complexes of the type $[CoHX(phosphine)_2]$ would be expected to be extremely unstable. Their existence is, however, possible, since the system $[CoCl_2(PPh_3)_2]$–$NaBH_4$ has similar catalytic behavior in the polymerization of acetylene to an analogous system containing nickel which, in turn, is known to contain a metal-hydride species (*201*).

Reactions of halide complexes with carbon monoxide and nitric oxide are described below (subheadings *4* and *5*).

3. Complexes with Polydentate Ligands

a. Co(II) and Co(III). With bidentate ligands, at least four types of Co(II) complex are formed:

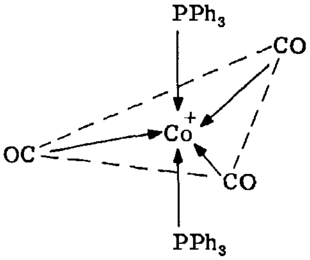
(1) $[CoX_2(chelate)_2]$, where chelate = dias (*374*) or a ditertiary phosphine (*90, 453*), are ionized in solution and tend to be hydrolyzed by water;
(2) $[CoX_2(chelate)]$, chelate = Cy_2PPCy_2 (*283*);
(3) $[Co(chelate)_2][CoX_4]$, chelate = dimethyl-*o*-methylthiophenylarsine (*133*);
(4) $[Co(dias)_3](ClO_4)_2$ (*59*).

In contrast to the monophosphine complexes, chelate complexes are readily oxidized to Co(III) complexes, e.g., $[CoX_2(dias)_2]X$ (*165, 374*). Tri- and tetradentate ligands also form stable Co(III) complexes, e.g., $[CoI_3(triarsine)]$ (*21*) and $[CoI_2(tetraarsine)]I$ (*20*).

b. Co(0). Several d^9 complexes of the type $[Co(diphosphine)_2]$ have recently been prepared; $[Co(Ph_2PC_2H_4PPh_2)_2]$ (*90*) and $[Co(Me_2PC_2H_4PMe_2)_2]$ (*125*) are obtained by reduction of halide complexes. They are isomorphous with the corresponding d^{10} Ni(0) complexes and thus have tetrahedral structures.

4. Carbonyl Complexes

Triphenyl-phosphine displaces carbon monoxide from dicobalt octacarbonyl; Reppe and Schweckendiek (*403*) first formulated the product as $[Co(CO)_3PPh_3]_2$, but Hieber (*256*) showed the compound to be ionic and it was later given the formula $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ (*238*, *406*). A trigonal bipyramidal structure (VIII) has been proposed for the cation (*436*). The nonionic, dimeric product can, however, be prepared in a nonpolar solvent (*238*). Both types of product have been prepared using other ligands, e.g., PEt_3 (*240*, *406*), $AsPh_3$, and $SbPh_3$ (*240*), but PCl_3 and PCl_2Ph did not give characterizable products (*405*). The salt $[Co(CO)_3(PPh_3)_2]$-$[Co(CO)_4]$ can be oxidized to $[Co(CO)_3(PPh_3)_2][CoCl_4]$ (*184*). The cation tricarbonylbis(triphenyl-phosphine)cobalt(I) is also produced by reacting $[CoI_2(PPh_3)_2]$ with carbon monoxide under vigorous conditions (*407*). In contrast, $[CoX_2(PEt)_2]$ reacts with carbon monoxide at atmospheric pressure to form $[CoX_2(CO)(PEt_3)_2]$ (*49*).



(VIII)

Tetracarbonyl cobaltates of mercury, and other metals, also lose carbon monoxide on treatment with triphenyl-phosphine and similar ligands with formation, for example, of $Hg[Co(CO)_3PPh_3]_2$ (*231–233*).

It has recently been shown that the anion $[Co(CO)_3PPh_3]^-$ is halogenated, using *N*-bromosuccinimide or trifluoromethyl iodide, to give Co(I) derivatives $[CoX(CO)_3PPh_3]$ (X = Br, I). Phenylation of the bromide gives the stable $[CoPh(CO)_3PPh_3]$ (*250*).

Heck and Breslow (*222–225*), in their work on reactions of cobalt carbonyl and its substitution products, have prepared stable triphenylphosphine complexes, e.g., $[Co(COMe)(CO)_3PPh_3]$, from unstable alkyl and acyl cobalt carbonyl derivatives. Hieber and Lindner (*229*, *249*, *251*) have prepared similarly stabilized derivatives and also $[CoH(CO)_3PPh_3]$, which decomposes at 20° compared with −20° for $[CoH(CO)_4]$.

There is a surprising lack of information concerning the action of polydentate ligands on dicobalt octacarbonyl. Tetraphenyl-diphosphine is reported to form the binuclear complex $[Ph_2PPPh_2\{Co(CO)_3\}_2]$ (*33*).

5. *Nitrosyl Complexes*

One carbon monoxide molecule is replaced from tricarbonyl-nitrosyl cobalt by triaryl-phosphine, -arsine, or -stibine with formation of $[Co(CO)_2(NO)L]$; with triphenyl-phosphine the disubstituted product $[Co(CO)(NO)(PPh_3)_2]$ can also be obtained (*318*, *402*). The trisubstituted derivative in this series, $[Co(NO)(PPh_3)_3]$, is obtained by reduction of $[CoCl(NO)_2]_2$ in the presence of the phosphine. Direct action of PPh_3 on the dinitrosyl cobalt halides splits the halogen bridge with formation of $[CoX(NO)_2PPh_3]$ (*241*, *243*). Another type of diamagnetic nitrosyl complex, which like the latter contains the metal with an inert-gas configuration, is $[CoX_2(NO)(PEt_3)_2]$, obtained by addition of NO to the phosphine-cobalt halide complex (*49*).

B. RHODIUM

1. *Halide Complexes*

Rhodium(III) halides with methyldiphenyl-arsine form the complexes $[RhX_3(AsMePh_2)_3]$ (*168*, *303*). In the presence of hypophosphorous acid these complexes are reduced to derivatives containing two halogens. These products were originally formulated as complexes of rhodium(II), $[RhX_2(AsMePh_2)_3]_2$ (*167*), but, when later found to be diamagnetic, were considered to be mixed salts of Rh(I) and Rh(III), e.g., $[Rh^{I}(AsMePh_2)_4][Rh^{III}Cl_4(AsMePh_2)_2]$ (*380*). More recent work has shown the presence of a metal hydride (ν_{Rh-H} ca. 2075 cm^{-1}) and the reduction products are correctly formulated $[RhHX_2(AsMePh_2)_3]$ (*303*). With dimethylphenyl-arsine, rhodium(III) halides, in the presence of hypophosphorous and hydrohalogen acids, are reported to form $[RhX_2(AsMe_2Ph)_4]$ (*169*). A further study of magnetic and other properties of these complexes is necessary for confirmation of their structure.

Tertiary phosphine complexes of the type $[RhX_3(\text{phosphine})_3]$ can be prepared and are particularly interesting in their reaction with alcohols, which forms carbonyl derivatives of Rh(I) (*110*, *111*, *269*):

$$[RhCl_3(PEt_3)_3] \xrightarrow[KOH]{EtOH} [RhCl(CO)(PEt_3)_2] \qquad (9)$$

and similarly

$$RhCl_3 + PPh_3 \xrightarrow[MeOC_2H_4OH]{} [RhCl(CO)(PPh_3)_2] \qquad (10)$$

This represents, of course, a further example of the "reductive carbonylation" reaction related to that described earlier for ruthenium and osmium (see Section VI,B,*1*).

The chelating diarsine reacts with rhodium(III) halides to form the salts $[RhX_2(dias)_2]X$ (*371*). With an alternative chelating ligand, dimethyl-*o*-methylthiophenyl-arsine (As-S), complexes with the same type of cation are obtained, $[RhX_2(As\text{-}S)_2][RhX_4(As\text{-}S)]$ (*135*). Analogous halide complexes containing tertiary diphosphines should be preparable but have not yet been described. A complex of unknown composition, but possibly a hydride, is obtained from rhodium metal and *o*-phenylenebisdiethylphosphine in the presence of hydrogen (*90*).

2. Carbonyl Complexes

The four-coordinate complexes $[RhX(CO)L_2]$ provide a striking example of the stabilization of the univalent state of the metal. This might have been anticipated to some extent, since the rhodium is isoelectronic with Pd(II) in, for example, such stable complexes as $[PdX_2L_2]$. Before their preparation by "reductive carbonylation" complexes of the type $[RhCl(CO)L_2]$ ($L = PPh_3, AsPh_3$) had been obtained from rhodium chlorocarbonyl. With triphenyl-stibine, Vallarino (*426*) obtained the analogous $[RhCl(CO)(SbPh_3)_2]$, although Hieber and co-workers (*245, 247*) report the preparation of a dicarbonyl, $[RhCl(CO)_2(SbPh_3)_3]$, by this reaction. These complexes are all diamagnetic (*237*) and the dipole moments of about 3 Debye units for the four-coordinate complexes suggest a *trans* arrangement of the tertiary phosphine or related ligands.

The complexes $[RhCl(CO)L_2]$ are remarkable for the difficulty with which Cl or CO is replaced or displaced by other ligands, although exchange with $C^{14}O$ and Cl^{36} anion occurs immeasurably quickly (*198*). Oxidation of the Rh(I) complexes with halogens produces the very stable Rh(III) complexes $[RhX_3(CO)L_2]$ ($X = Cl, I$) (*427*).

3. Nitrosyl Complexes

Dinitrosyl rhodium(I) chloride reacts with triphenyl-phosphine and related ligands to give $[Rh(NO)L_3]$ and $[RhCl_2(NO)L_2]$ (*242, 244*). Five-coordinate nitrosyl complexes of Co(II) analogous to the latter have been prepared, but not from $[CoCl(NO)_2]_2$.

4. Organic Complexes

Alkyl or aryl derivatives of rhodium stabilized by tertiary phosphine ligands are very difficult to prepare compared with those of other Group VIII metals. The aryl derivatives which have been prepared are typified by [$RhBr(1\text{-naphthyl})_2(PPr_3)_2$], obtained in very small yield from [$RhBr_3(PPr_3)_3$] (*116*).

Complexes of the type [$RhCl(diene)PPh_3$], where diene = cycloocta-1,5-diene (*121*) or norbornadiene (*43*), have been obtained from [$Rh_2Cl_2(diene)_2$] by a bridge-splitting reaction.

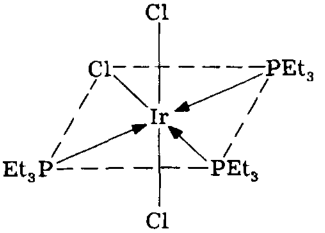
C. IRIDIUM

1. *Halide Complexes*

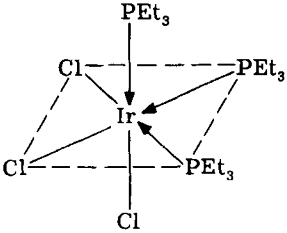
The Ir(III) complexes with tertiary arsines and phosphines are analogous to those of Rh(III). [$IrCl_3(AsMePh_2)_3$] (*171*) has been isolated in two isomeric forms and the complexes originally thought to be [$IrX_2(AsMePh_2)_3$]$_2$ (*170*) have been reformulated as hydrides, e.g., [$IrHBr_2(AsMePh_2)_3$] (*303*). The existence of complexes of the type [$IrBr_2(AsMe_2Ph)_4$] (*170*) has not been confirmed.

Dimethyl-*o*-methylthiophenyl-arsine with ammonium chloroiridate forms [$IrCl_3(As\text{-}S)_2$] (*135*), which is a seven-coordinate complex only if the ligand is fully chelated. The absence of information about iridium complexes with other chelating ligands is possibly indicative of difficulties in obtaining characterizable products.

The complexes [$IrX_3(phosphine)_3$] are readily prepared from chloroiridic acid and exist in two isomeric forms, e.g., structures (IX) and (X) (*79*).



(IX)



(X)

They react with alcohols to give hydride complexes and are presumably intermediate products in the reaction of various iridium halides with a tertiary phosphine and an alcohol to give hydride and carbonyl complexes. Compared with rhodium, many more types of products are obtained by the "alcohol reaction" mainly because of the increased stability of iridium hydride complexes.

2. *Hydride Complexes*

Three types of complex, [$IrHX_2(phosphine)_3$], [$IrH_2X(phosphine)_3$], and [$IrH_3(phosphine)_3$], have been prepared (*110, 111, 217, 429*):

$$[IrCl_3(PEt_3)_3] \xrightarrow{EtOH/KOH} [IrHCl_2(PEt_3)_3] \tag{11}$$

$$[IrCl_3(PEt_2Ph)_3] \longrightarrow [IrH_2Cl(PEt_2Ph)_3] \tag{12}$$

$$\begin{tikzcd}
(NH_4)_2IrCl_6 \arrow[r, "PPh_3", "aq.\ MeOC_2H_4OH\ 100^\circ"'] \arrow[dr, "C_2H_4(OH)_2 190^\circ"', "PPh_3"] & {[IrHCl_2(PPh_3)_3]} \arrow[r, "LiAlH_4"] & {[IrH_3(PPh_3)_3]} \arrow[dl, "HCl"'] \\
 & {[IrH_2Cl(PPh_3)_3]} &
\end{tikzcd} \tag{13}$$

These hydrides provide interesting cases of stereoisomerism which can be studied by several techniques (*3*). For example, two isomers of $[IrH_3(PPh_3)_3]$ were prepared by Malatesta and co-workers (*317*) by sodium borohydride reduction of $IrBr_3/PPh_3$. However, the properties of Hayter's product of this formula (*217*) (probably the isomer with *trans* hydrogens) are at some variance with those of either of Malatesta's compounds, so that a reliable comparison of isomers is at present difficult.

The trihydride is reported to form the dihydride $[IrH_2(PPh_3)_3]ClO_4$ on treatment with perchloric acid (*15*). The dihydride, $[IrH_2Cl(PPh_3)_3]$, is oxidized with chlorine to the Ir(IV) complex $[IrCl_4(PPh_3)_2]$ (*429*).

3. Carbonyl Complexes

Reactions of potassium tetraiododicarbonyl iridate(III) with triphenylphosphine and -arsine have given carbonyl complexes of Ir(I), (II), and (III), represented by $[IrI(CO)_2(PPh_3)_2]$, $[IrI_2(CO)(PPh_3)_2]$, $[IrI_3(CO)_2(AsPh_3)]$, and $[IrI_3(CO)(AsPh_3)_2]$ (*14*).

With iridium compounds it seems probable that carbonylation with alcohols proceeds via a hydride complex, since prolonged treatment of $IrCl_3$ with PPh_3 and an alcohol produces $[IrCl(CO)(PPh_3)_2]$. This complex is isomorphous with $[RhCl(CO)(PPh_3)_2]$ and has therefore a *trans*-square-planar configuration. Addition of chlorine or hydrogen chloride takes place with formation of $[IrCl_3(CO)(PPh_3)_2]$ and $[IrHCl_2(CO)(PPh_3)_2]$, respectively. The triphenyl-arsine analogue of this last complex may be obtained directly from the "alcohol reaction" (*432*).

A remarkable reaction, analogous to the addition of chlorine, is the formation of $[IrH_2Cl(CO)(PPh_3)_2]$ by the formal oxidation of $[IrCl(CO)(PPh_3)_2]$ with hydrogen(!) at atmospheric pressure and temperature (*433*). Vaska has also shown that $[IrCl(CO)(PPh_3)_2]$ adds oxygen to form $[IrO_2Cl(CO)(PPh_3)_2]$, and draws some analogy to these simple reactions with the chemisorption of hydrogen and oxygen on metals (*417*).

VIII. Group VIIIC

A. NICKEL

1. *Ni(II) Complexes*

a. Halide Complexes with Monodentate Ligands. Jensen (*290*) prepared the red to brown complexes $[NiX_2(PR_3)_2]$ (R = Et, *n*-Pr, *n*-Bu) and showed them to have a dipole moment of approximately zero. He therefore suggested a *trans*-square-planar configuration, which has since been confirmed by an X-ray examination of $[NiBr_2(PEt_3)_2]$ (*191*, *410*). The corresponding arsine and stibine complexes are much less stable and, of this class, only $[NiI_2(AsEt_3)_2]$ has been isolated. Nickel nitrate behaves differently than the halides, since the derived complex $[Ni(NO_3)_2(PEt_2)_2]$ is green and has a high dipole moment. Jensen suggested a *cis*-square-planar structure, but the magnetic moment of 3.1 B.M., later determined (*18*), led to suggestions of a tetrahedral configuration, although with a bidentate NO_3^- ligand an octahedral structure is possible (*17*). Preliminary X-ray examination of $[Ni(NO_3)_2(PEt_3)_2]$ favors a tetrahedral structure (*191*, *410*).

Triphenyl-phosphine does not complex quite so easily as the trialkyl-phosphines; Jensen (*290*) failed to obtain a product from reaction in ethanol, although other solvents, e.g., butanol (*454*) and acetic acid (*435*), have since been used successfully. Molten triphenyl-phosphine may alternatively be used (*266*). The complexes $[NiX_2(PPh_3)_2]$ are paramagnetic with magnetic moments corresponding to two unpaired electrons; the problem of their stereochemistry has only recently been resolved by an X-ray examination of $[NiCl_2(PPh_3)_2]$, showing it to be monomeric with a tetrahedral configuration (*435*). Other related complexes, e.g., $[NiX_2(PBuPh_2)_2]$ (*158*), are similarly paramagnetic and presumably tetrahedral in the solid state, although in these and other examples the reduced magnetic moments of solutions compared with solids suggest an equilibrium between diamagnetic and paramagnetic forms in solution. With special combinations of ligands, as for example in $[NiX_2(PBzPh_2)_2]$ (*55*) or $[NiBr_2(PEtPh_2)_2]$ (*220*), the two isomers (diamagnetic and paramagnetic) have actually been isolated. The reason for the formation of paramagnetic complexes must be associated with the force of the field generated by the ligands, and the formation of a tetrahedral, rather than an octahedral, complex is probably due mainly to the steric requirements of the particular combination of ligands involved. These factors have been fully discussed by Venanzi and co-workers (*55*).

Many other tertiary phosphines have given four-coordinate complexes (see Table V), but very few arsine complexes and no stibine complexes have been reported. Stable complexes are thus formed with ligands of

TABLE V
TERTIARY PHOSPHINE AND ARSINE COMPLEXES OF NICKEL(II)

Complex	Reference	Color	M.p. (or decomp.) (°C)	Magnetic moment (B.M.)	Dipole moment (D)	Remarks
$[NiX_2(PMe_3)_2]$	*40*	Red to brown	—	Diamag.	—	And X = SCN, NO_3
$[NiCl_2(PEt_3)_2]$	*290*	Dark red	112–113	Diamag. (*18*)	—	Spectra (*158*)
$[NiBr_2(PEt_3)_2]$	*290*	Dark red	106–107	—	~0	Spectra (*158*)
$[NiI_2(PEt_3)_2]$	*290*	Dark brown	91–92	—	—	Spectra (*158*)
$[Ni(SCN)_2(PEt_3)_2]$	*158*	Yellow	141–142	Diamag.	—	—
$[Ni(NO_2)_2(PEt_3)_2]$	*49*	Orange	163–169	—	1.5	—
$[Ni(NO_3)_2(PEt_3)_2]$	*290*	Green	131–132	3.1 (*18*)	8.85	Spectra (*17*, *189*)
$[NiI_2(AsEt_3)_2]$	*290*	Dark brown	54–55	—	—	—
$[NiCl_2(PPr_3{}^n)_2]$	*290*	Dark red	92–93	Diamag.	~0	—
$[NiX_2(PPr_3{}^i)_2]$	*192*	Red	—	—	—	UV spectra
$[NiCl_2(PBu_3{}^n)_2]$	*290*	Dark red	48–49	—	—	—
$[NiX_2(PBu_3{}^s)_2]$	*192*	Red	—	—	—	UV spectra
$[NiCl_2(PCy_3)_2]$	*424*, *425*	Red	227	Diamag.	0	—
$[NiBr_2(PCy_3)_2]$	*276*, *424*	Olive green	204 d	Diamag.	1.9	UV spectra
$[NiI_2(PCy_3)_2]$	*152*	Green	214	—	—	—
$[Ni(SCN)_2(PCy_3)_2]$	*424*	Orange-yellow	230	Diamag.	0	UV spectra
$[NiX_2(PBz_3)_2]$	*55*	—	—	Diamag.	1.35–3.7	—
$[NiCl_2(PPh_3)_2]$	*435*, *454*	Blue	247–250	3.07	—	—
$[NiBr_2(PPh_3)_2]$	*435*	Green	222–225	2.97	5.9	—
$[NiI_2(PPh_3)_2]$	*435*, *454*	Brown	225	2.92	8.5	—
$[Ni(SCN)_2(PPh_3)_2]$	*435*	Red	217–218	3.04	<3	—
$[Ni(NO_3)_2(PPh_3)_2]$	*435*	Green	224–227	3.04	—	—
$[NiX_2(PMe_2Ph)_2]$	*66*	Red	—	—	—	—

$[NiCl_2(PEt_2Ph)_2]$	*290*	Dark red	112–113	—	~0	—
$[NiBr_2(PEt_2Ph)_2]$	*109*	Dark red	114–116	—	—	—
$[Ni(NO_3)_2(PEt_2Ph)_2]$	*49*	Green	100–105	—	—	—
$[NiCl_2(PEtPh_2)_2]$	*220*	Dark red	146–151	Diamag.	3.2	—
$[NiBr_2(PEtPh_2)_2]$	*109, 220*	Dark green	173–175	3.2	5.9	—
		Brown (isomers)	160–175	Diamag.	—	—
$[NiI_2(PEtPh_2)_2]$	*220*	Brown-red	127–138	3.1	7.5	—
$[Ni(NO_3)_2(PEtPh_2)_2]$	*49*	Green	155–157	—	—	—
$[NiX_2(PBu_2Ph)_2]$	*158*	—	—	Diamag.	1.3–3.1	And X = NO_3, SCN
$[NiX_2(PBuPh_2)_2]$	*158*	—	—	ca. 3.3	3.3–6.8	And X = NO_3, SCN
$[NiX_2\{P(p\text{-anisyl})_3\}_2]$	*54*	Brown	—	ca. 3.25	7.4–9.2	And X = NO_3, SCN
$[NiX_2\{P(p\text{-tolyl})_3\}_2]$	*54*	Green	—	ca. 3.25	6.2–9.8	—
$[NiX_2\{AsMe_2(p\text{-}Me_2NC_6H_4)\}_2]$	*66*	Red	—	—	—	—
$[NiX_2\{PMe_2(p\text{-}Me_2NC_6H_4)\}_2]$	*66*	Red	—	—	—	—
$[NiBr_2\{P(CH_2Cl)_3\}_2]$	*158*	Red	158–159	Diamag.	1.5	—
$[NiI_2\{P(CH_2Cl)_3\}_2]$	*158*	Brown-black	125–126	Diamag.	—	—
$[NiX_2(PMe_2CF_3)_2]$	*40*	—	—	Diamag.	—	—
$[NiX_2(PAllPh_2)_2]$	*55*	—	—	—	—	—
$[NiX_2(PBz_2Ph)_2]$	*55*	—	—	Diamag.	1.7–3.2	—
$[NiX_2(PBzPh_2)_2]$	*55*	—	—	ca. 3	1.2–7.7	—

increased donor strength; this is further neatly demonstrated by a comparison of $AsMe_2Ph$ and $AsMe_2(p\text{-}Me_2NC_6H_4)$, where only the latter, with its increased availability of electrons on the arsenic atom, gave a stable complex (*66*).

Primary and secondary phosphines, as with halides of other metals, behave differently than tertiary phosphines. Phenyl-phosphine forms $[NiBr_2(PH_2Ph)_4]$ (*287*), and diethyl-phosphine similarly gives six-coordinate complexes, $[NiX_2(PHEt_2)_4]$ (*278*). However, dicyclohexyl-phosphine behaves "normally" to give $[NiBr_2(PHCy_2)_2]$ (*285*), and diphenyl-phosphine yields yet another type of product by reacting with nickel bromide to form the diphosphide $[Ni(PPh_2)_2(PHPh_2)_2]$ (*286*).

b. Halide Complexes with Polydentate Ligands. Nickel halides form complexes of the type $[NiX_2(\text{diphosphine})]$, where diphosphine = $Et_2PC_2H_4PEt_2$ (*453*), $Ph_2PC_2H_4PPh_2$, $Me_2PC_2H_4PMe_2$ (*50*), or $Cy_2P(CH_2)_3PCy_2$ (*280*), which are considered to have a *cis*-square-planar configuration. The structures of similarly formulated complexes derived from the diphosphines Cy_2PPCy_2 (*283*) or $Cy_2P(CH_2)_5PCy_2$ (*280*) are less certain. The diphosphines may also form 2:1, as well as 1:1, complexes, but dias differs in forming only 2:1 complexes with nickel halides (*372*). There is no doubt that this ligand is chelated in the complexes $[NiX_2(\text{dias})_2]$, although in other complexes of the type $[NiX_2L_2]$, where L is for example dimethyl-*o*-methylthiophenyl-arsine (*306*), Ph_2PPPh_2 (*282*), or $Ph_2PCH_2PPh_2$ (*50*), the ligand is probably behaving in a monodentate way. The complexes $[NiX_2(\text{dias})]$ may, however, be prepared from $[Ni(CO)_2\text{dias}]$ (*379*). This oxidation of Ni(0) complexes to Ni(II) complexes is a general one applied also to complexes of triphenyl-phosphine (*454*) and of *o*-phenylenebisdiethyl-phosphine (*86*). The complexes $[NiX_2(\text{dias})_2]$ (*210*) and the related $[NiX_2(\text{diphosphine})_2]$, although conducting in nitrobenzene solution, are probably fully covalent in the solid state.

The complex $[NiBr_2(\text{triarsine})]$ (*21, 22*) is of special interest as a five-coordinate derivative of nickel(II). An X-ray examination of this compound shows that the probable configuration is that of a distorted square pyramid (*314*). $[NiI_2(\text{tetraarsine})]$ (*20*) is a simple octahedral complex, assuming complete coordination.

c. Hydride and Organic Complexes. A very unstable hydride, possibly $[NiHCl(PPr_3)_2]$, has been shown to be present (NMR spectrum) in the system ($[NiCl_2(PPr_3)_2] + NaBH_4$) (*202*). Similar alkyl derivatives, e.g., $[NiClMe(PR_3)_2]$, and most aryl derivatives are also too unstable to be isolated in a pure condition. Nevertheless, stable aryl derivatives of the types $[NiXR(PR'_3)_2]$ and $[NiR_2(PR'_3)_2]$ (R = *o*-substituted aryl) have been prepared (*106, 109*). The complex $[NiIC_2F_5(Ph_2PC_2H_4PPh_2)]$, prepared by reacting $[Ni(CO)_2(Ph_2PC_2H_4PPh_2)]$ with perfluoroethyl iodide, provides a good example of the stabilization of metal-carbon σ-bonds through the influence of fluorine (*342*). The related acetylides $[Ni(C{\vdots}CR)_2(PR'_3)_2]$ are also stable, with $[Ni(C{\vdots}CPh)_2(PEt_2Ph)_3]$ providing an isolated example of a five-coordinate complex (*109*).

The π-allyl derivative of nickel, $[NiCl(\pi\text{-}C_3H_5)(PPh_3)]$, has recently been prepared by treatment of $[Ni(CO)_3PPh_3]$ with allyl chloride (*226*). Complexes of the type $[Ni(olefin)(PPh_3)_2]$ have been briefly described (*445*) and will doubtless be further investigated. A comparison with the analogous platinum complexes would be of considerable interest.

d. Cyanide Complexes. Complexes of nickel cyanide, since the CN^- anion is isoelectronic and isostructural with carbon monoxide, should resemble complexes of nickel carbonyl. They are thus of potential interest as catalysts, but, due mainly to difficulties of preparation, have been but little investigated (see Section VIII,A,*7*).

An unstable complex, thought to be $[Ni(CN)_2(PPh_3)_2]$ (*50*), was formed by reacting $Ni(CN)_2$ with molten triphenyl-phosphine; other complexes have been obtained by indirect methods:

(*24, 34*) $[NiCl_2(PPh_3)_2] + K_2Ni(CN)_4 \rightarrow [Ni_2(CN)_4(PPh_3)_2]$ (14)

(*350, 352*) $[Ni(CO)_2(PPh_3)_2] + C_2N_2 \rightarrow [Ni(CN)_2]_3PPh_3$ (15)

e. Complex Salts Containing Quaternary Phosphonium Ions. The early work of Reppe and Schweckendiek (*403*) with nickel halide–triphenylphosphine complexes as catalysts (see Section VIII,A,*7*) showed that the complexes $[NiX_2(PPh_3)_2]$ reacted with alkyl and aryl halides (RX') to form complexes of formulas $NiX_2(PPh_3)_2 \cdot RX'$ and $NiX_2(PPh_3)_2 \cdot 2RX'$.

It is only recently that the obviously correct formulations as $[PPh_3R][NiX_2X'PPh_3]$ and $[PPh_3R]_2[NiX_2X'_2]$ have been made (*152, 154*). Many complexes of these types (and with HX' in place of RX') have since been prepared, mainly for trial as catalysts, by the reactions:

(*151*) $[NiX_2(PPh_3)_2] + RX \rightarrow [PPh_3R][NiX_2X'PPh_3]$ (16)

(*267*) $NiX_2 + PPh_3 + PPh_3RX' \rightarrow [PPh_3R][NiX_2X'PPh_3]$ (17)

(*351*) $[NiX_2(PPh_3)_2] + ROH + X'_2 \rightarrow [PPh_3R][NiX_2X'PPh_3]$ (18)

(*151*) $[Ni(CO)_2(PPh_3)_2] + RX + ROH \rightarrow [PPh_3R][NiX_3PPh_3]$ (19)

(*28*) $Ni + PPh_3BuBr \rightarrow [PPh_3Bu][NiBr_3PPh_3]$ (20)

The four-coordinate anions contain tetrahedrally coordinated nickel, substantiated by magnetic moments ($\mu_{eff} = 3.4\text{–}3.9$) in a few cases. Table VI lists the known complexes, most of them necessarily reformulated.

In spite of showing that $NiBr_2(PPh_3)_2 \cdot BuBr$ and $NiBr_2(PPh_3)_2 \cdot 2PhBr$

TABLE VI

QUATERNARY PHOSPHONIUM SALTS OF NICKEL(II)

Complex	Reference	Color	M.p. (°C)	μ_{eff} (B.M.)
$[PPh_3Bu][NiCl_3(PPh_3)]$	*454*	Blue	176	—
$[PPh_3CH_2Ph][NiCl_3(PPh_3)]$	*28*	Green-blue	196	—
$[PPh_3Bu][NiCl_2Br(PPh_3)]$	*351, 403*	Blue-green	150	—
			171	—
$[PPh_3Bu][NiClBr_2(PPh_3)]$	*454*	Blue	167–168	—
$[PPh_4][NiClBr_2(PPh_3)]$	*454*	Green	203–205	—
$[PHPh_3][NiBr_3(PPh_3)]$	*267*	Green	178–180	—
$[PPh_3Et][NiBr_3(PPh_3)]$	*454*	Green	162	—
$[PPh_3Bu][NiBr_3(PPh_3)]$	*267, 403*	Green	177–178	—
$[PPh_3Bu^{iso}][NiBr_3(PPh_3)]$	*454*	Blue-green	167	—
$[PPh_3Bu^{tert}][NiBr_3(PPh_3)]$	*152*	Green	221	3.4 (*338*)
$[PPh_4][NiBr_3(PPh_3)]$	*454*	Green	210	—
$[PPh_3Et][NiBr_2I(PPh_3)]$	*454*	Violet-brown	160	—
$[PPh_3Bu][NiBr_2I(PPh_3)]$	*454*	Violet-brown	125	—
$[PPh_3Bu][NiBrI_2(PPh_3)]$	*353*	Green	217	—
$[PPh_3Bu][NiI_3(PPh_3)]$	*35, 267*	Blue	176	—
$[PEt_2Ph(1\text{-}C_{10}H_7)][NiBr_3(PEt_2Ph)]$	*109*	Blue	186–188	3.4
$[PPh_3Me]_2[NiCl_4]$	*194*	Blue	198	—
$[PPh_4]_2[NiCl_4]$	*454*	Blue	260	—
$[PPh_4]_2[NiCl_2Br_2]$	*454*	Blue	253–255	—
$[PHBu_3]_2[NiBr_4]$	*403*	—	117–118	—
$[PPh_4]_2[NiBr_4]$	*152, 403*	Blue	273	3.8 (*338*)
$[AsPh_3Me]_2[NiCl_4]$	*193*	Blue	—	3.89
$[AsPh_3Me]_2[NiI_4]$	*193*	Red	—	3.49
$[NEt_4][NiBr_3PPh_3]$	*152, 154*	Green	266	3.68
$[NBu_4][NiI_3PPh_3]$	*152, 154*	Red	132–135	3.46

had considerable molar conductivities in acetone and that the former gave PPh_3BuBr, and no PPh_3, on decomposition, Yamamoto and Oku (*458*) suggested fully covalent structures containing phosphorus(V).

2. Ni(III) Complexes

The red Ni(II) complex $[NiBr_2(PEt_3)_2]$ is readily oxidized with bromine to the black Ni(III) complex $[NiBr_3(PEt_3)_2]$ ($\mu_{eff} = 1.7$–1.9 B.M.) (*290, 292*). The structure of this five-coordinate complex is probably that of a tetragonal pyramid rather than a trigonal bipyramid, but the decisive X-ray analysis is difficult (*410*), due in part to the relative instability of the compound. The corresponding complexes with chelating ligands, $[NiBr_3(dias)]$ (*379*) and $[NiBr_3(diphosphine)]$ (*50, 453*), may well be octahedral polymers.

Much more stable complexes of Ni(III) are obtained by oxidation (air + HX) of [NiX_2(chelate)$_2$], chelate = dias (*373*) or $Me_2PC_2H_4PMe_2$ (*50*). The products, [NiX_2(chelate)$_2$]X, have magnetic moments corresponding to one unpaired electron for the metal.

3. Ni(IV) Complexes

Only one compound containing nickel(IV) has been isolated; the complex [$NiCl_2$(dias)$_2$]Cl is oxidized by nitric acid in the presence of perchloric acid to give [$NiCl_2$(dias)$_2$](ClO_4)$_2$ (*376*).

4. Nitrosyl Complexes

Blue nitrosyls of the type [Ni(OH)(NO)(MeOH)$_2$] have long been known. The first related complex containing phosphine ligands was [NiBr(NO)(PPh_3)$_2$], prepared by Feltham (*178*) by treatment of [$NiBr_2$(PPh_3)$_2$] with $NaNO_2$, possibly in an attempt to prepare the unknown [Ni(NO_2)$_2$(PPh_3)$_2$]. A series of analogous complexes, [NiX(NO)(PR_3)$_2$], has recently been prepared via reduction of [Ni(NO_3)$_2$(PR_3)$_2$] to [Ni(NO_3)(NO)(PR_3)$_2$] with carbon monoxide (*49*). The complexes [NiI(NO)($AsPh_3$)$_2$] and [NiI(NO)($SbPh_3$)$_2$] are obtained from [NiI(NO)]$_4$ (*228*), and [NiCl(NO)(PPh_3)$_2$] from [$NiCl_2$(NO)] (*8*). These four-coordinate nitrosyl complexes are deeply colored and possibly have a tetrahedral structure with the nickel atom, formally Ni(I), having the same electronic configuration as it has in Ni(0) complexes. Triphenyl-phosphine behaves differently than triphenyl-arsine and -stibine with [NiI(NO)]$_4$, since the product is the dimeric [NiI(NO)PPh_3]$_2$ (*228*).

The product obtained on treatment of [Ni(CO)$_2$(PPh_3)$_2$] with nitric oxide is claimed by Griffith *et al.* (*203*) to be [Ni(NO)$_2$(PPh_3)$_2$]. However, only one NO stretching frequency was observed and it is suggested here that an alternative product might be [Ni(NO_2)(NO)(PPh_3)$_2$], i.e., a member of the series [NiX(NO)(PR_3)$_2$]. This is, in fact, only one of the products which Feltham (as cited in *417*) claims to have isolated from this reaction.

5. Carbonyl Complexes

The carbon monoxide of nickel tetracarbonyl may be replaced in a stepwise manner by suitable ligands. Phosphines, arsines, and stibines normally replace one or two molecules of carbon monoxide to form [Ni(CO)$_3$L] and [Ni(CO)$_2$$L_2$] (see Table VII). Only [Ni(CO)(PMe_3)$_3$] (*45*) and possibly [Ni(CO)(PF_3)$_3$] (*131*) of the trisubstituted type have been described. The mono- and disubstituted types can be prepared by other methods, e.g.,

(*151*) $[NiBr_2(PPh_3)_2] + Ni(CO)_4 \rightarrow [Ni(CO)_2(PPh_3)_2]$ (21)
(*32*) $[ZnCl_2(PPh_3)_2] + Ni(CO)_4 \rightarrow [Ni(CO)_2(PPh_3)_2]$ (22)
(*455*) $[NiBr_2(PPh_3)_2] + CO \rightarrow [Ni(CO)_3PPh_3]$ (23)
(*354, 456*) $Ni + PPh_3 + CO \rightarrow [Ni(CO)_2(PPh_3)_2]$ (24)

Tri(β-cyanoethyl)-phosphine gives the disubstituted product $[Ni(CO)_2\{P(C_2H_4CN)_3\}_2]$ (*346*), but also behaves anomalously in forming $[Ni(CO)P(C_2H_4CN)_3]_n$ (*345*) containing bridging carbonyl groups.

Chelate ligands form the complexes $[Ni(CO)_2(chelate)]$, chelate = dias (*379*), other diarsines, and various diphosphines (*85, 199*), more stable than the dicarbonyl complexes with monodentate ligands.

TABLE VII
COMPLEXES OF THE TYPES $[Ni(CO)_3L]$ AND $[Ni(CO)_2L_2]$

Complex	Reference	Color	M.p. (°C)
$[Ni(CO)_2(PEt_3)_2]$	*46*	—	—
$[Ni(CO)_2(PBu_3)_2]$	*346, 403*	Orange	liq.
$[Ni(CO)_3PPh_3]$	*403, 454*	Colorless	123
$[Ni(CO)_2(PPh_3)_2]$	*403, 454*	Colorless	206–209
$[Ni(CO)_3P(p\text{-tolyl})_3]$	*354, 403*	—	158
$[Ni(CO)_3AsEt_3]$	*51*	Colorless	liq.
$[Ni(CO)_2(AsEt_3)_2]$	*51*	Yellow	liq.
$[Ni(CO)_3AsPh_3]$	*403*	—	105
$[Ni(CO)_3SbPh_3]$	*30, 403*	—	105–109
$[Ni(CO)_2(SbPh_3)_2]$	*29*	—	—
$[Ni(CO)_2PPh_3SbPh_3]$	*29*	—	—
$[Ni(CO)_2\{P(CF_3)_3\}_2]$	*56, 176*	—	−31
$[Ni(CO)_2\{P(C_2H_4CN)_3\}_2]$	*346*	White	140 d
$[Ni(CO)_3PCl_3]$	*346*	—	—
$[Ni(CO)_3SbCl_3]$	*449*	Buff	—

All these substitution products are assumed to have a tetrahedral configuration, like nickel carbonyl itself. Much has been written on the nature of the Ni—P or Ni—As bonds contained in the complexes. Infrared studies on $[Ni(CO)_2dias]$ and calculation of the stretching force constants showed the C—O bonds to be similar to those in $Ni(CO)_4$, and it was concluded that the structure involving Ni—C and Ni—As double bonds dominates (*384*). Comparison of the infrared spectra and dipole moments of a series of dicarbonyl derivatives showed that the P—Ni and As—Ni bonds in Ni(0) complexes have essentially the same bond order, estimated to lie between 1.4 and 1.7 (*86*). It is difficult to define the extent of double bonding from kinetic data, but Meriwether and Fiene (*346*) suggest that the bonds are primarily σ in character, with strong contributions from

π-bonding occurring only in complexes of phosphorus halides and phosphites. Finally, an attempt has been made to study the P—Ni bond by measuring the nuclear magnetic resonance spectra of P^{31}-phosphine complexes (*347*).

6. Complexes of Ni(0) Other Than Carbonyl Derivatives

By treatment of $Ni(CO)_4$ with PCl_3, Irvine and Wilkinson (*271*) prepared $[Ni(PCl_3)_4]$, the first example of a complex of Ni(0) containing four phosphorus donor atoms. Chatt (*131*) had suggested earlier the analogy between PF_3 and CO, but was unsuccessful in attempts to prepare $[Ni(PF_3)_4]$ from $Ni(CO)_4$. This phosphorus trifluoride complex and $[Ni(PBr_3)_4]$ (*416, 448*) may, however, be prepared from $[Ni(PCl_3)_4]$. Phenyldichloro-phosphine (*321*) and phosphorus triisocyanate and triisothiocyanate (*450*) replace all the carbon monoxide from $Ni(CO)_4$ in a similar way to PCl_3.

A further development in this field was the production of $[Ni(PCl_2Me)_4]$ from metallic nickel and the phosphine at reflux temperature (*400*). Methyldichloro-phosphine and methyldibromo-phosphine and -arsine (*312*) are thus the only monodentate ligands, apart from CO, known to form a Ni(0) complex directly from the metal. The aromatic diphosphines o-$C_6H_4(PEt_2)_2$ and $Ph_2PC_2H_4PPh_2$ behave similarly to PCl_2Me and form [Ni(diphosphine)$_2$] (*86*). This last type of complex may also be prepared from nickel carbonyl or by reduction of [NiX_2(diphosphine)$_2$] with, for example, sodium borohydride (*91*).

Monodentate organophosphines have not given fully substituted derivatives by these methods, but $[Ni(PEt_3)_4]$ has been prepared from bis-π-allylnickel (*444*); a method possibly capable of wider application.

All these Ni(0) complexes are considered to have tetrahedral structures; the Raman spectrum of $[Ni(PF_3)_4]$ is in accord with this (*452*). The points made about the nature of the P—Ni bond in the earlier discussion of substituted carbonyl complexes are relevant also to these Ni(0) complexes. It is clear that only ligands with increased double-bonding capacity (either by substitution with strongly electronegative atoms or groups or by the proximity of a suitable aromatic residue) are capable of directly forming "fully substituted" nickel derivatives. Other factors may also be important, for example, why PCl_3 and PCl_2Ph do not react with metallic nickel in the same way as PCl_2Me.

Bisacrylonitrile nickel, $[Ni(CH_2{=}CHCN)_2]$, prepared by Schrauzer (*411*) by interaction of nickel carbonyl and acrylonitrile, is a novel type of complex of Ni(0). It is coordinatively unsaturated and thus very unstable; further coordination with triphenyl-phosphine provides the derivatives $[Ni(CH_2{=}CHCN)_2PPh_3]$ and $[Ni(CH_2{=}CHCN)_2(PPh_3)_2]$ (*412, 413*). The latter is considerably more stable, possibly due to its ability to assume a tetrahedral configuration.

7. *Complexes of Nickel as Catalysts*

The catalytic properties of transition metal complexes containing phosphine, arsine, or stibine ligands are most marked when the metal is nickel. Reppe (*151*, *403*) studied the complexes, particularly those containing triphenyl-phosphine, of a large number of transition metals and invariably obtained the best results with nickel complexes. Later workers in the field of catalysis have, in consequence, usually restricted themselves to an examination of nickel complexes only.

a. Polymerization of Olefins. Ethylene, methylacrylate, vinyl acetate, and styrene are polymerized by using $[Ni(CO)_2(PPh_3)_2]$ as catalyst (*25*). With the same catalyst, butadiene is dimerized to cyclooctadiene (30–40%) and vinylcyclohex-1-ene (10%) (*402*); trimer (cyclododecatriene) may also be obtained when using alternative Ni(0) compounds (*446*).

b. Polymerization of Acetylenes. Acetylene itself is polymerized under suitable conditions (e.g., 100–120°/10 atm) to give mixtures of benzene and styrene when using the catalyst $[Ni(CO)_2(PPh_3)_2]$ (*348*, *403*, *456*), $[NiBr_3PPh_3][PPh_3Bu]$ (*29*), or $[Ni(CN)_2]_3PPh_3$ (*352*). When using more active catalyst systems, such as the unstable complexes $[NiHX(PR_3)_2]$ (*201*, *309*) or $[NiMe_2(PR_3)_2]$ (*50*), acetylene forms a brown-black linear polymer even at room temperature and pressure. Substituted acetylenes such as propargyl alcohol (*403*), phenylacetylene (*404*), and $(:CCH_2OR)_2$ (*190*) are trimerized when using the catalyst $[Ni(CO)_2(PPh_3)_2]$ or $[Ni(CO)_3PPh_3]$. Other catalysts used for the cyclic polymerization of acetylenes include $[Ni(PCl_3)_4]$ (*300*), $[Ni(CO)_2(Ph_2PC_2H_4PPh_2)]$ (*270*), and $[Ni(CH_2{=}CHCN)_2(PPh_3)_{1\text{ or }2}]$ (*414*).

c. Preparation of α,β-Unsaturated Carboxylic Acids. In the work concerned with the production of acrylic acid or its esters by the reaction,

$$C_2H_2 + CO + ROH \rightarrow CH_2 = CHCOOR \tag{25}$$

Reppe (cited in *151*) showed that phosphine complexes were more active catalysts than the nickel halides alone and, further, that the activity of complexes such as $[NiBr_2(PPh_3)_2]$ was enhanced by the presence of an alkyl halide. This led to a thorough study of complexes of the types $[NiBr_2(PPh_3)_2]$ (*268*, *349*), $[NiBr_3(PPh_3)][PPh_3Bu]$ (*27*, *457*) (see Section VIII,A,*1*,*e*), and $[Ni(CN)_2]_3PPh_3$ (*350*) as catalysts in the synthesis of unsaturated carboxylic acids and their derivatives.

d. Miscellaneous. Alcohols are carbonylated to give aliphatic carboxylic acids or their esters, using catalytic systems containing $[NiX_2(PPh_3)_2]$

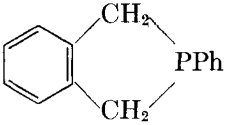
(*355*). Other catalytic applications of a number of complexes have been reported without specific exemplification.

B. PALLADIUM

1. *Halide Complexes*

a. Complexes with Monodentate Ligands. Tertiary phosphines, arsines, and stibines complex with palladium(II) salts to form the square-planar derivatives [PdX_2L_2] (see Table VIII). These derivatives are stable (the stibine complexes being least stable), readily crystallized, and of well-defined melting point. They have, in consequence, been used in many instances to characterize compounds of Group VB elements, particularly in the work of Mann and his co-workers (*37, 149, 150, 159, 221, 323, 324–326*). A *trans* arrangement of ligands with a consequent low dipole moment (measured value ca. 1 D) is invariably the case with the phosphine and arsine complexes, but solutions of the stibine complexes have been shown to contain up to 40% of the *cis* isomer in equilibrium and this less soluble isomer may separate from the solution (*129*). The ultraviolet spectra of certain simple complexes have been measured and shown to be affected by changes in constitution in the same way as related nickel complexes (*422*). Mixed complexes of the type [$PdX_2(PR_3)$(amine)] will be discussed below as products obtained from bridged complexes.

The vacant 5*p* orbital of the four-coordinate complexes is only rarely filled by further coordination. Complexes of the type [PdX_2L_3], where L = $AsMePh_2$ (*369*), $PMePh_2$ (*219*), PEt_2Ph (*50*), or



(*334*), may be d^8-dsp^3 complexes in the solid state. They readily dissociate to lose one molecule of ligand, L, but in the presence of excess ligand may ionize in solution to [$PdXL_3$]$^+X^-$.

b. Complexes with Polydentate Ligands. Chatt and Mann (*100*) prepared 1:1 and 2:1 complexes of the types [$PdCl_2$(diarsine)] and [$PdCl_2(\text{diarsine})_2$], from several ditertiary arsines. On mixing a palladium(II) salt and diarsine, the salt [$Pd(\text{diarsine})_2$][$PdCl_4$] is first formed, which breaks down on heating to the 1:1 complex, this latter coordinating with further diarsine to form the 2:1 complex. Analogous 1:1 complexes may also be obtained from [PdX_2en] by a ligand displacement reaction (*437*).

Further work on complexes of *o*-phenylenebisdimethyl-arsine(dias) (*208, 210, 211*) has shown that, although the complexes [$PdX_2(\text{dias})_2$] are

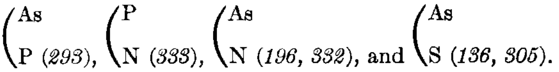
TABLE VIII

SIMPLE TERTIARY PHOSPHINE, ARSINE, AND STIBINE COMPLEXES OF PD(II) HALIDES

Complex	Reference	Color	M.p. (°C)
$[PdCl_2(PMe_3)_2]$	*335*	Yellow	282 d
$[PdCl_2(PEt_3)_2]$	*61, 327*	Yellow	139
$[PdBr_2(PEt_3)_2]$	*262*	Orange	132
$[PdI_2(PEt_3)_2]$	*50*	Orange	138
$[Pd(NO_3)_2(PEt_3)_2]$	*50*	Yellow	182 d
$[PdCl_2(PPr_3^n)_2]$	*327*	Yellow	96
$[PdBr_2(PPr_3^n)_2]$	*12*	Orange-yellow	88
$[PdX_2(PPr_3^i)_2]$	*422*	—	—
$[PdCl_2(PBu_3^n)_2]$	*327*	Yellow	66
$[PdBr_2(PBu_3^n)_2]$	*327*	Yellow	73
$[PdI_2(PBu_3^n)_2]$	*327*	Orange	65
$[Pd(NO_2)_2(PBu_3^n)_2]$	*70*	—	141–142
$[PdCl_2(PAm_3^n)_2]$	*327*	Yellow	47
$[PdCl_2(PEt_2Ph)_2]$	*50*	Yellow	138
$[PdBr_2(PEt_2Ph)_2]$	*262*	Orange	133
$[Pd(NO_3)_2(PEt_2Ph)_2]$	*50*	Yellow	174–176
$[PdCl_2(PBu_2Ph)_2]$	*100*	Orange	47
$[PdCl_2(PPh_3)_2]$	*100*	Yellow	270 d
$[PdCl_2(AsMe_3)_2]$	*327*	Pale yellow	235
$[PdBr_2(AsMe_3)_2]$	*335*	Orange	229
$[Pd(NO_2)_2(AsMe_3)_2]$	*335*	Lemon	234 d
$[Pd(SCN)_2(AsMe_3)_2]$	*335*	Yellow	124
$[PdCl_2(AsEt_3)_2]$	*62, 327*	Orange	116
$[Pd(NO_2)_2(AsEt_3)_2]$	*327*	—	—
$[PdCl_2(AsPr_3^n)_2]$	*327*	Orange	55
$[PdBr_2(AsPr_3^n)_2]$	*327*	—	49
$[PdCl_2(AsBu_3^n)_2]$	*327*	Orange	54
$[Pd(NO_2)_2(AsBu_3^n)_2]$	*70*	—	96
$[PdCl_2(AsAm_3^n)_2]$	*327*	Orange	10–11
$[PdCl_2(AsMe_2Ph)_2]$	*310*	Orange	170–173
$[PdBr_2(AsMePh_2)_2]$	*369*	Orange	178
$[PdI_2(AsMePh_2)_2]$	*307*	Brown-orange	—
$[PdCl_2(SbMe_3)_2]$	*129, 356*	—	150–165 d
$[PdCl_2(SbEt_3)_2]$	*288*	Yellow	90 d
$[PdCl_2(SbPr_3^n)_2]$	*129*	Yellow	66 d
$[PdCl_2(SbBu_3^n)_2]$	*129*	Yellow	65 d
$[PdCl_2(SbPh_3)_2]$	*129*	Yellow	140 d

conducting in nitrobenzene solution, they are six-coordinate in the solid state. The crystal structure of $[PdI_2(dias)_2]$ has been determined; the central metal atom is surrounded by four arsenic atoms in a square plane, and the two iodine atoms complete a distorted octahedral arrangement with elongated metal-iodine bonds.

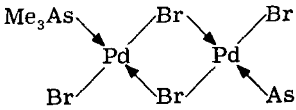
Complexes related to these diarsine complexes have been derived from many other chelating ligands, e.g., various ditertiary phosphines (*91*, *213*, *261*, *282*, *283*, *453*) and ligands containing two dissimilar donor atoms, which may be represented:



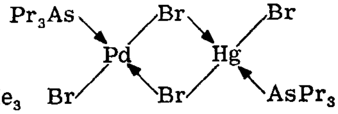
Complexes derived from tritertiary arsines and a tetratertiary arsine have been compared in order to study the factors influencing the coordination numbers in Pd(II) complexes (*409*).

2. Bridged Di-Palladium Derivatives

Treatment of a solution of the complex $[PdCl_2L_2]$ with ammonium chloro palladite results in the formation of a more deeply colored binuclear complex $[Pd_2Cl_4L_2]$ (*328*, *335*). Wells (*441*) has shown that $[Pd_2Br_4(AsMe_3)_2]$ has the *trans*-planar symmetrical structure (XI). The stibine complexes in this class are again the least stable (*119*). Chelate ligands do not form bridged complexes of this type (*100*). Bridged complexes containing a bridging nitro group (*70*) or oxalate radical (*101*), or with two different metal atoms, e.g., structure (XII) (*329*), may also be prepared.



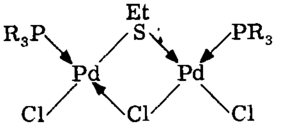
(XI)



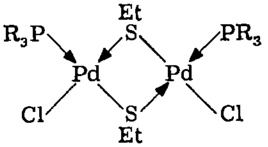
(XII)

When L is phosphine or arsine, the halogeno-bridged complexes react with monoamines (am) to form the stable derivatives *trans*-$[PdX_2Lam]$ (*120*, *328*). Studies of the infrared spectra of a series of these derivatives enabled the effect of L on the NH stretching frequency to be determined (*77*, *78*).

Treatment of $[Pd_2Cl_4(PR_3)_2]$ with ethane thiol results in replacement of the bridging chlorine atoms to yield (XIII) and (XIV) (*84*, *99*), this



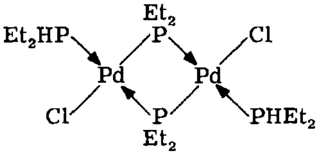
(XIII)



(XIV)

cis configuration being established by the high dipole moments of the compounds.

The initial work on complexes of palladium with primary and secondary phosphine suggests interesting developments in the field of bridged complexes. Issleib and co-workers have shown that both diphenyl-phosphine (*286*) and phenyl-phosphine (*287*) react with palladous chloride with elimination of HCl. The product $[PdCl(PPh_2)(PHPh_2)]_2$ and several related complexes have been shown by Hayter (*218*, *219*) to contain a phosphorus bridge rather than a chlorine bridge. The structure (XV), for the product from diethyl-phosphine, is supported by a preliminary X-ray examination. The bridge is split on treatment with tertiary phosphines to form a phosphide of the type $[PdCl(PR_2)(PEt_3)_2]$.



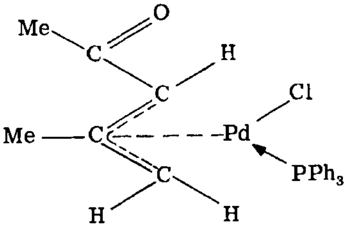
(XV)

3. Hydride and Organic Complexes

Palladium hydrides of the type $[PdHX(PR_3)_2]$ are more stable than the corresponding nickel compounds, although not sufficiently stable to be readily isolated in a pure state (*73*).

Alkyl and aryl derivatives of the types $[PdXR(PEt_3)_2]$ and $[PdR_2(PEt_3)_2]$ are also intermediate in stability between their unstable nickel and stable platinum analogues, being readily prepared by alkylation or arylation of $[PdX_2(PEt_3)_2]$ (*63*, *140*). The complexes *trans*-$[PdXR(PEt_3)_2]$ absorb carbon monoxide at room temperature and pressure to form the acyl derivatives *trans*-$[PdX(COR)(PEt_3)_2]$ (*48*).

Mesityl oxide forms a π-allylic complex with palladium(II) chloride from which may be derived a stable phosphine complex $[PdCl(C_6H_9O)PPh_3]$ of probable structure (XVI) (*394*).



(XVI)

4. Pd(0) Complexes

Malatesta and Angolette (*316*) have prepared complexes of the type $[PdL_4]$ (L = PPh_3 and $AsPh_3$) and $[Pd\{P(p—ClC_6H_4)_3\}_3]$, which by their method of preparation should not contain metal hydride as do some of the analogous derivatives of platinum. The complex $[Pd(PPh_3)_4]$ has also been prepared by the action of PPh_3 on $[Pd(\pi—C_5H_5)(\pi—C_6H_9)]$ (*183*). Compounds of this last type could be useful intermediates for the preparation of other Pd(0) complexes.

Complexes of Pd(0) containing monodentate ligands, apart from their ready oxidation, are prone to dissociation. Complexes of the type $[Pd(diphosphine)_2]$ are much more stable. These have been prepared by reduction of, for example, $[PdX_2(diphosphine)_2]$ (*91*), or by direct reaction of metal and *o*-phenylenebis(diethyl-phosphine) (*90*).

C. PLATINUM

1. Pt(II) Complexes

a. Halide Complexes with Monodentate Ligands. Square-planar complexes of the type $[PtX_2L_2]$ are readily formed by Pt(II) halides and related compounds (see Table IX). As described previously, Ni(II) and Pd(II) halides also form stable four-coordinate complexes, and in a *trans*-$[MX_2L_2]$ series the stability decreases M = Pt > Pd > Ni. However, platinum differs from nickel and palladium in also forming stable *cis* compounds; in fact only the *cis* isomers have been isolated in a pure condition with certain ligands, e.g., PPh_3. This applies in most examples of tertiary stibine complexes, although the very soluble *trans* isomers exist as the major component in equilibrium with the less soluble *cis* isomers in solution.

In many cases, particularly with trialkyl-phosphines and -arsines, mixtures of *cis* and *trans* isomers result from the preparation, and their separation and isomerization have been studied by Chatt and Wilkins (*126–128*, *130*). The fact that the isomerization is photochemically effected (*206*) may not always have been taken into account. The isomers differ in the following ways: (1) *trans* isomers are more strongly colored; (*2*) *cis* isomers are much less soluble in organic solvents and usually have higher melting points; (3) *cis* isomers have large dipole moments.

The dipole moments of the *cis* isomers are generally in the range 9–13 D and may be contrasted with a value of 4.4 D for *cis*-$[PtCl_2(PF_3)_2]$ (*131*), which demonstrates the effect of the increased drift of *d*-electrons from the Pt atom into the *d* orbitals of the phosphorus under the influence of the very electronegative fluorine atoms.

Nuclear-spin coupling constants (J_{Pt-P}) are larger for *cis*-$[PtCl_2(PBu_3)_2]$

TABLE IX

SIMPLE TERTIARY PHOSPHINE, ARSINE, AND STIBINE COMPLEXES OF PT(II) HALIDES

Complex	Reference	Color	M.p. (°C)	Dipole moment (D)
cis-[PtCl$_2$(PMe$_3$)$_2$]	*39, 62*	White	324–326	13.1
cis-[PtCl$_2$(PMe$_2$CF$_3$)$_2$]	*39*	White	188–190 d	9.2
trans-[PtCl$_2${PMe(CF$_3$)$_2$}$_2$]	*39*	Yellow	85–87	0
cis-[PtCl$_2$(PEt$_3$)$_2$]	*61, 288*	White	191–192	10.7
trans-[PtCl$_2$(PEt$_3$)$_2$]	*61, 288*	Yellow	142–143	∼0
cis-[PtBr$_2$(PEt$_3$)$_2$]	*288*	White	201–202	11.2
trans-[PtBr$_2$(PEt$_3$)$_2$]	*288*	Yellow	134–135	∼0
cis-[PtI$_2$(PEt$_3$)$_2$]	*288*	Pale yellow	→*trans*	8.2
trans-[PtI$_2$(PEt$_3$)$_2$]	*288*	Dark yellow	136–137	∼0
cis-[Pt(NO$_2$)$_2$(PEt$_3$)$_2$]	*288*	White	192–193 d	—
trans-[Pt(NO$_2$)$_2$(PEt$_3$)$_2$]	*288*	White	201–202	∼0
cis-[Pt(NO$_3$)$_2$(PEt$_3$)$_2$]	*288*	White	182–183	—
trans-[Pt(NO$_3$)$_2$(PEt$_3$)$_2$]	*288*	Yellow	125–126	2.75
cis-[PtCl$_2$(PPr$_3^n$)$_2$]	*288*	White	149–150	11.5
trans-[PtCl$_2$(PPr$_3^n$)$_2$]	*126, 288*	Yellow	85–86	∼0
cis-[PtBr$_2$(PPr$_3^n$)$_2$]	*68*	White	160–161	—
trans-[PtBr$_2$(PPr$_3^n$)$_2$]	*68*	Yellow	96–97	—
trans-[PtI$_2$(PPr$_3^n$)$_2$]	*130*	Yellow	118–119	—
cis-[PtCl$_2$(PBu$_3^n$)$_2$]	*288*	White	144	11.5
trans-[PtCl$_2$(PBu$_3^n$)$_2$]	*288*	Yellow	65–66	∼0
trans-[Pt(NO$_2$)$_2$(PBu$_3^n$)$_2$]	*70*	White	148	—
cis-[PtCl$_2$(PPe$_3^n$)$_2$]	*130*	White	124–125	—
cis-[PtCl$_2$(PPh$_3$)$_2$]	*288*	White	310 d	—
cis-[PtBr$_2$(PPh$_3$)$_2$]	*319*	Orange	300 d	—
cis-[PtI$_2$(PPh$_3$)$_2$]	*319*	Orange-yellow	285	—
cis-[PtCl$_2$(PMePh$_2$)$_2$]	*274*	Yellow-white	—	—
trans-[PtCl$_2$(PPh$_2$CF$_3$)$_2$]	*41*	Pale yellow	63–65	0
trans-[PtCl$_2${PPh(CF$_3$)$_2$}$_2$]	*41*	—	134–136	0
cis-[PtCl$_2$(PEt$_2$Ph)$_2$]	*288*	White	202–203	—
trans-[PtCl$_2$(PEt$_2$Ph)$_2$]	*288*	Yellow	123	∼0
trans-[PtI$_2$(PEt$_2$Ph)$_2$]	*288*	Yellow	137–138	—
[PtCl$_2$(PCl$_3$)$_2$]	*415*	—	—	—
cis-[PtCl$_2$(AsMe$_2$Et)$_2$]	*130*	Pale yellow	177–178	—
trans-[PtCl$_2$(AsMe$_2$Et)$_2$]	*130*	Yellow	173–174	—
cis-[PtCl$_2$(AsEt$_3$)$_2$]	*288*	Off-white	142	10.5
trans-[PtCl$_2$(AsEt$_3$)$_2$]	*288*	Yellow	120–121	∼0
cis-[PtBr$_2$(AsEt$_3$)$_2$]	*401*	Colorless	113–114	—
trans-[PtBr$_2$(AsEt$_3$)$_2$]	*288, 401*	Yellow	120	—
cis-[PtI$_2$(AsEt$_3$)$_2$]	*401*	Yellow	87–88	—
trans-[PtI$_2$(AsEt$_3$)$_2$]	*288*	Orange-yellow	93–94	—
cis-[Pt(NO$_2$)$_2$(AsEt$_3$)$_2$]	*288*	White	169–170	—
trans-[Pt(NO$_2$)$_2$(AsEt$_3$)$_2$]	*288*	White	199–200	—
cis-[PtCl$_2$(AsPr$_3^n$)$_2$]	*126*	—	131–132	—

TABLE IX (*Continued*)

Complex	Reference	Color	M.p. (°C)	Dipole moment (D)
trans-$[PtCl_2(AsPr_3^n)_2]$	*288*	Yellow	52	—
trans-$[PtCl_2(AsBu_3^n)_2]$	*288*	Yellow	54	$\sim$0
trans-$[Pt(NO_2)_2(AsBu_3^n)_2]$	*70*	White	102–103	—
cis-$[PtCl_2(AsPh_3)_2]$	*288*	Off-white	ca. 300 d	—
trans-$[PtCl_2(AsPh_3)_2]$	*288*	Yellow	ca. 300 d	—
$[PtI_2(AsPh_3)_2]$	*319*	Apricot	276	—
cis-$[PtCl_2(AsBu_2Ph)_2]$	*130*	White	120–121	—
trans-$[PtCl_2(AsBu_2Ph)_2]$	*130*	Yellow	40–41	—
cis-$[PtCl_2(AsMePh_2)_2]$	*58*	Pale yellow	211–215	—
$[PtBr_2(AsMePh_2)_2]$	*307*	Yellow	—	—
trans-$[PtI_2(AsMePh_2)_2]$	*368*	Orange	229	—
$[PtCl_2(AsMe_2Ph)_2]$	*58*	Yellow	167	—
$[PtBr_2(AsMe_2Ph)_2]$	*369*	Yellow	201	—
cis-$[PtCl_2\{As(CH{=}CH_2)_3\}_2]$	*313*	—	90	—
$[PtCl_2(SbMe_3)_2]$	*356*	Pale yellow	—	—
cis-$[PtCl_2(SbEt_3)_2]$	*288*	Green-yellow	104	9.2
cis-$[PtBr_2(SbEt_3)_2]$	*288*	Green-yellow	132	—
trans-$[PtI_2(SbEt_3)_2]$	*288*	Yellow	68–69	$\sim$0
trans-$[Pt(NO_2)_2(SbEt_3)_2]$	*288*	Green-yellow	200–205 d	$\sim$0
cis-$[PtCl_2(SbPr_3^n)_2]$	*288*	Green-yellow	80–81	—
cis-$[PtBr_2(SbPr_3^n)_2]$	*6*	Yellow	93–95	—
cis-$[PtCl_2(SbBu_3)_2]$	*288*	Green-yellow	62–63	10.9
cis-$[PtCl_2(SbPh_3)_2]$	*288*	Yellow	ca. 140 d	9.3

than for the *trans* isomer, suggesting that π-bonding is significantly stronger in the former (*396*). The far-infrared spectra of similar types of complexes have been measured in order to study the influence of the neutral ligand upon ν_{Pt-X} (*6*).

The Pt(II) complexes react in solution with further phosphine or other neutral ligand. For example, $[PtCl_2(PEt_3)_2]$ forms $[Pt(PEt_3)_4]Cl_2$ (*61*, *289*), $[Pt(PEt_3)_2(NH_3)_2]Cl_2$ (*296*), and $[Pt(PEt_3)_2(thiourea)_2]X_2$ (*204*). An application of this type of reaction was to show that $[PtCl_2(PPh_3)_2]$ (too insoluble for dipole moment measurement) formed the $[Pt(PPh_3)_2en]^{++}$ cation with ethylenediamine (en), thus demonstrating the *cis* configuration of the starting complex (*205*).

Complexes with dissimilar neutral ligands, e.g., $[PtX_2(PR_3)amine]$, are readily obtained from halogeno-bridged complexes as will be seen later. The spectra of a wide variety of these complexes have been studied (*75*, *76*, *78*, *80*, *164*).

Five-coordinate complexes of the type $[PtX_2L_3]$ are uncommon: $[PtBr_2(AsMePh_2)_3]$ dissociates very readily in solution and it is difficult to differentiate between a five-coordinate structure and the salt $[PtBr(AsMePh_2)_3]Br$ (*369*).

b. Halide Complexes with Polydentate Ligands. With bidentate ligands, Pt(II) complexes of the two types $[PtX_2(chel)]$ and $[PtX_2(chel)_2]$ are formed in an analogous way to the Pd(II) derivatives. Complexes with dias have been the most thoroughly investigated (*207*, *210*, *211*). $[PtI_2(dias)_2]$ has been shown to be isomorphous with $[PdI_2(dias)_2]$ and has thus a distorted octahedral structure in the solid state. Other bidentate ligands used include ditertiary phosphines (*50*, *102*), dimethyl-*o*-(methylthio)phenyl-arsine (*134*), α-picolyldimethyl-arsine (*196*), and dimethyl-pent-4-enylarsine $[Me_2As \cdot (CH_2)_3 \cdot CH{=}CH_2]$ (*297*). This last example is of particular interest since it involves a tertiary arsenic atom and a C═C double bond as the donor centers of a chelate group.

Tri- and tetratertiary arsines have been similarly employed as ligands (*22*, *53*). Preliminary X-ray examination of $[PtBr_2(trias)]$ shows it to be mainly ionic. On this evidence it may be concluded that the tendency to form five-coordinate complexes is Pt(II) < Pd(II) < Ni(II), although this may be a function of the particular ligands involved. The crystal structure of $[PtI(QAS)][BPh_4]$ (QAS = tris(*o*-diphenylarsinophenyl)-arsine) has been examined and the cation shown to have a trigonal bipyramidal arrangement of ligands at the Pt atom (*315*).

c. Hydride Complexes. Reduction of the complexes *cis*-$[PtX_2(MR_3)_2]$ (M = P or As) produces the complexes *trans*-$[PtHX(MR_3)_2]$ (*72*, *113*), which are much more stable than the corresponding palladium complexes. The usual reducing agent employed is hydrazine hydrate, but there are many other alternatives including ethanol and KOH (*110*).

The *trans*-square-planar structure has been confirmed by examination of the crystal structure of $[PtHBr(PEt_3)_2]$ (*391*). The hydrogen atom has a very high *trans*-effect and labilizes the anionic ligand in *trans* position to itself. Conversely, the anionic ligand influences the metal-hydrogen bond, as is shown by study of the infrared spectra of a series of hydrides $[PtHX(PR_3)_2]$ (*74*); for example, when $X = NO_2$, $\nu_{Pt-H} = 2242\ cm^{-1}$, and when X = CN, $\upsilon_{Pt-H} = 2041\ cm^{-1}$.

A series of complexes $[PtH_2(PPh_3)_n]$ (n = 2, 3, or 4) has recently been reported (*137*), being products previously formulated $[Pt(PPh_3)_n]$ (*319*). However, only $[PtH_2(PPh_3)_2]$ is substantiated by infrared spectra, a value of $\gamma_{Pt-H} = 1670\ cm^{-1}$ probably being indicative of a *trans*-dihydride.

d. Organic Complexes. Alkyl and aryl derivatives of the types $[PtXR(PR'_3)_2]$ and $[PtR_2(PR'_3)_2]$ are readily obtained (*107*, *108*), and the former react with carbon monoxide under pressure to form $[PtX(COR)(PR'_3)_2]$ (*48*). All these complexes are similar to, but considerably more stable than, their palladium analogues. It is usual to derive the alkyl and aryl complexes from the halides $[PtX_2(PR_3)_2]$, but the stabilizing phosphine ligand has been introduced by the unusual reaction (*163*):

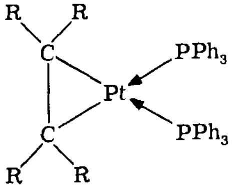
$$[Me_2PtC_8H_8PtMe_2] \rightarrow [PtMe_2(PPh_3)_2] \qquad (26)$$

It is interesting to speculate whether the complex obtained by reaction of platinic chloride with tri(β-chlorovinyl)-arsine, formulated $[Pt(CH{=}CHCl)_2\{As(CH{=}CHCl)_3\}_2]$, was really the first monomeric σ-bonded organo-platinum derivative (*326*).

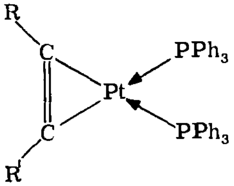
Studies of the infrared spectra of the alkyl and acyl complexes have shown the influence of various ligands on the metal-alkyl (*4*, *7*) and on the metal-acyl (*5*) groupings.

Kinetic studies on several series of compounds, typified by *trans*-[MCl(*o*-tolyl)$(PEt_3)_2$] (M = Ni, Pd, or Pt), show the rapid decrease in reactivity of the chloride ligand in passing from nickel to platinum [5,000,000(Ni) : 100,000(Pd) : 1(Pt)], and the relative *trans*-effect of a range of ligands substituted for (*o*-tolyl) in the above formula (*36*).

Olefins and acetylenes form the complexes $[Pt(olefin)(PPh_3)_2]$ (*114*) and $[Pt(acetylene)(PPh_3)_2]$ (*105*) by treatment of the reduction product of *cis*-$[PtCl_2(PPh_3)_2]$ with the unsaturated hydrocarbon. These products are *cis*-planar Pt(II) complexes of probable related structures (XVII) and (XVIII).



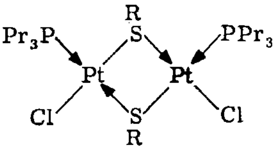
(XVII)



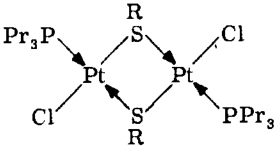
(XVIII)

e. Bridged Di-Platinum Derivatives. The binuclear halogen-bridged platinum complexes $[Pt_2X_4(MR_3)_2]$ (M = P, As, or Sb) have a *trans*-planar symmetrical structure like their palladium analogues. They are most conveniently prepared by heating together the complex $[PtX_2(MR_3)_2]$ and platinous chloride (*68*, *117*). Monoamines (am) react with these bridged compounds to form the complexes *trans*-$[PtX_2Lam]$ (*118*). These unsymmetrical complexes have proved particularly amenable to physical measurements directed at assessment of the part played by the filled *d* orbitals of Pt(II) in its complexes.

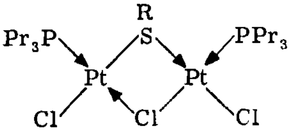
In contrast to the halogeno-bridged complexes, both thio-bridged and thiocyanato-bridged complexes exhibit isomerism (*83*). Separation of isomers by chromatography is only partially successful (*295*). With two sulfur atoms in the bridging positions, *cis* and *trans* isomers, typified by structures (XIX) and (XX), are obtained, but with one bridging sulfur



(XIX)



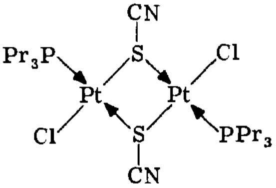
(XX)



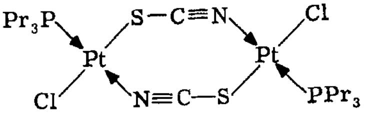
(XXI)

and one bridging chlorine atom only the *cis* isomer, e.g., (XXI), is obtained (*87*).

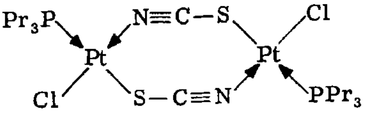
The thiocyanato-bridged complexes were first assumed to be related to the thio-bridged complexes as in structure (XXII) (*69*), but it has since



(XXII)



(XXIII)



(XXIV)

been shown that the two isomeric forms are represented by (XXIII) and (XXIV) (*71, 88, 392*).

2. Pt(IV) Complexes

The Pt(IV) state is in general considerably more stable than the Pd(IV) state, and it may be assumed that complexes of the latter are too unstable to be readily isolated.

Platinic salts are reduced by tertiary phosphines to give complexes of Pt(II). Complexes of Pt(IV) are, however, readily obtained by the oxidation of a phosphine (*67*) or arsine (*368*) complex of Pt(II) with halogens:

$$[PtX_2(MR_3)_2] + X_2 \rightarrow [PtX_4(MR_3)_2] \qquad (27)$$

Cis and *trans* isomers of the product may be obtained. Complexes of Pt(II) with polydentate ligands may be similarly oxidized (*22, 210*).

Alkyl and aryl derivatives of Pt(IV) can be obtained by the reactions (*107, 108*):

$$[PtIMe(PEt_3)_2] + MeI \rightarrow [PtI_2Me_2(PEt_3)_2] \qquad (28)$$

$$[PtPh_2(PEt_3)_2] + I_2 \rightarrow [PtI_2Ph_2(PEt_3)_2] \qquad (29)$$

3. Carbonyl Complexes

The halogeno-bridged carbonyl complexes $[Pt_2X_4(CO)_2]$ react with methyldiphenyl-arsine or phosphorus trichloride to give the unstable impure products $[PtX_2(CO)(AsMePh_2)]$ (*273*) and $[PtX_2(CO)(PCl_3)]$ (*274*). This type of complex can also be obtained by splitting the halogen bridge of $[Pt_2X_4(PR_3)_2]$ with carbon monoxide.

Malatesta and Cariello (*319*) treated $[Pt(PPh_3)_n]$ with carbon monoxide under pressure to obtain unstable mixtures of $[Pt(CO)_x(PPh_3)_y]$. Products of more definite composition, $[Pt_3(CO)_4(PR_3)_4]$, have been obtained by alternative methods but their structure is uncertain (*50*).

4. Pt(0) Complexes

The only established compounds of Pt(0) are of the type [Pt(diphosphine)$_2$], prepared by reduction of [PtCl$_2$(diphosphine)$_2$] (*102*). Although it has been suggested that the complexes $[Pt(PPh_3)_n]$ are really hydrides, several reactions (e.g., with methyl iodide, olefins, and acetylenes) have been described which give products not containing a metal hydride. The exact nature of all these complexes is thus still uncertain, and complexes of the type $[Pt(PR_3)_{3 \text{ or } 4}]$, free from hydride, almost certainly exist (*11, 322*).

By analogy with Pd(0), a possible preparative method for Pt(0) complexes would utilize a π-dienyl-π-enyl-Pt(II) complex.

IX. Group IB

A. COPPER

1. Halide Complexes

a. Complexes with Monodentate Ligands. Salts of Cu(II) are readily reduced by tertiary phosphine and arsine ligands and complexes of Cu(II) have not been established. Some complexes previously formulated to contain Cu(II), e.g., $[CuCl_2(PPh_3)_2]$ (*31*), are diamagnetic and thus contain only Cu(I). However, the complex $[CuCl_2(PCy_3)_2]$ (*276*) is green, which may be indicative of the presence of Cu(II); magnetic measurements are necessary to confirm this.

With Cu(II) compounds particular care is necessary in the interpretation of results. In one instance, the product from cupric chloride and methyldiphenyl-arsine was found to be paramagnetic and formulated as $[Cu_2Cl_3(AsMePh_2)_3]$ (*343*, *344*), a complex of Cu(I) and Cu(II). The product, when pure, was later shown to be $[Cu(OAsMePh_2)_4][CuCl_2]_2$ (*375*).

Complexes of Cu(I) are known with ligand to metal ratios of 4:1, 3:1, 2:1, and 1:1. Methyldiphenyl-arsine is notable in forming complexes of all four types. Nyholm (*378*) has formulated the products as $[Cu(AsMePh_2)_4]X$, $[CuX(AsMePh_2)_3]$, $[Cu(AsMePh_2)_4][CuX_2]$, and $[CuCl(AsMePh_2)]_4$, respectively. Other ligands give complexes of one or more of these types, although not necessarily with formulations analogous to those previous. The 1:1 complexes are probably best known, and cuprous iodide readily forms this type with trialkyl-phosphines and -arsines. All the products are tetrameric and thus formulated $[CuI(MR_3)]_4$ (*331*). X-ray analysis of $[CuIAsEt_3]_4$ shows it to have a structure with the four copper atoms, each four-coordinate, at the apices of a regular tetrahedron (*440*).

Other examples of 2:1 complexes may not all be dimeric salts. A product formulated as $[CuI(PEt_3)_2]$ (*348*) melts as low as 38°; $[CuI(PMe_2Ph)_2]$ is a nonelectrolyte, as are certain other related complexes (*66*). Three-coordination has not been firmly established, however, and the products are not necessarily monomeric. In any further investigation in this particular field, the related "mixed" complexes of the type $[CuBrP(OPh)_3AsPh_3]$ (*19*) may be worth further consideration.

The few 3:1 complexes described all readily dissociate, making their constitution difficult to determine.

Isolation of the 4:1 complexes may be aided by the use of anions having poor coordinating properties, as for example with $[Cu(PPh_3)_4]ClO_4$ (*155*).

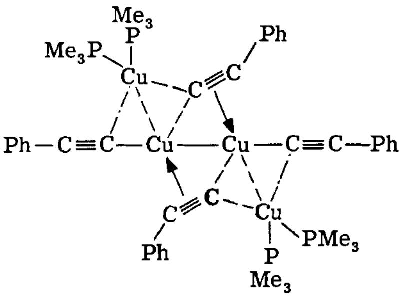
Cuprous halides form complexes $[CuX(PH_3)_2]$ which lose phosphine, the iodide least readily, to give $[CuX(PH_3)]$ (*264*). The structure of these products has not been determined; they apparently decompose at low temperature. Primary and secondary phosphine complexes are represented by $[CuCl(PH_2Ph)]_4$ (*287*) and $[CuCl(PHPh_2)]_4$ (*286*).

b. Complexes with Polydentate Ligands. From the above section it may be concluded that Cu(I) shows a strong tendency towards four-coordination even though it forms a variety of complexes with monodentate ligands. Complexes with polydentate ligands also show this tendency. With bidentate ligands two types of complex are formed: $[Cu(chel)_2]X$ and $[Cu(chel)_2][CuX_2]$ where chel = dias (*294*), *o*-diethylphosphino phenyl-diethyl-arsine (*145*), or dimethyl-*o*-methylthiophenyl-arsine (*132*). As might be anticipated, a tridentate ligand forms the complex [CuI(triarsine)] (*21*). The tri-α-pyrryl-phosphine ($PPyr_3$) in the monomeric complexes [$CuX(PPyr_3)$] is probably behaving as a tridentate ligand (*277*).

2. Organic Complexes

The product obtained from the action of cyclopentadiene and tripropyl-phosphine on cuprous oxide, formulated [$Cu(C_5H_6)(PPr_3)_2$] (*418*), has some historical interest as the first reported cyclopentadienyl compound of a transition metal. The analogous reaction with triethyl-phosphine has, however, since been shown to produce [$Cu(C_5H_5)PEt_3$] (*451*).

Acetylene complexes of copper have recently been investigated by Coates and co-workers (*47*, *141*, *142*). Treatment of a cuprous alkyl or aryl acetylide with a tertiary phosphine first gives [$RC{\equiv}C{\cdot}Cu{\cdot}PR'_3$]$_n$. The complex in which R = Ph and R′ = Me has been shown by Corfield and Shearer to be tetrameric (n = 4) in the solid state, with the rather unexpected structure (XXV). This polymerization may be reduced by further coordination with phosphine, resulting, for example, in [$PhC{\equiv}C{\cdot}Cu(PMe_3)_2$] and [$PhC{\equiv}C{\cdot}Cu(PMe_3)_3$], this last complex being particularly unstable.



(XXV)

B. Silver

Unlike the A subgroups, the IB subgroup shows greater similarity between its first two members than between its second and third.

1. Halide Complexes

a. Complexes with Monodentate Ligands. The 1:1 complexes [$AgI(MR_3)$]$_4$ (R = alkyl) (*336*) are all assumed to contain tetrahedrally coordinated Ag(I), since [$AgI(AsEt_3)$]$_4$ is isomorphous with [$CuI(AsEt_3)$]$_4$. Complexes of Ag(I) and Cu(I) of this type dissociate on heating and are much less stable than the corresponding complexes of Au(I). Tertiary alkyl phosphines are conveniently stored as their silver complexes, from which they can be regenerated when required. Where R = aryl, as for example in $[AgBr(PPh_3)]$ (*31*), it is not known whether the complexes exist in a similar tetrameric form. It is interesting that $[Ag(SCN)(PPr_3^n)]_n$ is polymeric in a different way. Ag—SCN—Ag—SCN chains are bound in pairs by Ag—S cross-linking and a distorted tetrahedral configuration results about the silver atom (*423*). The complex $Ph_3BiAgClO_4$ (*366*) requires further investigation to determine whether, as is unlikely, the bismuth is coordinated.

With the 2:1 complexes, for example $[AgX(AsMe_2Ph)_2]$, $[AgX(AsMePh_2)_2]$ (*57*), and related complexes (*65, 66*), the three-coordination, of interest due to its comparative rarity, appears to be more firmly established than with the Cu(I) analogues.

No 3:1 complexes have been described, but 4:1 complexes are exemplified by $[Ag(PPh_3)_4](ClO_4)$ (*155*).

b. Complexes with Bidentate Ligands. As was the case with copper, two types of complex are formed with chelating ligands. One obtains both types, viz., $[Ag(chel)_2]X$ and $[Ag(chel)_2][AgX_2]$, from a particular ligand (*132, 145, 196, 302, 453*) less often than with the corresponding copper complexes.

2. *Organic Complexes*

Complexes typified by $[Ag(C{\equiv}CPh)PEt_3]_n$ are obtained in a similar manner to their copper analogues, but are considerably less stable (*47, 142*). They are undoubtedly associated in solution but decomposition hinders more precise structural determination.

C. GOLD

1. *Halide Complexes*

a. Au(I). Cahours and Gal (*61, 62*) showed that auric chloride treated with triethyl-phosphine or -arsine gives the aurous complex $[AuCl(EEt_3)]$. The analogous complex $[AuClPPh_3]$ was later shown to be monomolecular (*301*). Mann and his co-workers (*336*) further investigated the trialkylphosphine and -arsine complexes. The former are much more stable and can be distilled without decomposition. Aurous halides with dimethylphenyl- and methyldiphenyl-arsine give the 1:1 complexes, but aurous cyanide behaves anomalously, possibly due to polymerization (*173*), although $[AuCNPEt_3]$ has been described (*418*).

Even though, in contrast to Cu(I) and Ag(I), the preferred coordination number for Au(I) is two, it is perhaps surprising that the 1:1 complexes only rarely coordinate further. The only 2:1 complex described is

[AuI(p-$Me_2NC_6H_4PMe_2$)$_2$], but this is largely ionized in solution (*65*). Another higher coordinate product is typified by [$AuClPEt_3(NH_3)_2$] (*301*).

Four-coordinate Au(I) is, however, well established in the complexes [Au(chel)$_2$]X, where chel = dias (*209, 212, 377*) and other tertiary diarsines and diphosphines (*145, 213*). The complex [Au(dias)$_2$]I has an X-ray diffraction pattern identical to that of [Cu(dias)$_2$]I, both being presumed to have a tetrahedral configuration about the metal (*212*). Certain ligands, which are capable of chelating with a metal, do not form chelate complexes with aurous halides. Formation of products of the type XAu(diphosphine)AuX, where diphosphine = triethylene-diphosphine (*261*) or 1,2-bis(diethylphosphine)ethane (*453*), demonstrates that high chelating power is necessary to overcome the preference for Au(I) to be two-coordinate.

An interesting application of [$AuClPPh_3$] has been recently reported by Nyholm (*381*) in the preparation of complexes containing metal-metal heterobonds, e.g.,

$$[Fe(CO)_4]Na_2 + [AuClPPh_3] \rightarrow [Fe(AuPPh_3)_2(CO)_4] \tag{30}$$

Similarly, the carbonyl manganates (-1) and -cobaltates (-1) react to form [$Mn(AuPPh_3)(CO)_5$] and [$Co(AuPPh_3)(CO)_4$]. This could be the start of a new field of work on metal-metal bonds.

b. Au(III). Gold differs from copper and silver in readily forming complexes other than with the metal in the univalent state. Mann and Purdie (*330*) found that the complexes [$AuXPR_3$] are oxidized by halogens to the Au(III) complex [AuX_3PR_3], which in turn may be reduced back to the Au(I) complex with sulfur dioxide. An X-ray analysis of [$AuBr_3PMe_3$] has shown it to have a square-planar structure (*395*). No *cis-trans* isomerism has been observed in complexes of the type [$AuXX'_2PR_3$], presumably due to ease of isomerization to the more stable form.

Four-coordinate complexes of Au(III) with bidentate ligands are exemplified by [Au(dias)$_2$]X$_3$ (*209, 212, 377*), formed by oxidation of [Au(dias)$_2$]X. The complexes [AuI(dias)$_2$](ClO_4)$_2$ and [AuI$_2$(dias)$_2$](ClO_4) have also been described. The former is more likely to be six-coordinate, although the hybridization involved in the formation of any six-coordinate Au(III) complex is difficult to explain.

2. Organic Complexes

The complexes [$AuXPR_3$] on treatment with the appropriate organometallic reagent (e.g., Grignard) form the stable derivatives [$AuR'PR_3$] (*64*). Alkynyl derivatives may be prepared similarly or by treatment of the aurous acetylide with a phosphine (*143*). The chemical and thermal stabilities of these products are intermediate between those of analogous organopalladium(II) and platinum(II) complexes.

Trimethyl gold forms complexes of the type [$AuMe_3PPh_3$], which liberate ethane on heating *(144)*.

X. Discussion

The nature of the ligand-metal bond and the significance of the vacant 3*d* orbitals of the phosphorus have been considered in several types of phosphine complex. Of possibly greater importance is the stabilization effect of phosphine and arsine ligands in assisting the study of the bonding of hydrogen and other anionic ligands in suitable stable complexes. The range of hydride and organic complexes stabilized by phosphine and arsine ligands is shown in Table X, which gives one example of each of the main types.

The other principal use of phosphine, arsine, and, to a lesser extent, stibine ligands lies in the stabilization of unusual oxidation states. Table XI gives one typical example for each oxidation state of the transition metals.

There are many spaces in both Tables X and XI which are likely to be subsequently filled. Oxidation states which ought to be exemplified include Ru(0), Os(0), Os(I), Tc(0), W(II and IV), Nb and Ta (various), and Ti(0).

Further speculation can readily be made by consideration of an alternative classification of complexes, according to electronic configuration and coordination number, as shown in Table XII. Types of complex which it ought to be possible to prepare would thus include: [$Ni^{I}XL_3$] (*a*) (other than [$NiX(NO)(PR_3)_2$]), [Ru^{0}(diphosphine)$_2$] (*b*), [$Cr^{I}X(CO)$(diphosphine)$_2$] (*c*), [$W^{II}X_2L_4$] (*d*), and [$V^{I}X(CO)_4L$] (*e*).

It may be seen from Tables X and XI that chelating ligands play an important part under the heading of stabilization. Of the many chelating ligands studied, *o*-phenylenebisdimethyl-arsine, first prepared by Chatt and Mann, is outstanding in its versatility. Nyholm and his co-workers have shown that it forms complexes with a large number of transition elements. The metal in these complexes often has an unusually high oxidation state and may exhibit also an unusual coordination number. More recent studies involving the use of tertiary diphosphines suggest that, as a class, they are equally versatile with particular emphasis on their ability to stabilize low oxidation states. Other polydentate ligands are being used increasingly to achieve unusual coordination numbers. The stereochemical arrangements involved, which are necessitated by the nature of the polydentate ligand, are of considerable interest. Structural determination by X-ray analysis, particularly of complexes of unusual coordination number (i.e., other than 2, 4, or 6) or otherwise novel types, should be the ultimate aim wherever practicable in order to increase our fundamental knowledge of the constitution of complexes. Information so far obtained from X-ray

TABLE X

HYDRIDE AND ORGANIC COMPLEXES STABILIZED BY TERTIARY ORGANOPHOSPHINES AND ARSINES

Group VII	Group VIIIA	Group VIIIB	Group VIIIC	Group IB
$[\mathrm{MnH(CO)_4PPh_3}]$	$[\mathrm{FeHCl(Me_2PC_2H_4PMe_2)_2}]$	$[\mathrm{CoH(CO)_3PPh_3}]$	—	—
$[\mathrm{MnMe(CO)_4PPh_3}]$	$[\mathrm{Fe(C_6Cl_5)_2(PEt_2Ph)_2}]$	$[\mathrm{CoPh(CO)_3PPh_3}]$	$[\mathrm{NiBr}(o\text{-}\mathrm{tolyl})(\mathrm{PEt_3})_2]$	—
$[\mathrm{Mn(COMe)(CO)_4PPh_3}]$	—	$[\mathrm{Co(COMe)(CO)_3PPh_3}]$	—	—
—	—	—	$[\mathrm{Ni(olefin)(PPh_3)_2}]$	—
—	$[\mathrm{RuH_2(Et_2PC_2H_4PEt_2)_2}]$	$[\mathrm{RhHX_2(AsMePh_2)_3}]$	$[\mathrm{PdHBr(PEt_3)_2}]$	—
—	$[\mathrm{RuClMe(Ph_2PC_2H_4PPh_2)_2}]$	$[\mathrm{RhBr(1\text{-}naphthyl)_2(PPr_3)_2}]$	$[\mathrm{PdClMe(PEt_3)_2}]$	—
—	—	—	$[\mathrm{PdCl(COMe)(PEt_3)_2}]$	—
—	—	$[\mathrm{RhCl(diene)(PPh_3)}]$	—	—
$[\mathrm{ReH_3(PPh_3)_4}]$	$[\mathrm{OsHCl(Et_2PC_2H_4PEt_2)_2}]$	$[\mathrm{IrH_3(PPh_3)_3}]$	$[\mathrm{PtHCl(AsEt_3)_2}]$	—
—	—	—	$[\mathrm{PtClPh(PEt_3)_2}]$	$[\mathrm{AuMePEt_3}]$
—	—	—	$[\mathrm{PtCl(COPh)(PEt_3)_2}]$	—
—	$[\mathrm{OsCl_2(diene)(PEtPh_2)_2}]$	—	$[\mathrm{Pt(olefin)(PPh_3)_2}]$	—
$[\mathrm{ReCl(acetylene)_2PPh_3}]$	—	—	$[\mathrm{Pt(acetylene)(PPh_3)_2}]$	—

TABLE XI

Examples of Oxidation States of Transition Metals in Complexes with P, As, and Sb Ligands

Oxidation state	Group IV	Group V	Group VI	Group VII
−1	—	$[V(CO)_5PPh_3]^-$	—	$[Mn(CO)_4PPh_3]^-$
0	—	$[V(CO)_4(PPh_3)_2]$	$[Cr(Me_2PC_2H_4PMe_2)_3]$	$[Mn(CO)_4PPh_3]$
1	—	—	—	$[MnCl(CO)_3(PPh_3)_2]$
2	—	—	$[CrCl_2(PEt_3)]_n$	$[MnI_2(PPh_3)_2]$
3	$[TiCl_3(Et_2PC_2H_4PEt_2)]$	$[VCl_3(PEt_3)_2]$	$[CrCl_3(PEt_3)_2]_2$	$[MnCl_2(dias)H_2O]ClO_4$
4	$[TiCl_4(dias)]$	$[VCl_4(dias)_2]$	—	—
0	—	—	$[Mo(CO)_5PPh_3]$	—
2	—	—	$[MoBr_2(CO)_3dias]$	$[TcCl_2(dias)_2]$
3	—	—	—	$[TcCl_2(dias)_2]Cl$
4	$[ZrCl_4(dias)_2]$	—	$[MoBr_4(dias)]$	—
5	—	—	—	$[TcCl_4(dias)]Cl$
0	—	—	$[W(CO)_4(PPh_3)_2]$	$[Re(CO)_4PPh_3]_2$
1	—	—	—	$[ReCl(CO)_3(PPh_3)_2]$
2	—	—	—	$[ReCl_2(Ph_2PC_2H_4PPh_2)_2]$
3	—	—	—	$[ReCl_3PPh_3]$
4	$[HfCl_4(dias)_2]$	—	—	$[ReI_4(PPh_3)_2]$
5	—	—	—	$[ReCl_4(dias)_2]ClO_4$

Oxidation state	Group VIIIA	Group VIIIB	Group VIIIC	Group IB
−1	—	$[Co(CO)_3PPh_3]^-$	—	—
0	$[Fe(CO)_3(PPh_3)_2]$	$[Co(CO)_3PEt_3]_2$	$[Ni(CO)_2(PPh_3)_2]$	—
1	$[FeI(CO)_2dias]$	$[CoBr(NO)_2PPh_3]$	$[NiBr(NO)(PPh_3)_2]$	$[CuIAsEt_3]_4$
2	$[FeCl_2(PPh_3)_2]$	$[CoCl_2(PEt_3)_2]$	$[NiBr_2(PEt_3)_2]$	$[CuCl_2(PCy_3)_2]$
3	$[FeCl_3(AsPh_3)_2]_2$	$[CoCl_2(Et_2PC_2H_4PEt_2)_2]Cl$	$[NiBr_3(PEt_3)_2]$	—
4	$[FeCl_2(dias)_2][FeCl_4]_2$	—	$[NiCl_2(dias)_2](ClO_4)_2$	—
0	—	—	$[Pd(Ph_2PC_2H_4PPh_2)_2]$	—
1	—	$[RhCl(CO)(PPh_3)_2]$	—	$[AgIAsEt_3]_4$
2	$[RuCl_2(AsMePh_2)_4]$	$[RhCl_2(AsMe_2Ph)_4]$	$[PdCl_2(PEt_3)_2]$	—
3	$[RuCl_3(AsMePh_2)_3]$	$[RhCl_3(PEt_3)_3]$	—	—
0	—	—	$[Pt(Ph_2PC_2H_4PPh_2)_2]$	—
1	—	$[IrCl(CO)(PPh_3)_2]$	—	$[AuClPEt_3]$
2	$[OsBr_2(SbPh_3)_4]$	$[IrBr_2(AsMe_2Ph)_4]$	$[PtCl_2(PEt_3)_2]$	—
3	$[OsBr_3(AsPh_3)_3]$	$[IrCl_3(PEt_3)_3]$	—	$[AuBr_3PMe_3]$
4	$[OsBr_4(AsPh_3)_2]$	$[IrCl_4(PPh_3)_2]$	$[PtCl_4(PPr_3)_2]$	—

TABLE XII

Some Relationships between Oxidation Number, Electron Configuration, and Coordination Number[a]

Configuration	Coordination number	Group V	Group VI	Group VII	Group VIIIA	Group VIIIB	Group VIIIC	Group IB
d^{10}	4	—	—	—	—	$[Co^{-I}(CO)_3PPh_3]^-$	$[Ni^0(CO)_2(PPh_3)_2]$	$[Cu^ICl(AsMePh_2)_3]$
		—	—	—	—	—	$[Pd^0(PPh_3)_4]$	$[Ag^IIPEt_3]_4$
		—	—	—	—	—	$[Pt^0(Ph_2PC_2H_4PPh_2)_2]$	$[Au^I(dias)_2]I$
d^9	4	—	—	—	—	$[Co^0(Me_2PC_2H_4PMe_2)_2]$	(*a*)	$[Cu^{II}Cl_2(PCy_3)_2]^b$
d^8	6	—	—	—	—	—	$[Ni^{II}(dias)_3]^{++}$	$[Au^{III}I_2(dias)_2]^+$
	5	—	—	$[Mn^{-I}(CO)_4PPh_3]^-$	$[Fe^0(CO)_4PPh_3]$	$[Co^I(CO)_3(PPh_3)_2]^+$	$[Ni^{II}Br_2trias]$	$[Au^{III}I(dias)_2]^{++b}$
	4	—	—	—	(*b*)	$[Rh^ICl(CO)(PPh_3)_2]$	$[Pd^{II}Cl_2(PEt_3)_2]$	$[Au^{III}Br_3PMe_3]$
d^7	5	—	—	$[Mn^0(CO)_4PPh_3]$	$[Fe^II(CO)_2dias]$	$[Co^{II}Cl_2(CO)(PEt_3)_2]$	$[Ni^{III}Br_3(PEt_3)_2]$	—
d^6	6	$[V^{-I}(CO)_5PPh_3]^-$	$[Cr^0(CO)_4(PPh_3)_2]$	$[Mn^II(CO)_4PPh_3]$	$[Fe^{II}Cl_2(CO)_2(PEt_3)_2]$	$[Co^{III}I_3trias]$	$[Ni^{IV}Cl_2(dias)_2]^{++}$	—
d^5	6	$[V^0(CO)_4(PPh_3)_2]$	(*c*)	$[Mn^{II}Br_2(CO)_2dias]$	$[Fe^{II}Br_2(dias)_2]^+$	—	—	—
d^4	6	(*e*)	(*d*)	$[Re^{III}Cl_3(PEt_2Ph)_3]$	$[Os^{IV}Cl_2(dias)_2]^{++}$	—	—	—

[a] See text for explanation of italic letters in parentheses.

[b] Constitution not fully established.

TABLE XIII
CRYSTAL STRUCTURE DETERMINATIONS (X-RAY)

Coordination number	Complex	Reference	Structure
2	$[AuCl(PCl_3)]$	*16*	Linear
4	$[Co(C_9H_{11})_2(PEt_2Ph)_2]$	*393*	*trans*-Planar
	$[NiBr_2(PEt_3)_2]$	*191, 410*	*trans*-Planar
	$[NiCl_2(PPh_3)_2]$	*435*	Tetrahedral
	$[Ni(NO_3)_2(PEt_3)_2]$	*191, 410*[a]	Favors tetrahedral
	$[Pd_2Br_4(AsMe_3)_2]$	*441*	*trans*-Planar Symmetrical
	$[Pd_2Cl_2(PEt_2)_2(PHEt_2)_2]$	*218*[a]	Phosphorus-bridged Planar
	$[PtBr_2(PEt_3)_2]$	*182*[a]	*trans*-Planar
	$[PtHBr(PEt_3)_2]$	*391*	*trans*-Planar
	[PtBrtrias]Br	*22*[a]	Ionic
	$[Pt_2Cl_2(SCN)_2(PPr_3)_2]$	*392*	Thiocyanato-bridge (two isomers)
	$[CuIAsEt_3]_4$	*440*	Tetrahedral
	$[PhC\vdots CCuPMe_3]_4$	*141*	(see structure XXV)
	$[Ag(SCN)PPr_3]_n$	*423*	Tetrahedral (distorted)
	$[AuBr_3PMe_3]$	*395*	Planar
5	$[NiBr_3(PEt_3)_2]$	*410*[a]	—
	$[NiBr_2trias]$	*314*	Square pyramid (distorted)
	$[PtI(tetraarsine)]^+$	*315*	Trigonal bipyramid
6	$[W(CO)_4(PEt_3)_2]$	*265*[a]	Octahedral
	$[ReOCl_3(PEt_2Ph)_2]$	*174*	*trans*-Octahedral
	$[OsHBr(CO)(PPh_3)_3]$	*389*[a]	Octahedral
	$[PdI_2(dias)_2]$	*211*[a]	Distorted octahedral (Pt analogue isomorphous)
8	$[TiCl_4(dias)_2]$	*138*[a]	Dodecahedral

[a] Preliminary results.

analysis is summarized in Table XIII. X-ray determination is usually concerned primarily with the stereochemistry of the central metal atom, but it may be mentioned that the arrangement of the three organic groups and the metal about the phosphorus or arsenic atom is, as expected, tetrahedral or nearly so.

Phosphine itself does not readily form well-characterized complexes, but primary and secondary phosphines form derivatives often notable for their dissimilarity to the complexes derived from the corresponding tertiary phosphine. Issleib and co-workers have demonstrated this in many instances, and it is clear that the further study of complexes from primary and secondary phosphines will be of value. A particular instance of the potential importance here is provided by the preparation of binuclear phosphorus-bridged compounds, recently prepared by other methods also.

The recent discovery of the reactions of alcohols with phosphine complexes, or with a phosphine plus a metal halide, provides an added incentive to the study of phosphine, arsine, and stibine complexes. So far the reactions, involving reduction or reductive carbonylation, have been applied to derivatives of Ru, Os, Rh, Ir, and Pt. The possible application to catalytic work involving alcohols (or other compounds capable of hydrogen ion transfer) is obvious, and it would be particularly valuable to extend the number of "active" metals to include some first-row transition elements.

It is clear that recent events in the field of phosphine and arsine complexes have provided a fresh impetus in a variety of directions. Further developments of considerable importance are inevitable.

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