TRANSITION METAL COMPLEXES WITH GROUP IVB ELEMENTS

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I. Introduction[1]

Metal-metal bonding in transition metal compounds has become widely recognized in the past decade. Hitherto interest has centered mainly around interactions between two or more transition metal atoms (*66*, *152*, *154*), but more recently there has been a renewed interest in bonding between transition and nontransition metals. Compounds with bismuth (*181*), zinc (*120*), cadmium (*120*), mercury (*109*, *113*, *120*, *156*, *187*, *188*), Group IIIB metals (*201*, *204*), and Group IVB metals bonded directly to transition metal ions have been prepared, and this variety has been a factor in stimulating further interest in metal-metal bonding in coordination chemistry. It has become apparent that the ability of nontransition metal elements to behave as ligands is widespread throughout the Periodic Table, and this constitutes an important link between the bonding of classical nonmetallic ligands and interactions between transition metal atoms.

Rather than to attempt to cover the whole of the emerging field of metal-metal bonding, this review has been confined to a survey of the complexes of Group IVB elements with transition metals. Nevertheless this restricted approach well illustrates the variety of complexes now known to contain metal-metal bonds, and allows them to be treated within the context of the periodic behavior of this group.

II. The General Chemistry of Group IVB

A survey of transition metal compounds can be made in terms of the general chemistry of the group as a whole. This approach proves a useful way of correlating the large number of compounds known and predicting further devlopments in the field. Group IVB well illustrates (*68*, *174*) several general trends found in other periodic groups: the change from electronegative to electropositive character going down the group, the presence of the "inert pair" and an increasingly stable lower oxidation state as one goes down the group, and the discontinuity between first- and second-row elements. Carbon must be considered separately, since the

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[1] Abbreviations used: X = Cl, Br (sometimes other anions); M = transition metal; E = Group IVB element; R = alkyl or aryl; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Ph = phenyl; Bz = benzyl; Cp = π-bonded cyclopentadienyl; NBD = norbornadiene; COD = cyclo-octa-1,5-diene; and diphosphine = bis(diphenylphosphino)ethane. L = neutral ligand, but, where ML_n is used to denote a coordinated metal atom, L may represent more than one type of ligand. The compound types $R_3E\text{-}ML_n$, $R_2E[ML_n]_2$, $RE[ML_n]_3$, and $E[ML_n]_4$ are referred to as mono-, di-, tri-, and tetrasubstituted complexes.

formation of carbon-metal bonds is largely determined by the unique factors of organic chemistry. For this reason organometallic compounds are not considered here except when useful comparisons can be made.

A. THE TETRAVALENT STATE

All the remaining four elements form the covalent tetravalent oxidation state to be expected from their electronic configuration. Typical EX_4 compounds have four equivalent covalent bonds described in valence bond terms by sp^3 hybridization. There is evidence (*58*, *69*, *90*) for some ($p \rightarrow d$) π-bonding in Si—X bonds when X has a lone pair of electrons, such as N, O, Cl, or has π-electrons, such as in the phenyl group. This tendency to use *d* orbitals for π-bonding appears to decrease rapidly down the group. *d* Orbitals are involved in σ-bonding in EX_6^{2-} compounds (where X is a highly electronegative group), and this is more common for tin and lead, but the formation of octahedral complexes depends on steric factors as well as energetic considerations. The ability of Group IVB elements to increase their coordination number (to both five- and six-coordination) makes EX_4 compounds, and their derivatives, good Lewis bases (*69*), particularly toward nitrogen and oxygen donors. Covalent bonds may be formed between like and unlike elements of the group, but this tendency to catenation, although greatly extended in recent years, never approaches that of carbon. Compounds of the type $(R_3E)_3ER$ and $(R_3E)_4E$ are now known, but E—E bonds are considerably weaker than carbon-carbon bonds and multiple bonding is unknown.

Transition metal complexes of the type $R_3E\text{-}ML_n$ and $R_2E[ML_n]_2$ are known for all Group IVB elements (with the exception of $R_2Si[ML_n]_2$), and may be regarded as normal tetravalent compounds. The tetrahedral environment of E has been confirmed by X-ray structure determinations (see Section VI,A). The extra *d* electrons on M can be involved in ($d \rightarrow d$) π-bonding between E and M, and there is chemical and physical evidence that this type of back-donation of electrons is occurring.

The M—E bond is more stable in the monosubstituted complexes than in the disubstituted, and is generally less reactive than the M—C bond in the corresponding alkyls. It is tempting to ascribe this to multiple bond character of the metal-metal bond. An order of stability, in so far as it can be assessed, is $Sn \sim Ge > Si > Pb$ and may reflect the degree of π-orbital overlap, although other factors must be important. Silicon complexes show more instability toward air and water than do those of germanium and tin, and this is in keeping with the general behavior of silicon. $H_3Si\text{-}ML_n$ complexes also react with nitrogen donors to form weak adducts through cleavage of the Si—M bond. π-Bonding should

TABLE I

MONOSUBSTITUTED TETRAVALENT COMPLEXES OF GROUP IVB ELEMENTS (MIXED ORGANOHALOGEN DERIVATIVES NOT INCLUDED)

Group VIA	Group VIIA	Group VIII
$R_3E\text{-}Cr(CO)_3Cp$ (R = Me, Ph; E = Ge, Sn, Pb) (*183, 200*)	$R_3E\text{-}Mn(CO)_5$ (R = H, Me, Et, Ph; E = Si, Ge, Sn, Pb) (*6, 59, 61, 105, 130, 179, 222*) $X_3E\text{-}Mn(CO)_5$ (X = Cl, Br; E = Si, Ge, Sn) (*5, 105, 130, 178a, 179, 181*) $R_3E\text{-}Mn(CO)_4(Ph_3P)$ (R = H, Ph; E = Si, Ge, Sn) (*5, 105, 179, 184*)	$R_3E\text{-}Fe(CO)_2Cp$ (R = Me, Ph; E = Si, Sn, Pb) (*82, 105, 137, 199, 209, 222*) $X_3E\text{-}Fe(CO)_2Cp$ (X = Cl, Br, I; E = Ge, Sn) (*28a, 30, 91, 105, 165, 180*) $(R_3E)_2Fe(CO)_4$ (R = Me, Ph, cyclohexyl; E = Sn, Pb) (*71, 110, 112, 115*)
$R_3E\text{-}Mo(CO)_3Cp$ (R = Me, Ph; E = Ge, Sn, Pb) (*183, 199, 200*) $X_3E\text{-}Mo(CO)_3Cp$ (X = Cl; E = Sn) (*28a, 30*)		
$R_3E\text{-}W(CO)_3Cp$ (R = Me, Ph; E = Ge, Sn, Pb) (*28a, 44, 183, 200*)	$R_3E\text{-}Re(CO)_5$ (R = Me, Ph; E = Si, Ge, Sn, Pb) (*130, 181, 184*) $X_3E\text{-}Re(CO)_5$ (X = Cl, Br; E = Ge, Sn) (*105, 130, 181, 184*) $R_3E\text{-}Re(CO)_4(Ph_3P)$ (R = Ph; E = Ge, Sn) (*184*)	

Group VIII	Group VIII	Group IB
R_3E-$Co(CO)_4$ ($R = H$, Me, Et, Bu, cyclohexyl, Ph; $E =$ Si, Ge, Sn, Pb) (*4, 33, 47, 48, 107, 115, 118, 207*) X_3E-$Co(CO)_4$ ($X =$ F, Cl, Br, I; $E =$ Si, Ge, Sn) (*47, 107, 207*) R_3E-$Co(CO)_3(R^1{}_3P)$ ($R =$ Me, Bu, Cl, Br; $E =$ Sn) (*28a, 118*)		R_3E-$Cu(Ph_3P)_n$ ($n = 1, 3$; $R =$ Ph; $E =$ Ge) (*102*) X_3E-$Cu(Ph_3P)$ ($X =$ Cl; $E =$ Sn) (*86*)
R_3E-$Rh(CO)_2(Ph_3P)_2$ ($R =$ Me; $E =$ Sn) (*64*)	$(R_3E)_2Pd(R^1{}_3P)_2$ ($R =$ Ph; $E =$ Ge) (*35*) $(R_3E)_2Pd(CN)_2^{2-}$ ($R =$ Ph; $E =$ Ge) (*35*)	R_3E-$Ag(Ph_3P)_n$ ($n = 1, 3$; $R =$ Ph; $E =$ Ge) (*102*) X_3E-$Ag(Ph_3P)$ ($X =$ Cl; $E =$ Sn) (*86*)
R_3E-$Ir(CO)_3(Ph_3P)$ ($R =$ Me, Ph; $E =$ Sn) (*64*) R_3E-$IrHCl(CO)(Ph_3P)_2$ ($R =$ Et, Ph; $E =$ Si) (*46*) X_3E-$IrHCl(CO)(Ph_3P)_2$ ($X =$ Cl; $E =$ Si, Sn) (*46, 234*)	$(R_3E)_2Pt(R^1{}_3P)_2$ ($R =$ Me, Ph; $E =$ Si, Ge) (*51, 75*) (R_3E)-$PtY(R^1{}_3P)_2$ ($R =$ Me, Ph; $E =$ Si, Ge, Sn, Pb) (*18, 44, 51, 75, 76, 104, 150, 198*) $(X_3E)PtY(R^1{}_3P)_2$ ($X =$ Cl; $E =$ Sn) (*15, 72, 158, 254*)	R_3E-$Au(Ph_3P)_n$ ($n = 1, 3$; $R =$ Me, Ph; $E =$ Si, Ge) (*18, 102*) X_3E-$Au(Ph_3P)$ ($X =$ Cl; $E =$ Sn) (*86*)

TABLE II

Disubstituted Tetravalent Complexes of Group IVB Elements (mixed organohalogen derivatives not included)

Group VIA	Group VIIA	Group VIII
	$R_2E[Mn(CO)_5]_2$ (R = H, Me, Et, Ph; E = Ge, Sn, Pb) (*105, 168, 179*)	$R_2E[Fe(CO)_2Cp]_2$ (R = H, Me, Et, Ph; E = Ge, Sn) (*94, 180*) $X_2E[Fe(CO)_2Cp]_2$ (X = Cl, Br, I, CNS, NO_3, OH, etc; E = Ge, Sn) (*28, 28a, 91, 94, 180, 182, 203, 228*) $[R_2E\text{-}Fe(CO)_4]_2$ (R = Me, Et, Pr, Bu, Am, Ph; E = Ge, Sn, Pb) (*70, 71, 110, 112, 113, 115, 118, 124, 132, 133, 145*) $[R_2E\text{-}Fe(CO)_3(Ph_3P)]_2$ (R = Bu; E = Sn) (*112, 113*)
$R_2E[Mo(CO)_3Cp]_2$ (R = Me, Ph; E = Sn) (*183, 200*) $X_2E[Mo(CO)_3Cp]_2$ (X = Cl; E = Sn) (*28a, 183*)		
$R_2E[W(CO)_3Cp]_2$ (R = Me, Ph; E = Sn) (*183*) $X_2E[W(CO)_3Cp]_2$ (X = Cl; E = Sn) (*183*)	$R_2E[Re(CO)_5]_2$ (R = Ph; E = Ge, Sn) (*181, 184*)	

Group VIII	Group VIII	Mixed Metal Complexes
$R_2E(Co(CO)_4]_2$ (R = Me, Bu, Ph; E = Ge, Sn, Pb) *(28, 115, 118, 207)*	$X_2E[Ni(CO)Cp]_2$ (X = Cl; E = Sn) *(203)*	$R_2E[Mn(CO)_5][Mo(CO)_3Cp]$ (R = Me, Ph, Cl; E = Sn) *(183a, 199)*
$X_2E[Co(CO)_4]_2$ (X = Cl, Br, I; E = Ge, Sn) *(28, 203, 207)*		$R_2E[Mn(CO)_5][W(CO)_3Cp]$ (R = Me, Ph, Cl; E = Sn) *(183a, 199)*
$R_2E[Co(CO)_3(R^1_3P)]_2$ (R = Me, Et, Bu; E = Sn) *(28, 118)*		$R_2E[Mn(CO)_5][Re(CO)_5]$ (R = Ph, Cl; E = Sn) *(183a)*
$X_2E[Co(CO)_3(R^1_3P)]_2$, (X = Cl, Br, I; E = Sn) *(28, 28a, 203)*		$R_2E[Mn(CO)_5][Co(CO)_4]$ (R = Ph, Cl; E = Sn) *(183a)*
$\{X_2E[Co(CN)_5]_2\}^{6-}$ (X = Cl; E = Sn) *(241)*		$R_2E[Mo(CO)_3Cp][Fe(CO)_2Cp]$ (R = Cl; E = Sn) *(28a)*
$R_2E[Ir(CO)_3(Ph_3P)]_2$ (R = Me; E = Sn) *(64)*		

generally affect the Lewis base character of E in its transition metal complexes.

The E—C bond in $R_3E\text{-}ML_n$ complexes is generally easily broken, when E is germanium or tin, by the action of halogen or hydrogen halides, although the E—M bond may be preferentially attacked. In the disubstituted complexes, one E—M bond is always broken in these reactions. Pb—M bonds are invariably broken, even in monosubstituted complexes, in spite of the reactivity of Pb—C bonds. It is unlikely that normally unreactive Si—C bonds will be easily broken in $R_3Si\text{-}ML_n$ complexes, although their behavior in this respect has not been reported.

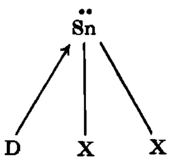
The higher substituted complexes $RE[ML_n]_3$ and $E[ML_n]_4$ are well known only for tin, although some have recently been reported for germanium and lead.

B. The Divalent State

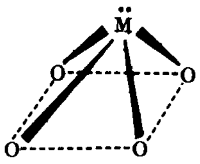
The formation of an "inert pair" of valency electrons, leading to the emergence of a lower valency state as the group is descended, is well illustrated in Group IVB. It first appears with germanium and becomes the dominant state with lead. It would be expected from modern ideas on stereochemistry (*100*) that the nonbonding pair in EX_2 compounds will influence their stereochemistries by occupying a spatially directed orbital. Tin and lead dihalides in the vapor state (*160*) have an angular structure, which can be described (*100*) by sp^2 hybridization. These compounds should then act as acceptor species toward certain electron donors by virtue of the vacant p orbital on the E atom to form compounds of the type EX_2(adduct). Addition compounds are known for divalent halides of germanium (*92*, *143*, *177*), tin, and lead (*87*). The solubility of divalent tin compounds in oxy-organic solvents is attributed to their acceptor properties and the formation of solvent adducts. The divalent elements seem to act primarily as monofunctional acceptors; although a few compounds of the type $EX_2 \cdot 2$(adduct) are known, it is not certain if both donors are bonded directly to E: in $SnCl_2 \cdot 2H_2O$ only one water molecule is coordinated directly to the tin atom (*134*).

The crystal structures of tin(II) compounds, of which a large number are now known (*87*, *219*), clearly show the influence of the nonbonding electrons on stereochemistry and the acceptor character of the tin atom. The basic unit of all tin(II) compounds in the solid state is the pyramidal structure (see structure I) with the lone pair at the apex and a donor species that may be halogen, oxygen, sulfur, or selenium. It can be regarded as a distorted tetrahedral configuration with the nonbonding pair of electrons occupying a directed sp^3 hybrid orbital.

Although fewer germanium compounds have had their structures determined, it is known (*87*, *244*) that GeS and GeSe are isomorphous with the tin compounds while $CsGeF_3$ (*177*) and $CsGeCl_3$ (*57*) show distortions from the true perovskite structure, which probably reflects the stereochemical significance of the "inert pair." GeF_2 is a fluorine-bridged chain polymer (*236*) with the structural unit a trigonal pyramid, but the chains are cross-linked by weak fluorine bridges so that each germanium atom can be considered to bond to four fluorines and hence *d* orbitals must be used in the bonding. *d* Orbitals are probably also involved in the SnO and PbO structures (see structure II) (*176*), which are based on the square pyramid with the lone pair at the apex. Lead compounds are generally more ionic in character, but the distortion of the perovskite structure in $CsPbX_3$ (X = Cl, Br, I) (*173*) can be taken as indicative of a sterically active lone pair. The structure of $NH_4Pb_2Br_5$ (*214*) seems more likely to be based on the $Pb_2Br_5^-$ ion rather than on the $PbBr_2$ group and thus to have a pyramidyl structure similar to $Sn_2F_5^-$ (*163*).



(I)



(II)

Salts of the halide complexes EX_3^- are known for all halogens, and these ions are the predominant species in solutions for the systems that have been studied (*87*), provided an excess of halide ion is maintained. The Raman spectra of the ions $GeCl_3^-$ (*78*), SnF_3^- (*148*), $SnCl_3^-$ (*78*, *251*), and $SnBr_3^-$ (*251*) have confirmed that the pyramidal configuration of the solid state remains in solution. The existence of higher complexes of the type EX_4^{2-} seems to be limited at best to extremely low concentrations, although PbX_4^{2-} and higher complexes are said to exist (*87*, *186*). $K_2SnCl_4 \cdot 2H_2O$ has been shown (*135*) to be the double salt $KSnCl_3 \cdot KCl \cdot 2H_2O$ with a pyramidal $SnCl_3^-$ ion.

Other MEX_3 complexes are known (*87*) for tin and lead, where X can be acetate, formate, thiocyanate, or hydroxide, and EX_3^- again appears to be the predominant species in most solutions containing an excess of these ions.

The predictions made from theory are therefore confirmed by experimental results, and it seems well established that divalent EX_3^- ions and $EX_2 \cdot$(adduct) compounds have pyramidal structures with a directed lone pair analogous to the trivalent Group VB compounds. Therefore Group IVB compounds may be expected also to exhibit donor properties through the nonbonding pair, and should behave as coordinating ligands with transition metals. Furthermore, vacant *d* orbitals are likely to be energetically and sterically favorable (at least in the case of Ge and Sn) for overlap with transition metal *d* orbitals to occur. Thus there could be significant d_π-d_π back-bonding, as is the case with trialkyl- and triarylphosphine, -arsine, and -stibine ligands.

In accord with theoretical predictions, the trichlorostannite ion (*72*, *254*) and tribromostannite ion (*1*) behave as conventional donor ligands toward transition metals. There is chemical and physical evidence for a considerable π-contribution to the bonding, although the recent isolation of $Ph_4AsSnCl_3 \cdot BX_3$ (X = F, Cl) (*131*) shows that nonbonding electrons are capable of forming a pure σ-coordinate link. The occurrence of $Ph_4AsGeCl_3 \cdot BX_3$ (*131*) is evidence of similar donor properties for divalent germanium, and, although no complexes between GeX_3^- and transition metals have yet been reported, they are undoubtedly capable of existence.

However, no coordination is observed (*247*) between divalent lead and transition metal compounds under similar conditions. Lead(II) compounds are more ionic in character than tin(II) compounds, and the nonbonding electrons are thus more likely to approximate to a pure *s* orbital and to show less donor ability. Moreover, the *d* orbitals in lead are likely to be less favorable for $(d \rightarrow d)$ π-bonding. The situation in Group VB, where bismuth is the only member of the group not to show significant coordinating power, is thus paralleled here.

III. Tetravalent Compounds

A. SILICON

The first recorded example of a silicon transition metal complex is $Me_3Si\text{-}Fe(CO)_2Cp$, prepared by Piper and associates (*209*) in 1956. The reaction employed,

$$Me_3SiCl + NaFe(CO)_2Cp \rightarrow Me_3Si\text{-}Fe(CO)_2Cp \qquad (1)$$

is now a standard procedure for preparing tetravalent complexes of all Group IVB elements. The complex is sensitive to oxidation and hydrolysis in contrast to the phenyl analog (*137*). Although $Ph_3Si\text{-}Mn(CO)_5$ was originally reported (*105*) to be unstable toward oxygen, it has been shown (*130*) to have been incorrectly formulated, and authentic $Ph_3Si\text{-}Mn(CO)_5$ and its rhenium counterpart are actually air-stable solids prepared by the reaction of triphenylsilane on the metal carbonyl at elevated temperatures. A likely reaction scheme is (M = Mn, Re):

$$Ph_3SiH + M_2(CO)_{10} \rightarrow Ph_3Si\text{-}M(CO)_5 + HM(CO)_5 \qquad (2)$$

$$Ph_3SiH + HM(CO)_5 \rightarrow Ph_3Si\text{-}M(CO)_5 + H_2 \qquad (3)$$

However, silane does not react stoichiometrically (*168*) with manganese carbonyl hydride.

Silicon complexes of manganese and rhenium generally show greater stability than their alkyl counterparts. Carbon monoxide will not insert (*6*) into the Si—M bond, but the action of tertiary amines on $H_3Si\text{-}Mn(CO)_5$ leads (*6*) to weak five-coordinate adducts $[H_3Si\cdot 2B]^+[Mn(CO)_5]^-$ (B = amine base). Other silanes are known to react in this way (*7*, *42*, *43*), although the structure of the five-coordinate ions has not been elucidated. Hydrogen chloride can replace the hydrogen atoms of the H_3Si— group without affecting the Si—Mn bond (*5*). Similarly, triphenylphosphine will replace one carbonyl group (*5*) and leave the metal-metal bond intact.

Cobalt complexes of the type $R_3Si\text{-}Co(CO)_4$ (*47*, *48*) are also remarkably stable to air and moisture in comparison with alkyl cobalt carbonyls (*34*, *121*). Nevertheless the Si—Co bond is still comparatively reactive, being readily broken by protic reagents, halogens, and alkali (*4*, *107*, *162*). $H_3Si\text{-}Co(CO)_4$ forms the adducts $[H_3Si\cdot 2B]^+[Co(CO)_4]^-$ (*6*) with tertiary amines, which are stronger than those with manganese, but again carbon monoxide insertion is not observed.

The cobalt complexes are prepared (*47*, *48*, *107*) by reacting dicobalt octacarbonyl with the parent silane, but the hydride complex (*4*) was formed from the reaction of iodosilane with the tetracarbonylcobaltate(−1) ion.

A series of complexes with iridium-silicon bonds is formed (*46*) by the reversible addition of silanes to the square planar d^8 complex, *trans*-$(Ph_3P)_2Ir(CO)Cl$:

$$trans\text{-}(Ph_3)P_2Ir(CO)Cl + R_3SiH \rightleftharpoons (Ph_3P)_2Ir(SiR_3)H(CO)Cl \qquad (4)$$

This is yet another example of what is now a very common addition reaction (*63*, *240*). Electronegative substituents attached to silicon are necessary to promote the reaction, since trialkyl- and triarylsilanes do not react.

Although platinum(II) phosphine complexes behave as homogeneous catalysts for the hydrosilation of olefins (*47*), stable silicon complexes of platinum have not been isolated. However, treatment (*104*) of *cis*-$(Et_3P)_2PtCl_2$ with bis(trimethylsilyl)mercury quantitatively replaces one chlorine atom, but not both, with the trimethylsilyl moiety:

$$cis\text{-}(Et_3P)_2PtCl_2 + (Me_3Si)_2Hg \rightarrow (Et_3P)_2PtCl(SiMe_3) + Me_3SiCl + Hg \qquad (5)$$

The complex is sensitive to air and moisture, but Chatt and his co-workers (*51*) found that aromatic silylplatinum derivatives are quite stable. The bis-silyl complex was the only product when *cis*-$(PhMe_2P)_2PtCl_2$ was treated with methyldiphenylsilyllithium:

$$cis\text{-}(Me_2PhP)_2PtCl_2 + 2MePh_2SiLi \rightarrow (Me_2PhP)_2Pt(SiMePh_2)_2 \qquad (6)$$

However, the reaction between $(Et_3P)_2PtCl_2$ and Ph_3SiLi gave (*18*) an unstable hydride, $(Et_3P)_2PtH(SiPh_3)$.

The metal-metal bonds in the bis-silyl complex are destroyed stepwise by two molecules of hydrogen chloride, with the second molecule cleaving in the opposite sense:

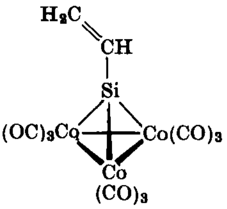
$$(Me_2Ph)_2Pt(SiMePh_2)_2 \xrightarrow{HCl} trans\text{-}(Me_2PhP)_2PtCl(SiMePh_2) + HSiMePh_2 \qquad (7)$$

$$trans\text{-}(Me_2PhP)_2PtCl(SiMePh_2) \xrightarrow{HCl} (Me_2PhP)_2PtHCl + ClSiMePh_2 \qquad (8)$$

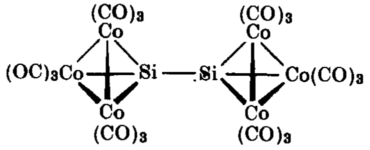
Infrared data on monosilyl complexes indicate that the silyl group has a high inductive *trans* effect, and this accounts for the different stepwise attack by hydrogen chloride. It might also explain why with —$SiMe_3$ the bis-silyl complex is not formed and the monosilyl is unstable, since the —$SiMe_3$ group would be expected to have an even greater *trans* effect than —$SiMePh_2$ (*51*). Trialkylsilyllithium has also been used (*18*) to prepare a silicon-gold complex:

$$(Ph_3P)AuCl + Me_3SiLi \rightarrow (Ph_3P)AuSiMe_3 \qquad (9)$$

This is to date the only silicon complex of this type, but the germanium compounds have been studied (*102*) in some detail and will be discussed (Section III,B,5).



(III)



(IV)

Two unusual silicon cobalt compounds, $C_2H_3Si\text{-}Co_3(CO)_9$ and $[SiCo_3(CO)_9]_2$, have been prepared (*138, 139*) by reacting R_4Si (R = vinyl, Ph) with dicobalt octacarbonyl. $C_2H_3Si\text{-}Co_3(CO)_9$ is considered to have a tetrahedral array of metal atoms (structure III), as is found (*79, 149, 231*) for $RC\text{-}Co_3(CO)_9$. The bonding in these complexes has been discussed (*139*), and the interaction of silicon *d* orbitals with the cobalt cluster is possible.

A comparison (*138*) of the carbonyl stretching frequencies between $CH_2{\cdot}CH{\cdot}Si\text{-}Co_3(CO)_9$ and $RC\text{-}Co_3(CO)_9$ suggests that the silicon *d* orbitals are involved. $[SiCo_3(CO)_9]_2$ (structure IV) is analogous to $[C\text{-}Co_3(CO)_9]_2$ reported by Bor *et al.* (*32*), with the two metal tetrahedra most probably joined by an E—E bond. The silicon bond can have multiple bond character (*139*).

B. GERMANIUM

1. *Monosubstituted Complexes*

Compounds of the type $R_3Ge\text{-}ML_n$ are now well known (see Table I) and have been prepared by reacting the appropriate germane with the sodium salt of the transition metal anion ML_n^- (Eq. 1). The phenyl derivatives are all stable compounds, resistant to air and to moisture; the methyl derivatives are less stable.

The phenyl groups in $Ph_3Ge\text{-}Re(CO)_5$ can be substituted by bromine without breaking the metal-metal bond only by avoiding excess of bromine or long reaction times (*184*):

$$Ph_3Ge\text{-}Re(CO)_5 + Br_2 \rightarrow Br_3Ge\text{-}Re(CO)_5 \qquad (10)$$

Under similar conditions the Ge—Mn bond in the manganese compound is always broken (*179*),

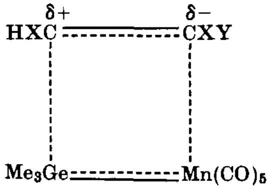
$$Ph_3Ge\text{-}Mn(CO)_5 + Br_2 \rightarrow Ph_3GeBr + BrMn(CO)_5 \qquad (11)$$

but it can be quantitatively brominated with dibromoethane. $Ph_2BrGe\text{-}Mn(CO)_5$ can be prepared from the disubstituted complex (Eq. 16), and the other mixed bromophenyl derivative can be prepared by a redistribution reaction (*179*):

$$Ph_2BrGe\text{-}Mn(CO)_5 + Br_3Ge\text{-}Mn(CO)_5 \xrightarrow{160^\circ C} 2PhBr_2Ge\text{-}Mn(CO)_5 \qquad (12)$$

Redistributions with organogermanium halides do not generally proceed readily without the aid of catalysts (*215*, *216*). Although free bromine breaks the metal-metal bond in $Ph_3Ge\text{-}Mn(CO)_5$, chlorine substitutes completely to $Cl_3Ge\text{-}Mn(CO)_5$; however, hydrogen chloride does not react at temperatures up to 76°C. $Cl_3Ge\text{-}Mn(CO)_5$ has been prepared directly (*178a*) from $ClMn(CO)_5$ and trichlorogermane, and more recently (*180*) $Cl_3Ge\text{-}Fe(CO)_2Cp$ was prepared this way. The halogen derivatives are more stable to air and light than the phenyl compounds. They sublime under high vacuum.

In both the manganese and rhenium complexes, one carbonyl group may be replaced by triphenylphosphine, -arsine, or -stibine (*179*, *184*) without breaking the metal-metal bond. An interesting reaction of $Me_3Ge\text{-}Mn(CO)_5$ is the insertion (*59*) of tetrafluoroethylene into the Ge—Mn bond to give $Me_3Ge{\cdot}CF_2{\cdot}CF_2{\cdot}Mn(CO)_5$. Other reaction products identified indicate that there is also complete cleavage of the metal-metal bond. Reactions with other halogenated olefins gave only products resulting from total bond cleavage, and no stable insertion products were isolated. In these cases olefin insertion may well be the initiating step, although a four-center intermediate (structure V) may be the closest approach to a separate insertion reaction.



(V)

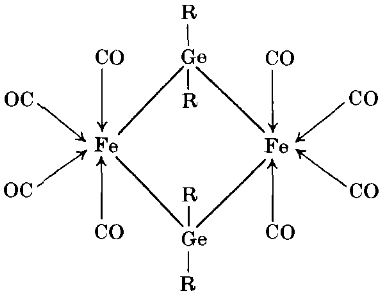
The preparation of several germanium complexes of cobalt-tetracarbonyl has recently been reported (*207*). The general method of preparation is the reaction of the cobalt carbonyl anion with an appropriate substituted germane, but different stoichiometries can lead to different products. Thus phenyltrichlorogermane can give either $Ph_2ClGe\text{-}Co(CO)_4$ or $PhClGe[Co(CO)_4]_2$, and $GeCl_4$ (which reacts similarly with dicobalt carbonyl) gives either $Cl_3Ge\text{-}Co(CO)_4$ or $Cl_2Ge[Co(CO)_4]_2$.

2. *Disubstituted Complexes*

Disubstituted germanium complexes of the type $R_2Ge[ML_n]_2$ can be prepared by the same route used for the monosubstituted complexes:

$$R_2GeX_2 + 2ML_n^- \rightarrow R_2Ge[ML_n]_2 + 2X^- \qquad (13)$$

During the preparation of $Ph_2Ge[Mn(CO)_5]_2$ by this method (*184*), a second compound is formed in about equal amount at 15°C, but in only very low yield at −2°C. The structure of this second compound, formulated as $[Ph_2GeMn(CO)_5]_2$, is not known; but its stoichiometry would seem to rule out the dimeric structure (VI) proposed (*133*) for $[R_2GeFe(CO)_4]_2$, as this would suppose seven-coordination for manganese. A possible explanation is the linear structure $(OC)_5Mn\text{-}GeR_2\text{-}GeR_2\text{-}Mn(CO)_5$, but this remains only a speculation until the compound has been investigated in greater detail.



(VI)

The cleavage of metal-metal bonds by germanium(II) halides (*94*, *180*, *205*) is a useful method for preparing disubstituted complexes of germanium, e.g.:

$$[Fe(CO)_2Cp]_2 + GeCl_2 \rightarrow Cl_2Ge[Fe(CO)_2Cp]_2 \qquad (14)$$

$$Co_2(CO)_8 + GeI_2 \rightarrow I_2Ge[Co(CO)_4]_2 \qquad (15)$$

The halogen atoms in $X_2Ge[Fe(CO)_2Cp]_2$ (X = Cl, I) may be replaced (*94*) by the methyl group, using methyllithium, or by the hydride ion on treatment with sodium borohydride. The behavior of $I_2Ge[Co(CO)_4]_2$ toward these reagents has not been reported, and it is not known whether the monosubstituted complexes show the same reactivity.

$Ph_2Ge[Mn(CO)_5]_2$ will react with bromine (*179*), breaking one Ge—Mn bond and forming a monosubstituted complex:

$$Ph_2Ge[Mn(CO)_5]_2 + Br_2 \rightarrow Ph_2BrGe\text{-}Mn(CO)_5 + BrMn(CO)_5 \qquad (16)$$

A similar reaction takes place between $Ph_3Ge\text{-}Re(CO)_5$ and hydrogen chloride at low temperatures:

$$Ph_2Ge[Re(CO)_5]_2 + HCl \rightarrow Ph_2ClGe\text{-}Re(CO)_5 \qquad (17)$$

$H_2Ge[Mn(CO)_5]_2$ has been prepared (*168*) by reacting dimanganese decacarbonyl with germane, but is obtained in better yield from manganese carbonyl hydride:

$$2HMn(CO)_5 + GeH_4 \rightarrow H_2Ge[Mn(CO)_5]_2 + 2H_2 \qquad (18)$$

This reaction may involve intermediate reduction to GeH_2, as mono- or trisubstituted complexes are not formed and there is no reaction with manganese pentacarbonyl halides. Silane reacts differently, although the air-sensitive reaction products have not been characterized.

It was not possible to prepare $RGe[Re(CO)_5]_3$ (*184*), although the tin complex is known; $Ge[Fe(CO)_4]_4$ has been reported (*71*).

3. *Platinum Complexes*

Bis(triphenylgermanyl) complexes of platinum $(R_3P)_2Pt(GePh_3)_2$ (Table III) have been prepared (*75*) by the method used for the corresponding silicon complexes (Eq. 6), although the germanium complexes were the first to be characterized. The triethyl- and tri-*n*-propylphosphine complexes have been isolated and both show *cis-trans* isomerism as expected for square planar platinum(II) complexes. $(Me_2PhP)_2Pt(GeMePh_2)_2$ has also been prepared (*51*).

These complexes are very stable, being unaffected by air, water, or alkali, but show some very interesting chemistry. In spite of good thermal stability the Pt—Ge bond is readily cleaved on treatment with 1,2-dibromoethane, in contrast to $Ph_3Ge\text{-}Mn(CO)_5$ (Section III,B,1):

$$(R_3P)_2Pt(GePh_3)_2 + C_2H_4Br_2 \rightarrow (R_3P)_2PtBr_2 + 2Ph_3GeBr \qquad (19)$$

This behavior is similar to the Ge—Ge bond in hexaphenyldigermane, which although of high thermal stability is easily cleaved in like manner (*103*). Other halogen derivatives (e.g., carbon tetrachloride and iodine) react similarly, but with hydrogen chloride $(R_3P)_2PtHCl$ and triphenylgermane are also formed. It is postulated that, in addition to direct cleavage of the Pt—Ge bond, hydrogen chloride may form an octohedral platinum(IV) complex, which will break down as follows:

$$\begin{tikzcd}
(Et_3P)_2Pt^{II}(GePh_3)_2 \arrow[r, "HCl"] & (Et_3P)_2Pt^{IV}HCl(GePh_3)_2 \arrow[d] & (20) \\
Ph_3GeH + (Et_3P)_2PtHCl & (Et_3P)_2PtH(GePh_3) + Ph_3GeCl \arrow[l, "HCl"'] & (21)
\end{tikzcd}$$

Methyl iodide may react in a similar way since both Ph_3GeI and Ph_3GeMe are isolated; the addition of both methyl iodide and hydrogen chloride to platinum(II) complexes is well known (*54, 55*).

However, Eqs. (20) and (21) conflict with the results of Chatt and his associates (*51*), who found that $(Et_3P)_2Pt(SiMePh_2)_2$ reacts stepwise with hydrogen chloride (Eqs. 7 and 8) to give only $(Et_3P)_2PtHCl$. This behavior is attributed to the high *trans* effect of the silyl group, and the germanyl group has a comparable *trans* effect (see Section VI,B,2). The two observations can be rationalized if $(\mathrm{Et_3P})_2\mathrm{PtCl_2}$ is formed from an octahedral intermediate:

$$\begin{tikzcd}(\mathrm{Et_3P})_2\mathrm{Pt(GePh_3)_2} \arrow[r, "\mathrm{HCl}"] & (\mathrm{Et_3P})_2\mathrm{PtCl(GePh_3)} \arrow[r, "\mathrm{HCl}"] \arrow[d, "{[\mathrm{HCl}]}"] & (\mathrm{Et_3P})_2\mathrm{PtHCl} + \mathrm{ClGePh_3} \quad (22) \\ & (\mathrm{Et_3P})_2\mathrm{PtHCl_2(GePh_3)} \arrow[r] & (\mathrm{Et_3P})_2\mathrm{PtCl_2} + \mathrm{HGePh_3} \quad (23)\end{tikzcd}$$

A most interesting reaction (*75*) is the cleavage of one Pt—Ge bond in the digermanyl complex by molecular hydrogen at room temperature and pressure. The resulting hydrides $(\mathrm{R_3P})_2\mathrm{PtH(GePh_3)}$ are also very stable compounds. The reaction is first order with respect to digermanyl complex, and has a low activation energy of 9 kcal/mole. An octahedral species may again be the intermediate, decomposing as follows:

$$(\mathrm{R_3P})_2\mathrm{PtH_2(GePh_3)_2} \rightarrow (\mathrm{R_3P})_2\mathrm{PtH(GePh_3)} + \mathrm{Ph_3GeH} \qquad (24)$$

The detection of small amounts of hexaphenyldigermane in the reaction mixture suggests that some decomposition of the intermediate takes place the other way, although $(\mathrm{R_3P})_2\mathrm{PtH_2}$ was not detected under the experimental conditions.

The reaction of $(\mathrm{Et_3P})_2\mathrm{PtI_2}$ with triphenylgermanyllithium appears to involve halogen-metal exchange and the formation of novel lithioplatinum intermediates (*76*, *102*). Different products, among them $(\mathrm{Et_3P})_2\mathrm{PtHI}$, $(\mathrm{Et_3P})_2\mathrm{PtH(GePh_3)}$, and a novel ethoxy complex $(\mathrm{Et_3P})_2\mathrm{Pt(OEt)(GePh_3)}$, can be isolated according to the initial ratio of the reactants, and lithio derivatives $(\mathrm{Et_3P})_2\mathrm{PtILi}$ and $(\mathrm{Et_3P})_2\mathrm{PtLi(GePh_3)}$ have been postulated as intermediates. However, the reaction with phenyllithium gave no evidence for lithio derivatives:

$$(\mathrm{R_3P})_2\mathrm{Pt(GePh_3)_2} + \mathrm{PhLi} \rightarrow (\mathrm{R_3P})_2\mathrm{PtPh_2} + \mathrm{Ph_3GeLi} \qquad (25)$$

The reactions between $(\mathrm{R_3P})_2\mathrm{Pt(GePh_3)_2}$ and $\mathrm{MgI_2}$ give a similar range of products, and the formation of platinum "Grignards" is proposed. $(\mathrm{Et_3P})_2\mathrm{PtI(GePh_3)}$ is also a likely intermediate in these reactions but was not isolated. The chloro complex $(\mathrm{Et_3P})_2\mathrm{PtCl(GeMe_3)}$ has since been prepared by reacting bis(trimethylgermanyl)mercury on $(\mathrm{Et_3P})_2\mathrm{PtCl}$ (see Eq. 5).

4. *Palladium Complexes*

Bis(triphenylgermanyl) complexes of palladium are known (*35*) (Table III). $(\mathrm{Et_3P})_2\mathrm{Pd(GePh_3)_2}$ has been isolated pure below $-20°\mathrm{C}$, but decomposes above this temperature. Triethylphosphine has been replaced by the cyanide ion to give the stable ionic complex $[\mathrm{Pd(CN)_2(GePh_3)_2}]^{2-}$, but ligand replacement is complicated by the thermal instability of the phosphine complex. Complexes with triphenylphosphine, diphosphine, and dipyridyl probably also exist.

As in the case of platinum compounds, the Pd—Ge bonds are cleaved by ethylene dibromide, while molecular hydrogen gives $(Et_3P)_2PdH(GePh_3)$. With hydrogen chloride only triphenylgermane and $(Et_3P)_2PdCl_2$ are obtained, so octahedral palladium(IV) may also be formed. Trimethylgermane and $(Et_3P)_2PdCl_2$ at 40°C give the hydride $(Et_3P)_2PdHCl$, and similar exchange is observed (*47*) between some corresponding platinum phosphine halides and silanes, although apparently not with germanes (*75*).

5. *Complexes of Copper, Silver, and Gold*

Triphenylgermanyllithium has also been used to prepare complexes of Group IB (*102*):

$$(Ph_3P)_nMX + Ph_3GeLi \rightarrow (Ph_3P)_nM\text{-}GePh_3 \qquad (26)$$

where M = Cu, Ag, Au, $n = 1, 3$. The stability of these compounds varies in the order Au > Ag > Cu, but depends very much on the number and nature of the phosphine groups. $(Ph_3P)AuGePh_3$ is the only monophosphine complex stable to air and moisture, but the tris-phosphine complexes are generally more stable. Like the palladium and platinum complexes, the metal-metal bond is rapidly cleaved with 1,2-dibromoethane.

Gold provides the first example of a germanium transition metal complex without familiar π-bonding ligands being present:

$$2(Ph_3P)AuGePh_3 + PhLi \xrightarrow{Et_2O} Li[Au(GePh_3)_2]\cdot 4Et_2O + (Ph_3P)AuPh \qquad (27)$$

The solvated lithium salt precipitates from solution, and is rapidly hydrolyzed to gold, lithium hydroxide, and hexaphenyldigermane. The tetraethylammonium salt is unsolvated and more stable. The reaction depends on the initial formation of triphenylgermanyllithium, which subsequently replaces the phosphine molecule in the initial complex:

$$(Ph_3P)AuGePh_3 + PhLi \rightarrow Ph_3GeLi + (Ph_3P)AuPh \qquad (28)$$

$$(Ph_3P)AuGePh_3 + Ph_3GeLi \rightarrow LiAu(GePh_3)_2 + Ph_3P \qquad (29)$$

C. TIN

Tin can be considered as the representative metal of group IV since it forms a wider range of compounds with transition metals than does any other member of the group, except carbon. Complexes containing both tetravalent and divalent tin are now well characterized; the latter are discussed separately. Tetravalent tin is the only Group IV element to form stable compounds ranging from $R_3E\text{-}ML_n$ to $E[ML_n]_4$. In addition, nearly every type of complex formed by the other elements also exists for tin. This unique behavior of tin makes it a useful element for extending the chemistry in this field.

1. Monosubstituted Complexes

Tin forms a very wide range of compounds of the type $R_3Sn\text{-}ML_n$ (Table I). The most general method of preparation is that used for silicon and germanium derivatives involving transition metal anions and organotin halides (Eq. 1). Using this approach, Collman and co-workers (*64*) have prepared new anionic carbonyls of rhodium and iridium as intermediates in the formation of the five-coordinate transition metal species $Me_3Sn\text{-}Rh(CO)_2(Ph_3P)_2$ and $R_3Sn\text{-}Ir(CO)_3(Ph_3)P$. The reverse reaction,

$$Ph_3Sn^- + IFe(CO)_2Cp \rightarrow Ph_3Sn\text{-}Fe(CO)_2Cp \qquad (30)$$

where Ph_3Sn^- is added as triphenylstannyllithium (*18*) or generated *in situ* by the electrolytic reduction of hexaphenyldistannane (*82*).

A novel reaction, likely to become a very useful synthetic procedure, is the elimination of an amine in the reaction between a Group IVB amido derivative and a transition metal hydride (*44*):

$$R_3ENMe_2 + HML_n \rightarrow R_3E\text{-}ML_n + Me_2NH \qquad (31)$$

$Me_3Sn\text{-}W(CO)_2Cp$ and $(Ph_3P)_2PtCl(SnPh_3)$ have been prepared by this method. A related method involving the use of triphenyltin nitrate has also been used (*18*):

$$Ph_3SnNO_3 + (Ph_3P)_2PtHCl \rightarrow (Ph_3)P_2PtCl(SnPh_3) \qquad (32)$$

Alternatively, this latter complex can be prepared (*150*) from the reaction of tetrakis(triphenylphosphine) platinum with triphenyltin chloride:

$$(Ph_3P)_4Pt + Ph_3SnCl \rightarrow (Ph_3P)_2PtCl(SnPh_3) + 2Ph_3P \qquad (33)$$

Halogen derivatives $X_3Sn\text{-}ML_n$ may be prepared by substituting the organo groups in $R_3Sn\text{-}ML_n$, or more directly by addition of tin(II) halides to the halogen derivative of the appropriate transition metal group. $Cl_3Sn\text{-}Fe(CO)_2Co$ (*30*) and $Cl_3Sn\text{-}M(PPh_3)$ (M = Cu, Ag, Au) (*86*) have been prepared by this method, and also mixed halogen complexes (*165*), but the reaction of $SnCl_2$ with $ClNi(Ph_3P)Cp$ does not form a nickel-tin bond (*161*). Pentacarbonylmanganese chloride is unreactive (*30*), although the diphosphine derivatives $XMn(CO)_3$(diphosphine) and $XMn(CO)$(diphosphine)$_2$ react readily (*29*). Clearly the nature of the ligands around the transition metal atom exert considerable influence on its reactivity. However, steric factors may be the main cause of the inertness of $IMo(CO)_3Cp$ toward stannous chloride (*165*) if an eight-coordinate intermediate is required for the reaction to proceed. Herein may lie the clue to why the cyclopentadienyltricarbonylmolybdenum dimer forms $Cl_3Sn\text{-}Mo(CO)_3Cp$ with stannous chloride (*30*), and not the disubstituted compound that is the usual product in this type of reaction (see Eq. 39).

A related reaction involves displacement of mercury from its organometallic halide (*28a*):

$$XHg\text{-}ML_n + SnX_2 \rightarrow X_3Sn\text{-}ML_n + Hg \tag{34}$$

Compounds of $\text{-}Fe(CO)_2Cp$, $\text{-}M(CO)_3Cp$ (M = Mo, W), and $\text{-}Co(CO)_3(Bu_3P)$ have been prepared by this reaction.

Cyclopentadienyldicarbonyliron dimer reacts with tin(IV) halides (*91*) to give monosubstituted derivatives:

$$[Cp(CO)_2Fe]_2 + SnX_4 \rightarrow X_3Sn\text{-}Fe(CO)_3Cp + XFe(CO)_2Cp \tag{35}$$

Decacarbonyldimanganese is unreactive (*28*) toward both tin(II) and tin(IV) chlorides, but the paramagnetic substituted monomers $Mn(CO)_3$(diphosphine) and $Mn(CO)(\text{diphosphine})_2$ react with tin(II) chloride or bromide to give monosubstituted derivatives only.

Iron pentacarbonyl reacts (*71*) with R_2SnCl_2 (R = Et, Pr, Bu) to form unstable $(R_2ClSn)_2Fe(CO)_4$, which is readily converted to other tin-iron clusters (discussed in Section III,C,3). Reaction with R_3SnCl leads directly to other products with the above compound isolated in only trace amounts. However, Me_3SnH gives a high yield of $(Me_3Sn)_2Fe(CO)_4$ from iron pentacarbonyl, while Me_2SnH_2 gives the dimeric species $[Me_2SnFe(CO)_4]_2$.

The tin-metal bonds are resistant to halogen attack and this fact, together with the general stability of the complexes, suggests that there may be considerable double bond character in the metal-metal bond. However, $(Ph_3P)_2PtCl(SnPh_3)$ is cleaved by hydrogen chloride (*18*) to give triphenylstannane and $(Ph_3P)_2PtCl_2$, and this behavior is similar to that of the germanium complexes.

In contrast, chlorine or bromine will replace all phenyl groups in $Ph_3Sn\text{-}M(CO)_5$ (M = Mn, Re) (*105, 181*) without breaking the metal-metal bond. Hydrogen chloride will also substitute all these phenyl groups in the rhenium compound (*181*) but only two (*105*) in the manganese one:

$$Ph_3Sn\text{-}Mn(CO)_5 \xrightarrow{HCl} PhCl_2Sn\text{-}Mn(CO)_5 \tag{36}$$

$Ph_2ClSn\text{-}Mn(CO)_5$ has been formed via a redistribution reaction (*105*) rather than by direct substitution:

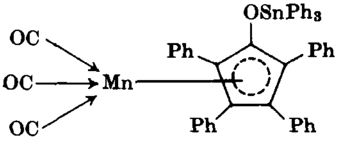
$$2Ph_3Sn\text{-}Mn(CO)_5 + Cl_3Sn\text{-}Mn(CO)_5 \rightarrow 3Ph_2ClSn\text{-}Mn(CO)_5 \tag{37}$$

This type of reaction is a general feature of organotin chemistry (*125*) but occurs here under milder conditions than are usually required. Mixed bromophenyl derivatives of rhenium can be prepared by heating Ph_3Sn-$Re(CO)_5$ with the appropriate amount of bromine (*184*).

Hydrogen chloride will also replace only two phenyl groups (*181*) in Ph_3Sn-$M(CO)_3Cp$ (M = Mo, W). Ph_3Sn-$Fe(CO)_2Cp$ gives the trichloro-derivatives (*105*) under similar conditions, but the Sn—Fe bond is sufficiently weak to be cleaved by chlorine.

The carbonyl derivatives R_3Sn-$M(CO)_n$ ($M = Mn, Re, n = 5$; $M = Co$, $n = 4$) can take part in ligand substitution reactions without affecting the metal-metal bond. Triphenylphosphine replaces one carbonyl group (*105*, *118*, *184*) at elevated temperatures or under ultraviolet light. At room temperatures no substitution occurs, and CO exchange is slow (*33*) in contrast to the lability of the carbonyl groups in $Hg[Co(CO)_4]_2$ and $CH_3CO \cdot Co(CO)_4$. The substituted compounds are stable, high-melting solids sensitive to hydrolysis. Ethylene will substitute in like manner (*61*) in Me_3Sn-$Mn(CO)_5$ but, in sharp contrast, tetrafluoroethylene inserts (*60*, *61*) into the Sn—Mn bond to give principally Me_3Sn-$CF_2 \cdot CF_2$-$Mn(CO)_5$ together with some trimethylfluorostannane and fluorocarbon derivatives of manganese pentacarbonyl. Only the latter products are formed with other halogenated olefins, and no insertion adducts were isolated although they are possible intermediates (see Section III,B,1).

The use of diphosphine (*29*) allows two and even four carbonyl groups to be replaced, as in X_3Sn-$Mn(CO)_3$(diphosphine) and X_3Sn-$Mn(CO)$(diphosphine)$_2$. However, substitution with tetraphenylcyclopentadienone does not give a simple substituted complex as was first thought (*105*), since it breaks the Sn—Mn bond to form (*106*) the cyclopentadienyl derivative (VII). This may also be regarded as an insertion reaction.



(VII)

2. *Disubstituted Complexes*

Preparation of the complexes $R_2Sn[ML_n]_2$ is generally by the method (Eqs. 1, 13) used for the monosubstituted derivatives. The procedure has been used (*183a*, *199*) to prepare the mixed metal compounds $R_2Sn[Mn(CO)_5][ML_n]$, where ML_n is a different transition metal group such as $-Mo(CO)_3Cp$, $-W(CO)_3Cp$, $-Re(CO)_5$, or $-Co(CO)_4$.

TABLE III

Germanium Complexes of Platinum and Palladium

Compound	Color[a]	M.P. (°C)	IR spectra (cm^{-1})	Remarks	Ref.
$(PhMe_2P)_2Pt(GeMePh_2)_2$	—	—	—	—	*(51)*
$(Et_3P)_2Pt(GePh_3)_2$	p-y	d160	—	—	*(75)*
$(Pr_3P)_2Pt(GePh_3)_2$	p-y	d120	—	*trans-*	
$(Et_3P)_2PtH(GePh_3)$	w	d150	ν(Pt—H) 2051	*cis-?*	
$(Pr_3P)_2PtH(GePh_3)$	—	—	ν(Pt—H) 2051	(not pure)	
$(Et_3P)_2Pt(OH)(GePh_3)$	—	d153–156	ν(O—H) 3630	From ethoxy complex	
$(Et_3P)_2Pt(OMe)(GePh_3)$	—	d172–180	Methoxy bands		
$(Et_3P)_2Pt(OEt)(GePh_3)$	c	d160–170	Ethoxy bands		
$(Et_3P)_2Pt(O^iPr)(GePh_3)$	—	d162–172	*i*-Propoxy bands		
$(Et_3P)_2PtCl(GeMe_3)$	—	—	—	—	*(104)*
$(Et_3P)_2Pd(GePh_3)_2$	p-y	d97–107	—	Unstable in solution	*(35)*
$(Et_3P)_2PdH(GePh_3)$	g	—	ν(Pd—H) 1890		
$K_2[(CN)_2Pd(GePh_3)_2]$	w	d112–120	ν(C≡N) 2084	—	
$(Me_4N)_2[(CN)_2Pd(GePh_3)_2]$	c	—	ν(C≡N) 2088	—	

[a] p-y = pale yellow, w = white, c = colorless, g = gray.

TABLE IV

Metal Cluster Compounds: Tri- and Tetrasubstituted Complexes with Group IVB Elements

Compound	E	R or X	References
$RE[Re(CO)_5]_3$	Sn	Ph, Br	*(181)*
$\{E[Re(CO)_5]_3\}_2$	Sn	—	
$XE[Mn(CO)_5][Fe(CO)_2Cp]_2$	Sn	Cl	*(182)*
$XE[Re(CO)_5][Fe(CO)_2Cp]_2$	Sn	Cl	
$RE[Fe(CO)_2Cp]_3$	Sn	Ph	
$E[Fe(CO)_2Cp]_2[Mo(CO)_3Cp]_2$	Sn	—	*(85)*
$E[Fe(CO)_2Cp]_4$	Sn	—	*(182)*
$E[Fe(CO)_3NO]_4$	Sn	—	*(117)*
$E[Fe(CO)_4]_4$	Ge, Sn, Pb	—	*(70, 71)*
$R_4E_3[Fe(CO)_4]_4$	Ge, Sn, Pb	Me, Bu	*(70, 71, 232)*
$RE[Co(CO)_3]_3$	Si	Vinyl	*(138)*
$\{E[Co(CO)_3]_3\}_2$	Si	—	*(139)*
$RE[Co(CO)_4]_3$	Sn	Me, Bu, vinyl, Ph	*(202, 205)*
$XE[Co(CO)_4]_3$	Sn	Cl, Br, I	

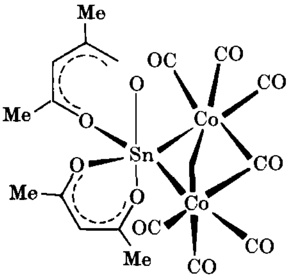
The reaction between bis(acetylacetone)tin dichloride and the tetracarbonylcobalt anion gives a novel compound (*206*):

$$(Acac)_2SnCl_2 + Co(CO)_4^- \rightarrow (Acac)_2SnCo_2(CO)_7 \quad (38)$$

The infrared spectrum shows the complex to have a bridging carbonyl group, and structure (VIII) is postulated with a cobalt-cobalt bond to explain the observed diamagnetism. The complex may well be formed from $(Acac)_2Sn[Co(CO)_4]_2$, which could spontaneously lose one carbonyl group because of the smaller Co-Sn-Co angle required by the octahedral configuration of the tin atom.

Halogen derivatives are most conveniently prepared (*30*, *203*) by the insertion of a tin(II) halide into the metal-metal bond of the appropriate dimer, e.g.:

$$[Fe(CO)_2Cp]_2 + SnX_2 \rightarrow X_2Sn[Fe(CO)_2Cp]_2 \quad (39)$$



(VIII)

The complexes $\{Cl_2Sn[Co(CN)_5]_2\}^{6-}$ (*241*) and $Cl_2Sn[Ni(CO)Cp]_2$ (*203*), which are prepared this way, are the only compounds known with these particular transition metal groups. Cyclopentadienyldicarbonyliron dimer gives the disubstituted complex with stannous chloride (Eq. 39) and the monosubstituted complex with stannic chloride (Eq. 35). However, both the mono- and disubstituted complexes are obtained (*91*) when using $SnPh_2Cl_2$:

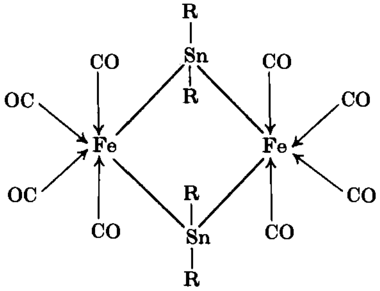
$$[Fe(CO)_2Cp]_2 + SnPh_2Cl_2 \rightarrow Cl_2Sn[Fe(CO)_2Cp]_2 + PhCl_2Sn\text{-}Fe(CO)_2Cp + FeCp_2 \quad (40)$$

SnX_2 will also insert into transition metal-mercury bonds (*28a*) to form disubstituted complexes according to the equation:

$$Hg[ML_n]_2 + SnX_2 \rightarrow X_2Sn[ML_n]_2 + Hg \quad (41)$$

In some cases the monosubstituted derivatives are also formed, while the reaction between $Hg[Co(CO)_3(Bu_3P)]_2$ and $SnBr_2$ gives $Br_3Sn\text{-}Co(CO)_3Bu_3P$ as the sole product, although the disubstituted derivative is known.

The interaction of dialkyltin dichlorides with $Fe(CO)_4^{2-}$ gives $[R_2Sn\text{-}Fe(CO)_4]_2$ (*132*, *133*), and on the basis of infrared spectra and dipole moments, structure (IX) is proposed. The reaction with iron pentacarbonyl at elevated temperatures (*70*, *71*) also gives (IX) from the breakdown of intermediate $(R_2ClSn)_2Fe(CO)_4$. R_3SnCl reacts similarly with both iron pentacarbonyl and dodecacarbonyltri-iron.



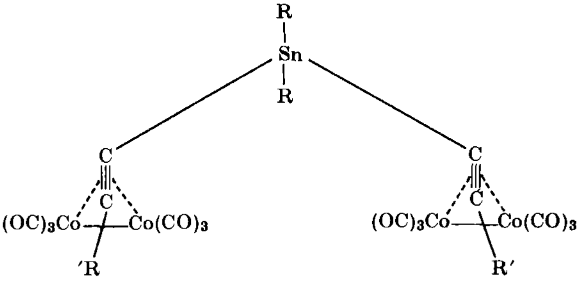
(IX)

Tetraorganotins gave only traces of (IX) with iron pentacarbonyl (*145*), unless two of the organo groups were either vinyl or phenyl. Dialkyldialkynyltins give (IX) with dodecacarbonyltri-iron (*124*) by loss of the alkynyl groups. Dicobalt octacarbonyl under milder conditions reacts without loss of acetylenes to give compound (X) bridging through the carbon triple bonds. Iron compounds of this type may be intermediates in the former reaction.

Complete substitution of the organo groups in $R_2Sn[ML_n]_2$ without breaking the metal-metal bonds is achieved by the use of hydrogen chloride (*105*, *182*, *183*) and bromine (*181*). The use of chlorine (*105*) breaks one metal-metal bond:

$$[R_2Sn\text{-}Mn(CO)_5]_2 \xrightarrow{Cl_2} Cl_3Sn\text{-}Mn(CO)_5 + ClMn(CO)_5 \qquad (42)$$

Also, alkylation of the halogen derivatives by Grignard reagents (*28*, *30*) or alkyl lithiums (*94*) is possible. Mixed organohalogen derivatives have not been prepared, with the exception of $PhXSn[Co(CO)_3(Bu_3P)]_2$ (*28*) and complete substitution of either alkyl or halogen derivatives takes place. Steric hindrance by the tributylphosphine group is considered to be preventing substitution of both halogens in $X_2Sn[Co(CO)_3(Bu_3P)]_2$ by phenyl groups. Metathetical reactions of $Cl_2Sn[Fe(CO)_2Cp]_2$ replace (*182*) the chloride ion with thiocyanate, acetate, hydroxyl, nitrate, ethylmercapto, and sulfide ions.



(X)

3. *Tri- and Tetrasubstituted Derivatives*

A logical extension of the general method (Eq. 1) has been used (*182*, *205*) to prepare these highly substituted compounds (see Table IV):

$$RSnCl_3 + 3NaCo(CO)_4 \rightarrow RSn[Co(CO)_4]_3 \quad (43)$$

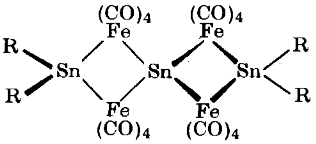
$$SnCl_4 + 4NaFe(CO)_2Cp \rightarrow Sn[Fe(CO)_2Cp]_4 \quad (44)$$

The reaction of $NaFe(CO)_3NO$ with $(NH_4)_2SnCl_6$ (*117*) gives both $ClSn[Fe(CO)_3NO]_3$ and $Sn[Fe(CO)_3NO]_4$. The former is also prepared from stannous chloride and $NaFe(CO)_3NO$, and disproportionates in solution to $Sn[Fe(CO)_3NO]_4$ and the lower substituted complexes.

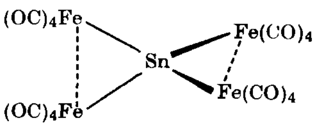
Many workers have found it convenient to start with mono- or disubstituted complexes, e.g. (*181*):

$$PhBr_2SnRe(CO)_5 + 2NaRe(CO)_5 \rightarrow PhSn[Re(CO)_5]_3 \quad (45)$$

The mixed metal derivatives $Sn[Fe(CO)_2Cp]_2[Mo(CO)_3Cp]_2$ (*85*) and $ClSn[Fe(CO)_2Cp]_2[M(CO)_5]$ (M = Mn, Re) (*182*) have been prepared from $Cl_2Sn[Fe(CO)_2Cp]_2$. $Sn[Fe(CO)_2Cp]_2[M(CO)_5]_2$ has not been reported. Attempts to prepare $Sn[Re(CO)_4]_4$ (*181*) gave instead $Sn_2[Re(CO)_4]_8$ with bonding between the tin atoms.



(XI)



(XII)

The reaction of $MeSnCl_3$ with tetracarbonyliron anion gives (*232*) the complex $Me_4Sn_3[Fe(CO)_4]_4$ (XI), which contains both di- and tetrasubstituted tin (the carbonyl groups complete octahedral coordination of the iron atoms). The same complex (with methyl and other alkyl groups) is formed (*70, 71*) along with $Sn[Fe(CO)_4]_4$ (XII) when R_xSnCl_{4-x} ($x = 2, 3$) reacts with iron pentacarbonyl or dodecacarbonyltri-iron. The complexes $(R_2ClSn)_2Fe(CO)_4$ and $[R_2SnFe(CO)_4]_2$, discussed previously, may be intermediates in their formation. $Sn[Fe(CO)_4]_4$ is the only product in the reaction between hexabutylditin and iron pentacarbonyl, and is also formed by reacting stannic chloride with the tetracarbonyliron anion. The compound contains iron-iron bonds to achieve a stable rare gas configuration, but such bonds are not required in $Sn[Fe(CO)_3NO]_4$ since the nitrosyl group donates an extra electron.

A novel compound $Sn[Co(CO)_4]_2$ (*120*) is formed from cobalt(II) bromide and metallic tin under high pressures of carbon monoxide. The structure of this compound is unknown as yet, but it probably contains divalent tin since the experimental conditions are reducing. Under similar conditions, lead(IV) is reduced to lead(II) without complexing and germanium failed to react. The series $M[Co(CO)_4]_n$ ($n = 1$, $M = Tl^I$; $n = 2$, $M =$ Zn, Cd, Hg; $n = 3$, $M = In^{III}, Tl^{III}$) is well known (*120, 221*).

Hieber and his co-workers (*119*) have also prepared the compound $Sn_2Fe_5(CO)_{20}$ of unknown structure. The iron is undoubtedly present as $Fe(CO)_4$ groups, and its preparation from $Fe(CO)_4^{2-}$ and $(NH_4)_2SnCl_6$ in alkaline solution allows the possibility of hydroxyl groups in the molecule.

D. LEAD

Although lead forms a more limited and less stable range of compounds than tin, some of the first complexes to be isolated were from reactions between R_3PbX compounds and iron pentacarbonyl, studied by Hein and his co-workers (*110, 111, 113, 114*). The reaction between Ph_3PbOH and iron pentacarbonyl gave (*113*) tetraphenyllead, benzophenone, and an unknown iron-lead compound. The reaction scheme proposed assumed the existence of two complexes between iron and lead:

$$Ph_3PbOH + Fe(CO)_5 \rightarrow (Ph_3Pb)_2Fe(CO)_4 + H_2O + CO_2 \qquad (46)$$

$$(Ph_3Pb)_2Fe(CO)_4 \rightarrow Ph_4Pb + Ph_2PbFe(CO)_4 \qquad (47)$$

$$Ph_4Pb + Fe(CO)_5 \rightarrow Ph_2PbFe(CO)_4 + Ph{\cdot}CO{\cdot}Ph \qquad (48)$$

$R_2Pb\text{-}Fe(CO)_4$ with $R = Et$ was first characterized (*113*) in the reaction between $H_2Fe(CO)_4$ and triethyllead hydroxide. Although the methyl analog was not isolated by this reaction (*111*), the formation of methane is consistent with an intermediate hydridocarbonyl species:

$$R_3PbOH + H_2Fe(CO)_4 \rightarrow R_3Pb(H)Fe(CO)_4 \rightarrow R_2Pb\text{-}Fe(CO)_4 + RH \qquad (49)$$

When the calcium hydrogen salt of the tetracarbonyliron anion was used (*110*, *111*), both $R_2Pb\text{-}Fe(CO)_4$, now shown to be dimeric, and $(R_3Pb)_2Fe(CO)_4$ were isolated. In this case there was no evidence for a hydridocarbonyl intermediate:

$$2R_3PbX + Ca[HFe(CO)_4]_2 \rightarrow (R_3Pb)_2Fe(CO)_4 \quad (X = OH, Cl, Br) \tag{50}$$

$$2(R_3Pb)_2Fe(CO)_4 \rightarrow [R_2PbFe(CO)_4]_2 + R_4Pb \tag{51}$$

When R is an acyclic alkyl group, $(R_3Pb)_2Fe(CO)_4$ breaks down spontaneously to the dimer and tetraalkyllead. This rearrangement does not occur so readily when R is phenyl or cyclohexyl, although $[Ph_2PbFe(CO)_4]_2$ has since been isolated (*112*). More recently Stone and his co-workers (*71*) also isolated the cluster compounds $Me_4Pb_3[Fe(CO)_4]_4$ and $Pb[Fe(CO)_4]_4$ from the reactions of iron pentacarbonyl with methyllead halides.

The dimer has also been obtained by direct interaction (*132*) between dialkyllead dihalides and the iron tetracarbonyl anion:

$$2R_2PbX_2 + 2Fe(CO)_4^{2-} \rightarrow [R_2PbFe(CO)_4]_2 \tag{52}$$

This type of reaction (see also Eq. 1) has been used to prepare most of the other lead compounds known. The insertion reactions of germanium(II) and tin(II) halides do not proceed with divalent lead (*30*). The only complex of lead reported that does not have carbonyl groups attached to the transition metal is $(Ph_3P)_2PtCl(PbPh_3)$, prepared from the reaction of $(Ph_3P)_2PtHCl$ with triphenyllead nitrate (*18*).

The overall instability of lead compounds compared to their tin analogs reflects a weaker metal-metal bond. Thus the Pb—Mn bond in $Ph_3Pb\text{-}Mn(CO)_5$ is readily broken by hydrogen chloride and chlorine (*105*) under conditions where the Sn—Mn bond is not. This behavior may be due to a lower π-contribution in the metal-metal bond due to less favorable overlap, although changes in polarity, hybridization, etc., must also be important.

IV. Complexes of Divalent Tin

A. ANIONIC COMPLEXES

1. *Historical*

Platinum metal salts have long been known to react with tin(II) chloride in hydrochloric acid to give intensely colored solutions (*128*, *250*), which have been used for the detection (*136*, *212*, *235*, *249*) of the platinum metals. Similar color reactions occur with tin(II) bromide and iodide (*24*, *26*, *27*, *196*). The colored solutions can generally be extracted into organic solvents (*9–11*, *99*) capable of coordinating to tin(II). Detailed spectrophotometric studies of these color reactions have been made with platinum (*8*, *9*, *25*, *169*, *172*), rhodium (*12*, *170*), palladium (*11*), and iridium (*27*), and they form the basis of quantitative determinations of the metals.

However, the nature of the chemical species in solution remained uncertain until quite recently. A cationic species $(PtSn_4Cl_4)^{4+}$ was reported by Ayres and Meyer (*10*), but it was later established (*151*, *189*, *223*) that the colored species are ionic in hydrochloric acid solutions for most of the platinum metals.

2. *General Chemistry*

The interesting properties of these compounds of divalent tin are best discussed by considering mainly the behavior of the transition metal, in contrast to most of this review. For this reason the complexes are written as conventional coordination complexes. The chloro complexes were formulated in this way (*77*, *254*): $[PtCl_2(SnCl_3)_2]^{2-}$, $[Rh_2Cl_2(SnCl_3)_4]^{4-}$, $[RuCl_2(SnCl_3)_2]^{2-}$, $[Ir_2Cl_6(SnCl_3)_4]^{4-}$, and $[OsCl_2(SnCl_3)_4]^{4-}$ (*247*).

The trichlorostannite ion is considered to be acting as a donor ligand, using its lone pair of electrons. By this approach the platinum metals maintain well-known oxidation states and stereochemistries, and this is supported by magnetic and conductometric data. Furthermore, tin may be displaced, as tin(II) chloride, from these complexes (*254*) by strong π-bonding ligands such as carbon monoxide and triphenylphosphine. Conversely, stannous chloride can replace more weakly bound ligands such as amines from their complexes, and some replacements with strong ligands (e.g., olefins and carbon monoxide) are reversible.

All the complexes, however, are most conveniently prepared by replacing chloride ion in the chloro complexes by tin(II) chloride in hydrochloric acid (necessary to prevent the hydrolysis of the tin salt) at room temperature (Pt, Rh) or under mild heating (Ir, Ru, Os). Excess of the reagent acts as the reducing agent when the transition metal is converted to a lower oxidation state. The bromo complex of rhodium $[Rh_2Br_2(SnBr_3)_4]^{4-}$ (*1*) has been prepared similarly, and that of iridium detected (*27*) in solution.

3. *Rhodium and Iridium*

Spectrophotometric studies of the rhodium^{III}–tin^{II}–chloride system shows two species whose proportions depend principally on the

$SnCl_3^-:Cl^-$ ratio (*99*). From solutions with a low concentration of the trichlorostannite ion the binuclear anion $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ is precipitated (*77*, *254*), and the electronic spectra of its salts and the original solutions (maxima at 419 mμ and 310 mμ) are the same. In the presence of a large excess of stannous chloride (*12*, *99*, *170*, *254*) the spectrum shifts to higher wavelengths (maxima 470 mμ and 330 mμ), and the intensity of the visible absorption peak increases. The first spectrum can be restored by dilution with hydrochloric acid, since the change is controlled by the $Cl^-:SnCl_3^-$ ratio rather than the Rh : Sn ratio. The tin-rich solutions can be extracted into isoamyl alcohol, and the ion $[Rh(SnCl_3)_4]^{3-}$ has been precipitated (*99*) with large cations as impure salts:

$$(Me_3BzN)_3[Rh(SnCl_3)_4]\cdot 2(Me_3BzN)SnCl_3\cdot SnCl_2 \quad \text{and} \quad (Ph_4As)_3[Rh(SnCl_3)_4]\cdot SnCl_2$$

Similar spectral changes are found when the $Cl^-:SnCl_3^-$ ratio is varied in the iridium^{III}–tin^{II}–chloride system at room temperature (*98*), but only one spectrum results on heating (*27*, *98*, *254*). Whereas Young *et al.* (*254*) isolated the binuclear species $[Ir_2Cl_6(SnCl_3)_4]^{4-}$ from heated solutions, Furlani and co-workers (*98*) report the isolation of $[IrCl_2(SnCl_3)_4]^{3-}$ as double salts with $SnCl_2$ from both aqueous solution and isoamyl alcohol extracts.

4. *Palladium*

In contrast to the behavior of other platinum metals, the palladium^{II}–tin^{II}–chloride system is unstable (*247*), and eventually metallic palladium is deposited from ethanolic solutions. A series of color changes is observed (*11*, *247*) as tin(II) chloride is added to palladium(II) chloride in hydrochloric acid. The addition of mercury salts (*11*, *224*) gives a further color change. A complex between palladium and tin(II) chloride has been isolated (*140*) and formulated as a palladium(I) species $[PdCl(SnCl_3)_2]_2^{4-}$ on the basis of analytical data only. Its chemical properties are not reported, but in view of the complexity of the system it could be impure and may well be either a complex of palladium(II) or (0).

5. *Platinum*

Cis and *trans* isomers of $[PtCl_2(SnCl_3)_2]^{2-}$ have been isolated (*254*) as the tetramethylammonium salts. In solution the interconversion between the two isomers can be followed spectrophotometrically since their electronic spectra are distinct. At Pt : Sn ratios of 1 : 2 a red isomer is first formed in solution, which rapidly changes completely to a yellow form on standing. By selective precipitation both isomers can be obtained separately from the one solution in quantitative yield. The interconversion of the two forms is dependent on the relative concentration of stannous chloride (the Pt:Sn ratio), temperature, and nature of the cation. Both have distinct X-ray powder patterns.

The red and yellow forms are considered to be the *trans* and *cis* isomers, respectively. Several interdependent equilibria probably exist simultaneously in solution:

$$\begin{aligned} SnCl_2 + Cl^- &\rightleftharpoons SnCl_3^- \\ PtCl_4^{2-} + SnCl_3^- &\rightleftharpoons PtCl_3(SnCl_3)^{2-} + Cl^- \\ PtCl_3(SnCl_3)^{2-} + SnCl_3^- &\rightleftharpoons \textit{trans}\text{-}PtCl_2(SnCl_3)_2^{2-} + Cl^- \\ \textit{trans}\text{-}PtCl_2(SnCl_3)_2^{2-} &\rightleftharpoons \textit{cis}\text{-}PtCl_2(SnCl_3)_2^{2-} \end{aligned}$$

In a two-step substitution of tetrachloroplatinite by $SnCl_3^-$ the strong *trans* effect of the latter (see below) favors the initial formation of the *trans* isomer. The conversion to the *cis* form probably occurs via a dissociative mechanism that is suppressed by the addition of excess stannous chloride.

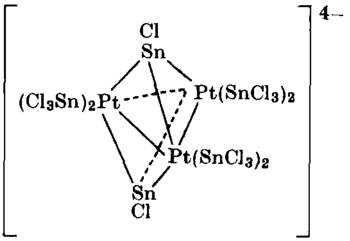
Further coordination by stannous chloride in solutions where the Pt:Sn ratio is >5 forms (*72*) an unusual five-coordinate species $[Pt(SnCl_3)_5]^{3-}$. But complex equilibria must exist in these solutions since under similar conditions Young *et al.* (*254*) isolated only impure solids, which are probably mixtures of $[Pt(SnCl_3)_5]^{3-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$ and possibly other tin species. Complexes of rhodium and iridium could not be isolated from tin-rich solutions (*98*, *99*) without extra tin(II) chloride being precipitated also. However, a preliminary X-ray structure determination (*74*) of $[Pt(SnCl_3)_5]^{3-}$ shows that the five tin atoms are disposed in a trigonal bipyramid about the central platinum atom.

Salts of other five-coordinate species $[HPt(SnCl_3)_4]^{3-}$ and $[HPt(SnCl_3)_2(PEt_3)_2]^-$ have also been prepared (*74*). Another unusual ionic complex, $[Pt_3Sn_8Cl_{20}]^{2-}$, has been prepared (*159*) by treating platinum(II) chloride or $[PtCl_2(SnCl_3)_2]^{2-}$ with stannous chloride according to the equations:

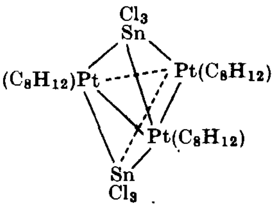
$$3PtCl_2 + 11SnCl_2 + 10Cl^- \rightarrow (Pt_3Sn_8Cl_{20})^{4-} + 3SnCl_6^{2-} \qquad (53)$$

$$3PtCl_2(SnCl_3)_2^{2-} + 5SnCl_2 + 2Cl^- \rightarrow (Pt_3Sn_8Cl_{20})^{4-} + 3SnCl_6^{2-} \qquad (54)$$

The complex is formulated as a platinum-tin cluster (XIII) with platinum formally zerovalent. The terminal trichlorostannite groups can be replaced by cyclo-octa-1,5-diene to give the neutral complex (XIV). Hydrolysis of solutions of (XIII) gives a brown precipitate of empirical formula $PtSn_3Cl_3\cdot 6H_2O$, which probably also has a trimeric structure related to (XIII) with the $SnCl_3$ groups partially hydrolyzed.



(XIII)



(XIV)

B. Carbonyl and Hydride Complexes

1. *Anionic Carbonyls*

Compounds of platinum and rhodium react normally with tin(II) chloride in organic solvents (*254*) to give solutions considered to contain the neutral species, $PtCl_2(SnCl_2{\cdot}solvent)_2$ and $Rh_2Cl_2(SnCl_2{\cdot}solvent)_4$, from which the salts can be precipitated on the addition of bulky cations. However, the reaction between sodium chloroiridate(IV) and tin(II) chloride in alcohols involves the solvent. Refluxing in ethanol or 2-methoxyethanol gives the neutral, binuclear species initially, which subsequently reacts with carbon monoxide, formed from reduction of the solvent, to give the carbonyl complex $[Ir(CO)Cl_3(SnCl_3)_2]^{2-}$ (*234*, *252*). This reaction parallels the formation of carbonyl species from the reaction between iridium salts and triphenylphosphine in alcohols (*239*). Analogous solvent interactions are known for ruthenium (*238*) and, when ruthenium trichloride is refluxed with excess stannous chloride in ethanol or 2-methoxyethanol, carbonyl species are formed (*252*) but have not been identified.

However, ruthenium trichloride reacts directly with carbon monoxide in hot ethanol (*56*), and the subsequent addition (*147*, *227*) of tin(II) halides forms the anion $[Ru(CO)_2X_2(SnX_3)_2]^{2-}$ ($X = Cl, Br$). The chloro complex is formed (*252*) when the chlorine bridges in polymeric $[Ru(CO)_2Cl_2]_n$ are cleaved by stannous chloride. The chlorine bridges in $Rh_2Cl_2(CO)_4$ are also broken (*254*), but one carbonyl group per rhodium atom is also displaced to form $[RhCl(CO)(SnCl_3)_2]^{2-}$. Alternatively, this complex can be formed by cleaving the chlorine bridges in $(Me_4N)_4[Rh_2Cl_2(SnCl_3)_4]$ with carbon monoxide. Air-sensitive $Ir(CO)_3Cl$ (*53*) also reacts with stannous chloride (*252*) to give air-stable solutions containing mixed carbonyl species, which have not been identified. In contrast, stannous chloride completely eliminates carbon monoxide from its platinum complexes (*254*) to give $[PtCl_2(SnCl_3)_2]^{2-}$

2. *Ruthenium Carbonyls*

When ruthenium trichloride is refluxed in ethanol under carbon monoxide, deep red solutions are obtained (*56*). Their composition is unknown but they contain (*227*) a mixture of species. By adding donor ligands, different products can be obtained depending on the conditions and the nature of the ligands. Principal products are $Ru(CO)_2Cl_2L_2$ ($L =$ amines, R_3P, $SnCl_3^-$, R_2S) (*146, 147, 227*) and $Ru(CO)Cl_2(R_3P)_3$ (*227*). The addition of excess of stannous chloride to the red solution gives a yellow solution from which $[Ru(CO)_2Cl_2(SnCl_3)_2]^{2-}$ can be isolated. Subsequent addition of pyridine (*146*) gave $Ru(CO)_2(SnCl_3)_2(pyridine)_2$, but diethyl sulfide gave $[Ru(CO)_2(Et_2S)_3(SnCl_3)]Cl$. Addition of triphenylphosphine (*227*) gives the unusual complex $Ru_2Cl_3(SnCl_3)(CO)(Ph_3P)_3(acetone)_2$ as the initial product. The compound contains free and coordinated acetone and is a 1 : 1 electrolyte, although the $SnCl_3$ group is not ionized. On warming in benzene it changes to $Ru_2Cl_3(SnCl_3)(CO)(Ph_3P)_4$, and on repeated recrystallization gives $Ru(CO)_2Cl_2(Ph_3P)_2$. Addition of triphenylstibine to the yellow solution gives $Ru(CO)_2Cl_2(Ph_3Sb)_2$, which cannot be obtained directly from the original red solution.

3. *Iridium Carbonyls and Hydrides*

Iridium salts are known to react with alcohols and related solvents in the presence of triphenylphosphine to form hydrides (*237*), carbonyls (*239*), and carbonyl hydrides (*239*). In the presence of stannous chloride alone, iridium salts form the carbonyl complex discussed in Section IV,B,1, and their reactions with both triphenylphosphine and stannous chloride in alcoholic solvents have been investigated (*234*). In ethanol, $(Ph_3P)_3IrHCl(SnCl_3)$ is formed under milder conditions than were used by Vaska (*237*) to prepare $(Ph_3P)_3IrHCl_2$. Successive recrystallizations result in complete loss of stannous chloride to give the latter complex. In 2-methoxyethanol, a dihydride complex $(Ph_3P)_3IrH_2(SnCl_3)$ is the main product, and can also be formed by treating $(Ph_3P)_3IrH_2Cl$ with stannous chloride.

Another versatile reaction in iridium chemistry is the formation of iridium(III) complexes by addition reactions (*63, 239*) of the square planar d^8 complex $(Ph_3P)_2Ir(CO)Cl$ (Eq. 4). Treatment with stannous chloride in acetone (*234*) involves the unusual addition of $HSnCl_3$ to form the solvated complex $(Ph_3P)_2Ir(CO)HCl(SnCl_3)acetone$. This compound may also be obtained directly from $(Ph_3P)_2Ir(CO)HCl_2$. The solvent molecule is not coordinated and is lost on recrystallization, but repeated recrystallization leads to a breakdown of the complex to both $(Ph_3P)_2Ir(CO)HCl_2$ and $(Ph_3P)_2Ir(CO)Cl$.

Ethyl methyl ketone and ethyl acetate also promote the addition of $HSnCl_3$, but alcohols, aldehydes, and aliphatic acids do not. If D_2O is added to the active solvents the deuterated complexes are formed. Thus the origin of the hydride ion is from trace amounts of water, and the selectivity suggests that keto-enol equilibria may be responsible for this novel hydrogen transfer reaction.

Stannous chloride also reacts with $(Ph_3P)_2Ir(CO)H_2Cl$ to give $(Ph_3P)_2Ir(CO)H_2(SnCl_3)$, but $(Ph_3P)_2Ir(CO)Cl_3$ remained inert in accordance with other observations (*52*).

4. Rhodium Hydrides

A reversible reaction occurs between *trans*-$(Ph_3P)_2Rh(CO)Cl$ and stannous chloride (*247*) but a hydride species was not formed, and it is considered that the orange product is most probably $(Ph_3P)_2Rh(CO)(SnCl_3)$ although analytical data were unsatisfactory. However, stannous chloride can catalyze the formation of rhodium hydrides. The reaction between rhodium trichloride and stannous chloride in acidified ethanol in the presence of phenyldimethylarsine gave $(PhMe_2As)_3RhHCl_2$ (*252*). The complex is a different isomer from the product of the hypophosphorous acid reduction of $(PhMe_2As)_3RhCl_3$ (*155*).

5. Platinum Hydrides

$(Me_4N)_3[Pt(SnCl_3)_5]$ absorbs hydrogen at 30°C and 50 atm (*74*) to give $(Me_4N)_3[PtH(SnCl_3)_4]$, and the reaction may be followed spectroscopically at lower pressures. A solution of $(Et_3P)_2PtCl_2$ containing two molecules of stannous chloride rapidly absorbs hydrogen at 1 atm, and $[(Et_3P)_2PtH(SnCl_3)_2]^-$ can be isolated as the tetraethylammonium salt. This complex is also formed by the reaction of $[(Et_3P)_2PtH(SnCl_3)]$ (*158*) with $(Et_4N)SnCl_3$. Two distinct isomers of $(Ph_3P)_2PtH(SnCl_3)$ (*15*, *18*) have been prepared from *trans*-$(Ph_3P)_2PtHCl$ and stannous chloride. A trace of $SnCl_2$ will catalyze *cis-trans* isomerization in the hydrido complexes.

C. COMPLEXES WITH GROUP V LIGANDS

Addition of triphenylphosphine to ethanolic $PtCl_2(SnCl_2{\cdot}solv.)_2$ precipitates $(Ph_3P)_2PtCl(SnCl_3)$ (*254*). The complex disproportionates readily in acetone to form $(Ph_3P)_2PtCl_2$, which will react (*18*, *72*, *254*) with excess stannous chloride to give the tin complex again. Two isomers of the complex have been isolated (*18*), and $(Ph_3P)_2Pt(SnCl_3)_2$ has been reported (*72*) when a large excess of stannous chloride is used. $(Ph_3As)_2PtCl(SnCl_3)$ is less easily dissociated (*254*) and requires excess of chloride ion to completely displace $SnCl_3^-$. Stannous chloride also adds readily to other phosphine complexes to give $(R_3P)PtX(SnCl_3)$, where X = fluorophenyl, phenyl (*158*, *198*), hydroxide (*15*), and hydride (*15*, *18*). $(Ph_3P)_2PtHCl$ also reacts (*18*) with stannic chloride to give the platinum(IV) complex $(Ph_3P)_2PtCl_2(SnCl_3)_2$, which readily reverts to the divalent species on recrystallization.

Treatment of $Rh_2Cl_2(SnCl_2{\cdot}solv.)_4$ with triphenylphosphine gives $(Ph_3P)_3RhSnCl_3$ (*254*) on refluxing. A phosphine group and $SnCl_2$ both readily dissociate from the complex in solution. The lability of the phosphine molecule must be related to the behavior of $(Ph_3P)_3RhCl$ (*20*, *193*), since the tin(II) complex can be prepared directly from the chloride (*247*). $(PhMe_2As)_3RhCl_2(SnCl_3)$ is formed (*252*) when rhodium trichloride and the arsine are refluxed in ethanol with excess of stannous chloride. The compound is unusual in that rhodium has not been reduced to the +1 state, but $(PhMe_2As)_3RhCl$ may be an intermediate since, when hydrochloric acid is present, $(PhMe_2As)_3RhHCl_2$ is formed. This system was first investigated by Dwyer and Nyholm (*88*), who described several compounds containing both tin and rhodium; it now seems likely that these compounds contained the trichlorostannato ligand.

D. OLEFIN COMPLEXES

The addition of diolefins to ethanolic $Rh_2Cl_2(SnCl_2{\cdot}solv.)_4$ generally gives (*254*) the well-known dimeric species $(diolefin)_2Rh_2Cl_2$ by direct displacement of the tin groups. But when norbornadiene (NBD) (2.2.1-bicyclohepta-1,5-diene) is used, a new tin complex $(NBD)_2RhSnCl_3$ is formed (*254*). The complex is monomeric and nonconducting in nitromethane, but shows appreciable conductance in dimethylformamide (*252*). From hot aqueous solutions a tetraphenylborate salt can be precipitated (*254*), leaving tin(II) chloride in solution:

$$(NBD)_2RhSnCl_3 \rightleftharpoons (NBD)_2Rh^+ + SnCl_3^- \qquad (55)$$

One diolefin molecule can be replaced by another bidentate or two monodentate ligands (see Table V). The complex also adds chlorine (*247*) to form an insoluble rhodium(III) complex, $(NBD)_2RhCl_2(SnCl_3)$. The compound is probably six-coordinate, since the infrared spectrum shows the characteristic absorption of an uncoordinated double bond; in solution it readily reverts back to its rhodium(I) precursor. The dipyridyl derivative also adds chlorine (*247*) to form $(NBD)(dipyridyl)RhCl_2(SnCl_3)$ but, since no free double bond was detected in this compound, the dipyridyl molecule may be acting as a monodentate ligand.

TABLE V

OLEFIN COMPLEXES OF RHODIUM AND IRIDIUM WITH $SnCl_3$

Compound	Color	M.P. (°C)	Λm mhos (10^{-3} M)		Reference
			$MeNO_2$	DMF[a]	
$(NBD)_2RhSnCl_3$	Yellow	d170–177	3.3	75	(*254*)
$(NBD)_2RhBPh_4$	White	—	—	25	
$(NBD)(Ph_3P)_2RhSnCl_3$	Orange	134–135	8.7	9.1	
$(NBD)(Ph_3As)_2RhSnCl_3$	Orange	d177–179	5.1	7.7	
$(NBD)(Ph_3Sb)_2RhSnCl_3$	Orange	d200	5.0	—	
$(NBD)(diphosphine)RhSnCl_3$	Yellow	—	—	—	(*247*)
$(NBD)(dipyridyl)RhSnCl_3$	Purple	135–136	—	—	
$(NBD)_2RhCl_2(SnCl_3)$	Orange-pink	—	(dissociates)		
$(NBD)(dipyridyl)RhCl_2(SnCl_3)$	Orange-pink	—	—	—	
$(NBD)_2IrSnCl_3$	Pale yellow	d230–240	(insol.)	65	(*254*)
$(COD)_2IrSnCl_3$	Yellow	d178–180	9.7	68	(*213, 254*)
$(COD)_2IrBPh_4$	White	d225–230	—	—	(*254*)
$(COD)(Ph_3P)IrSnCl_3$	Yellow	d127–130	21	30	
$(COD)(Ph_3As)_2IrSnCl_3$	Yellow	171–174	11	16	
$(QAS)IrSnCl_3$	Orange	330	—	—	(*213*)
$[(QAS)IrClSnCl_3]Cl$	Pale yellow	330	—	—	

[a] DMF = dimethylformamide.

Iridium also forms diolefin complexes of the type $(diolefin)_2IrSnCl_3$ (*213*, *254*) with norbornadiene and cyclo-octa-1,5-diene. Cyclo-octa-1,3-diene is isomerized on reaction to form the 1,5 complex, a well-known rearrangement in transition metal chemistry (*97*, *185*, *217*), but the less common isomerizations of 4-vinylcyclohex-1-ene to cyclo-octa-1,5-diene (COD) and cycloheptatriene to norbornadiene are also observed (*254*).

$(NBD)_2IrSnCl_3$ is rather inert; it does not ionize appreciably, does not undergo substitution, and has high thermal stability. However, $(COD)_2IrSnCl_3$ ionizes in aqueous dimethylformamide solutions and both diolefin molecules are displaced (*213*) by the quadridentate arsine, tris(diphenylarsinophenyl)arsine (QAS) to give $(QAS)IrSnCl_3$. The latter can be oxidized by chlorine to give $[(QAS)IrCl(SnCl_3)]Cl$, although addition of chlorine to $(R_3P)_2(COD)IrSnCl_3$ was not observed (*247*). A crystal structure determination (*213*) of $(COD)_2IrSnCl_3$ shows it to have a distorted trigonal bipyramid configuration with the $SnCl_3^-$ group occupying an equatorial position.

V. Catalytic Behavior of Group IVB Complexes

There has been renewed interest in recent years in the role of transition metal complexes in the catalytic reactions of unsaturated organic molecules. Group IVB complexes have been found to have useful catalytic properties toward some reactions of olefins.

A. HYDROGENATION OF OLEFINS

Methanolic solutions of tin(II) chloride and chloroplatinic acid will quantitatively reduce (*72*) ethylene and acetylene with hydrogen at ambient temperature and pressure. It is one of the few catalysts that will reduce simple olefins and acetylenes under these conditions without the presence of activating groups. The reaction is first order with respect to platinum and is a maximum at Sn:Pt ratios >5:1. A hydride species $[PtH(SnCl_3)_4]^{3-}$ has been detected (*74*) under the conditions of catalysis, while the action of ethylene alone forms Zeiss's salt $K[PtCl_3\cdot C_2H_4]\cdot H_2O$ (*72*) and rapid exchange between free and coordinated ethylene is observed in solution. Thus the ability of the platinum-tin(II) chloride species in solution, probably $Pt(SnCl_2\cdot solv.)_5$, to cleave the hydrogen molecule, and to coordinate both a hydrogen atom and the organic molecule, allows reaction between the two to take place at the metal probably via an alkyl intermediate. These factors, which are relevant to current ideas on catalytic hydrogenation, have been discussed at length elsewhere (*193*). The failure of this system to hydrogenate higher olefins appears to be due to their inability to complex with platinum as a result of steric and electronic factors.

The same system has also been used successfully (*15*, *17*, *96*) to hydrogenate polyunsaturated fatty esters, such as occur in soybean oil, at moderate temperatures and pressures (90°C, 500 psi). The products are predominantly mono-olefinic esters with only small amounts of the saturated esters being formed. Complexes with Group V donors, $(R_3M)_2PtCl_2$ (M = P, As, Sb), which are soluble in organic solvents, give only limited hydrogenation. This is increased by the addition of Group IV halides (*17*). For $(Ph_3P)_2PtCl_2$, catalytic activity decreases in the order $SnCl_4 > SnCl_2 > GeCl_4 > GeCl_2 > PbCl_2 > SiCl_4 > SiHCl_3$. Reactions between tin chlorides and $(Ph_3P)_2PtCl_2$ are known (*18*, *72*, *254*) to give trichlorostannato complexes, so it is likely that a direct reaction between the other Group IV halides and platinum also takes place. Both $(Ph_3P)_2Pt(GePh_3)_2$ and $(Ph_3P)_2PtCl(SnCl_3)$ can activate hydrogen (*74*, *102*) under catalytic conditions to give hydride complexes.

The catalytic activity of $(Ph_3P)_2PdCl_2$ is also enhanced (*126*) by the addition of stannous chloride and to a lesser extent by germanous chloride, and it is more effective than the platinum complex. The cyanide complex $(Ph_3P)_2Pd(CN)_2$ is a good catalyst on its own and does not react with stannous chloride, but the platinum compound is inactive. By contrast, the catalytic action of bis(triphenylphosphine)nickel halides is inhibited (*127*) by the addition of stannous chloride.

With these catalysts, hydrogenation essentially stops at the mono-enes and considerable isomerization of the double bonds is also observed. It is considered (*17*, *96*) that the double bond migration precedes hydrogenation and continues until a conjugated system is formed. The conjugated olefin can coordinate strongly enough for hydrogenation, but the ensuing mono-ene does not remain at the platinum atom for further reduction. This is in keeping with the failure of $Pt(SnCl_2\cdot solv.)_5$ to reduce olefins higher than ethylene (*72*), so that isomerization (*31*, *73*) becomes the dominant reaction.

The formation of platinum hydrides under the conditions of catalysis is observed (*15*, *17*) but, since hydrogenation can occur in methanol in the absence of hydrogen (*17*), hydride abstraction from the solvent must occur. Hydride ion transfer from alcohols to a transition metal ion is now a common synthetic procedure (*101*), and the dehydrogenation of isopropanol to acetone is catalyzed (*49*) by $Rh_2Cl_2(SnCl_2\cdot solv.)_4$.

The coordinating power of the solvent also affects the rate of hydrogenation, and the nature of the ligands is important too. Thus the catalytic activity depends on the π-bonding abilities of the Group VB ligands (*17*) and the nature of the halide ion (*127*), but the efficiency of such catalysts probably depends not only on the lability and stability of the intermediate hydride complexes, as determined by electronic factors, but also on the ability of the metal to increase its coordination number (*17*, *193*).

$(Ph_3P)_2PtH(SnCl_3)$ has been used (*129*) to reduce the chelating non-conjugated diolefin norbornadiene to norbornane. $(Ph_3P)_3IrH_2(SnCl_3)$ forms a complex with norbornadiene and hence does not reduce it, but sodium hexachloroiridate(IV) with stannous chloride will catalyze this reaction. The rate is a maximum at $Sn:Ir = 3.5$, which suggests that $Ir_2Cl_6(SnCl_2\cdot solv.)_4$ is the active species. $Rh_2Cl_2(SnCl_2\cdot solv.)_4$ has been used (*194*) to hydrogenate hex-1-ene to hexane, whereas under similar conditions but-1-ene was only isomerized (*126*).

B. HYDROSILATION OF OLEFINS

The addition of silicon halides to carbon double bonds, as catalyzed by chloroplatinic acid, has been studied in detail by Speier and his coworkers (*220*, *226*). It has recently been shown (*46*, *220*), contrary to earlier assumptions (*19*), that the catalysis is homogeneous. Olefin complexes of platinum(II) and rhodium(I) (*46*) and dicobalt octacarbonyl (*48*, *108*) are also good hydrosilation catalysts, although extensive isomerization occurs in all cases.

The major requirements for good hydrosilation catalysts (*46*) are similar to those for hydrogenation (*193*), namely: (*i*) the ability to activate the silane (Si—H bond breaking), (*ii*) the ability to activate the olefin, and (*iii*) the resistance to destructive reduction. The failure of palladium compounds as catalysts is due to factor (*iii*), while platinum(II)- and iridium(I)-phosphine complexes are probably ineffective as the result of (*ii*). However, the formation of stable silicon complexes with the latter may be the real problem, since it has been shown (*48*) that the catalytic power of dicobalt octacarbonyl is decreased by the formation of silicon complexes. This will inhibit olefin coordination by the effective blocking of a coordination site.

C. HYDROGERMANATION OF OLEFINS

Recently evidence has been obtained (*93*) that the addition of alkylgermanes to olefins is also catalyzed homogeneously by chloroplatinic acid. The 1,4 addition of trimethylgermane to cyclopentadiene and butadiene is an example of "coordination control" by the catalyst. Similarly, 1,4- and 1,5-cyclo-octadiene are converted to the 1,3 isomer in the presence of both chloroplatinic acid and trimethylgermane, at a much faster rate than hydrogermanation. In the absence of either chloroplatinic acid or trimethylgermane, there is no isomerization (and no hydrogermanation).

D. ISOMERIZATION OF OLEFINS

Mention has been made of the concurrent migration of double bonds in olefins during reduction reactions by transition metal catalysts. The features of catalytic isomerization (*73*) are similar to those of reduction reactions, namely, the formation of a metal hydride, generally from a cocatalyst such as hydrogen, alcohol, or acid, and the simultaneous coordination of an olefin molecule that can rearrange via an alkyl complex. The isomerization of butenes by $Pt(SnCl_2{\cdot}solv.)_5$ and $Rh_2Cl_2(SnCl_2{\cdot}solv.)_4$ has been studied in detail (*126*). The rearrangement of diolefins during the preparation of $(\text{diene})_2IrSnCl_3$ was mentioned earlier.

E. REDOX REACTIONS

It is possible that the reduction of metal ions to a lower oxidation state by tin(II) chloride can in many cases involve an intermediate complex between the two. Thus the reduction of chloroplatinic acid to $[PtCl_2(SnCl_3)_2]^{2-}$ may involve an initial complex between platinum(IV) and tin(II) chloride, which decomposes to the platinum(II) complex [see, for example, Baird (*18*)]. The chloro complexes of platinum(II), rhodium(I), and ruthenium(II) (see p. 118) have very intense bands in their visible spectra, which indicate considerable charge transfer between the two metal atoms. A redox reaction will be initiated by a complete charge transfer from the metal to the tin atom in the higher valency complexes, and this process can continue right to the metal, as with palladium, or to a stable zerovalent complex (*159*). During the reduction of uranium(VI) to uranium(IV) a 1:1 complex between U(IV) and Sn(II) (*175*) was detected spectrophotometrically. The kinetic first order dependence of both reagents suggests that the formation of this complex may be the rate-determining step. A 1:1 complex between U(IV) and Sn(II) was also observed, but no further reduction takes place. It has been suggested (*89*) that complex formation may also be involved in the reduction of vanadium(V). However, it is considered (*225*) that an electron transfer process can take place between divalent tin and a transition metal ion across a bridging chelate ligand, such as tartrate or citrate.

VI. Bonding in Group IVB Complexes

A. STRUCTURAL STUDIES

The bonding between a coordinated transition metal and Group IVB moiety creates nothing new in the stereochemistry observed for either the transition metal or the Group IVB atom. Therefore it is only necessary to consider effects causing distortions of coordination and the lengths of the metal-metal bonds. Table VI lists data from reported crystal structure determinations, which are relevant to the following discussions.

1. Bond Angles

Monosubstituted complexes, whose structures are known, all show slight but significant deviations from regular tetrahedral coordination

TABLE VI

STRUCTURAL DATA FOR GROUP IVB COMPLEXES

Compound	Bond lengths (Å)		Contraction[a]	Bond angles (°)[b]		Ref.
	M—E	e.s.d.		C-E-C or Cl-E-Cl	M-E-M or M-E-C	
Cl_3Si-$Co(CO)_4$	2.254	0.003	0.015	105	113[c]	(*218*)
Ph_3Ge-$Mn(CO)_5$	2.54	0.02	0.05	—	—	(*141*)
	2.60	—	0.01	—	—	(*229*)
$Cl_2Ge[Fe(CO)_2Cp]_2$	2.36	0.01	0.10	96	128	(*41*)
Me_3Sn-$Mn(CO)_5$	2.674	0.003	0.10	107	112[c]	(*40*)
Ph_3Sn-$Mn(CO)_5$	2.674	0.004	0.10	106	113[c]	(*242*)
Ph_3Sn-$Mn(CO)_4(Ph_3P)$	2.627	0.01	0.14	105	115[c]	(*38*)
$Ph_2Sn[Mn(CO)_5]_2$	2.70	0.01	0.07	100	117	(*142*)
Ph_3Sn-$Fe(CO)_2Cp$	2.536	0.003	0.10	105	113[c]	(*39*)
$Cl_2Sn[Fe(CO)_2Cp]_2$	2.49	—	0.15	94	128	(*65*)
$Me_4Sn_3[Fe(CO)_4]_4$	2.747 (internal)	0.008	−0.11[d]	—	99, 115	(*232*)
	2.265 (terminal)	0.008	0.01	108	105	
$Sn[Fe(CO)_4]_4$	2.54	0.01	0.10	—	69, 133	(*70, 71, 157*)
Cl_3Sn-$Ir(COD)_2$	2.642	0.002	0.12	—	113, 124[c]	(*213*)

[a] Comparison with the sum of metallic covalent radii (see text).
[b] Average values.
[c] Values for M-E-C angles.
[d] Bond lengthening.

about E. The more marked distortion from regular tetrahedral bond angles at the tin atom that occurs in $Ph_2Sn[Mn(CO)_5]_2$ (*142*), compared with Ph_3Sn-$Mn(CO)_5$ (*242*), probably arises from mutual repulsion of the two bulky manganese pentacarbonyl groups. It has been suggested (*232*) that the molecular geometry of $Me_4Sn_3[Fe(CO)_4]_4$ (structure XI), which has similarly distorted bond angles, is the result of distortion from normal octahedral and tetrahedral valency angles and bond lengths to relieve steric interactions. The bond angles in $Cl_2E[Fe(CO)_2Cp]_2$ [E = Ge (*41*), Sn (*65*)] are even more distorted and approach those in $Sn[Fe(CO)_4]_4$ (*71, 157*), where three-center Fe—Sn—Fe bonds involving *d* orbitals on the tin atom have been postulated. Thus it is likely that the localized E—Fe bonds have some multiple bond character arising from d_π-d_π overlap.

2. *Bond Lengths*

Reported metal-metal distances provide evidence for multiple bonding. Nearly all observed metal-metal bonds show appreciable shortening from the theoretical bond lengths calculated from metallic covalent radii (*230*). [Examination of reported bond lengths (*22*, *152*, *190*, *230*) shows that the metallic radii are reasonable values for effective covalent radii in organometallic complexes.] It is realized that bond lengths will be sensitive to other electronic and steric factors. In crystallographic studies, only differences greater than 3 times the estimated standard deviation (e.s.d.) are considered significant. The reported bond lengths for a number of other Group IVB complexes (*195, 229*) have not been considered, since calculations were made from two-dimensional determinations and e.s.d.'s are not reported. Values of e.s.d.'s are quoted in Table VI.

In R_3Sn-$Mn(CO)_5$ (*40*, *242*) the observed Sn—Mn bond length is independent of R and about 0.1 Å less than the sum of the covalent metal radii. Substitution of the carbonyl group *trans* to R_3Sn by a phosphine molecule of lower π-acceptor properties shortens the Sn—Mn bond still further (*38*). This is consistent with an increase in multiple bond character in the metal-metal bond as a result of less competition by the phosphine group for the electrons in *d* orbital on the manganese atom, which are used in Sn—Mn π-bonding. Bond shortening in Ph_3Sn-$Fe(CO)_2Cp$ (*39*) is similar to that in Ph_3Sn-$Mn(CO)_5$, which suggests that, in the first transition period at least, the important factor is the π-bonding abilities of the remaining ligands. An order of π-bonding ability appears to be $Cl_3Sn > Ph_3Sn > Ph_3Ge$; the presence of the highly electronegative chlorine atom attached to E is expected to increase the π-acceptor properties of a group.

In $Ph_2Sn[Mn(CO)_5]_2$ (*142*) the Sn—Mn bond is longer than in Ph_3Sn-$Mn(CO)_5$ (*242*), and competition for the *d* orbitals of the tin atom might be expected to reduce the π-contribution in each Sn—Mn bond. In $Me_4Sn_3[Fe(CO)_4]_4$ (structure XI), the four iron atoms attached directly to the central tin atom actually have bonds longer than the sum of the atomic radii, and this fact, together with the observed bond angle distortions, may be deemed solely the result of steric interactions (*232*). Thus there is a progressive lengthening in the metal-metal bonds when more transition metal groups bond to tin. The molecule $Sn[Fe(CO)_3]_4$ (*71*, *157*) has Sn—Fe bonds shorter than expected and severely distorted bonding angles, and in this case there are iron-iron interactions involving the tin *d* orbitals. Therefore even shorter Sn—Fe bonds in $Cl_2Sn[Fe(CO)_2Cp]_2$ (*65*) give good evidence for considerable π-bonding in the separate metal-metal bonds. There are no Fe-Fe interactions, but there are only two irons attached to tin and two electronegative chlorines. Furthermore, the Sn—Cl and Ge—Cl bonds are close to the covalent radii sum and longer than those in the ECl_4 compounds (*230*), and it seems plausible that a significant ($d \rightarrow d$) π-bonding between the metals is preferred to any ($p \rightarrow d$) π-bonding in the E—Cl bond. From bond length data an order of π-bonding ability for disubstituted compounds would be $Cl_2Sn > Cl_2Ge > Ph_2Sn$.

Effects on σ-bonding can effectively be ignored. Electronegative substituents on E will be expected to lengthen the metal-metal σ-bond, by increasing the positive charge on E, and shorten E—X bonds. Distortions in coordination affect bond lengths and this may be considered by using the concept of hybridization. There is NMR evidence that the *s* character in the metal-metal σ-bond is increased to about 30 %, and distortions from tetrahedral symmetry at E are generally observed in the crystalline state. Bent (*23*) finds that changes in bond length are less than 0.05 Å for first-row elements when changing from sp^3 to sp^2 hybridization. E—E bond lengths in X_3E-EX_3 compounds where there is no π-bonding vary only slightly with the nature of X.

B. Infrared Spectra

1. *Carbonyl Stretching Frequencies*

R_3E-$Mn(CO)_5$ complexes have a ($2A + E$) band pattern in the carbonyl region (*130*) consistent with C_{4v} symmetry for the $Mn(CO)_5$ group (*67*, *192*), and this is confirmed by structural determinations in the solid state. A further band is observed in some cases and can be assigned to the Raman-active B_1 mode. Accidental degeneracy can also occur. The appearance of this normally infrared inactive mode is due to the nonspherical top symmetry of the R_3E group, and is most marked when the group is asymmetric as for Me_2ClSn— (*130*). Infrared data and band assignments for the R_3E-$Mn(CO)_5$ complexes and some related compounds are given in Table VII. Qualitatively, the lowering of the carbonyl frequencies is of the order expected for changes in electronegativity: $Cl > Br > Me > Ph_3E$, but it can be seen that by this criterion the higher apparent electronegativity of X_3Sn compared with X shows that inductive effects are not the only factor to be considered.

Force field calculations (*130*) by the method of Cotton and Kraihanzel (*67*) give force constants that separate the inductive and mesomeric effects. In Table VII, the k_1 and k_2 listed refer to stretching force constants for the carbonyl groups *trans* (axial) and *cis* (equatorial), respectively, to the substituent group; k_1 will be affected more by changes in the *d*-orbital interactions between E, M and *trans*-CO, while k_2 is influenced mainly by inductive electronic effects. Increasing values of k_1 reflect increasing π-acceptor properties of the substituent group, and increasing values of k_2 reflect increasing electron-withdrawing power, although inductive effects will probably contribute to some extent to the values of

TABLE VII

INFRARED SPECTRA OF MANGANESE PENTACARBONYL COMPLEXES

Compound	Carbonyl stretching frequencies (cm^{-1}) $A_1^{(1)}$	E	B_2[a]	$A_1^{(2)}$	k_2[b]	k_1[b]	$10^2(k_2 - k_1)$[b]	Ref.
$ClMn(CO)_5$	2138	2054	2022	1999	17.48	16.22	126	(*122*)
HCF_2-$CF_2Mn(CO)_5$	2134	2044, 2041	2073	2015	17.33	16.51	82	(*246*)
$MeMn(CO)_5$	2116	2011	—	1990	16.82	16.11	71	
Ph_3Si-$Mn(CO)_5$	2098	2003	2030	2003	16.67	16.36	31	(*130*)
Ph_3Ge-$Mn(CO)_5$	2097	2006	2032	2002	16.70	16.33	37	
Ph_3Pb-$Mn(CO)_5$	2091	2003	2029	2003	16.64	16.35	29	
Ph_3Sn-$Mn(CO)_5$	2093	2002	2027	2002	16.64	16.34	30	
Me_3Sn-$Mn(CO)_5$	2089	1991	2021[c]	1998	16.49	16.29	20	
Me_2ClSn-$Mn(CO)_5$	2101	2006	2039	2015	16.72	16.57	15	
Br_3Sn-$Mn(CO)_5$	2126	2046	2060	2039	17.26	16.88	38	
Cl_3Sn-$Mn(CO)_5$	2122	2043	2070[c]	2037	17.31	16.91	40	

[a] Normally infrared inactive mode.

[b] Values in mdynes/Å from Jetz *et al.* (*130*).

[c] B_2 mode not observed, calculated value given.

k_1. Such criteria indicate that R_3E groups have better π-accepting properties than the chloride ion, and the replacement of the organo groups on E by halogens greatly enhances this. The order of π-acceptor abilities based on force constant data is $Cl_3Sn \sim Br_3Sn > Me_2ClSn > Ph_3E > Me_3Sn > Cl > Me$, whereas that of inductive effects is $Cl > X_3Sn > Me > Me_2ClSn > Ph_3E > Me_3Sn$. Similar results are obtained (*130*) from a consideration of the corresponding rhenium derivatives. However, such calculations are approximate, and it would be unwise to predict the order of π-accepting properties in the Ph_3E series from the small differences observed in their k_1 values. The difference $(k_2 - k_1)$ might give a better measure of the π-bonding of a substituent, provided the inductive effects are the same for both force constants. It is found that the R_3E groups cause much smaller $(k_2 - k_1)$ differences $(k_2 > k_1)$ than occur when strong σ-bonding substituents are present. This can be attributed to their greater effect on k_1 through π-bonding, although the values for Ph_3Ge and Cl_3Sn seem anomalously high.

Hagen and MacDiarmid (*107*) have recently analyzed the spectra of silicon cobalt tetracarbonyls. The carbonyl stretching frequencies are consistent with C_{3v} symmetry both in the gas phase and in solution (*47*) and have been assigned to $(2A + E)$ modes (Table VIII). (Splitting of the E mode is observed in solution and when the silicon group is asymmetric.)

This finding is in agreement with the structure determination of Cl_3Si-$Co(CO)_4$ (*218*). From these assignments, force constants k_e (for the equatorial carbonyl) and k_a (for the axial carbonyl, *trans* to the substituent) have been calculated by Cotton and Kraihalzel's method (*67*). By arguments similar to those used for the manganese pentacarbonyl complexes,

TABLE VIII

INFRARED SPECTRA OF COBALT TETRACARBONYL COMPLEXES

Compound[a]	A_1 (equatorial)	A_1 (axial)	E (equatorial)	k_e[b]	k_a[b]	$10(k_e - k_a)$	Ref.
HCF_2-$CF_2Co(CO)_4$	2126m	2060s	2052vs, 2048vs	17.62	17.15	47	(*245*)
$CF_3Co(CO)_4$[c]	2103m	2066vs, sh	2051s	17.67	17.25	42	(*116*)
$MeCo(CO)_4$[c]	2111w	2046m	2031s	17.34	16.91	43	(*167*)
$(MeO)_3Si$-$Co(CO)_4$	2105s	2040vs	2025vs, 2010vs, sh	17.17	16.81	36	(*47*)
F_3Si-$Co(CO)_4$[c]	2128w	2073m	2049s	17.63	17.36	27	(*107*)
Cl_3Si-$Co(CO)_4$[c]	2125w	2071m	2049s	17.60	17.33	27	
Ph_3Si-$Co(CO)_4$	2100s	2040s	2015vs, 2010s, sh	17.08	16.81	27	(*47*)
Me_3Si-$Co(CO)_4$[c]	2100m	2041ms	2009s	17.07	16.83	24	(*107*)
Cl_3Ge-$Co(CO)_4$	2122ms	2069ms	2050vs	17.59	17.30	29	(*207*)
Br_3Ge-$Co(CO)_4$	2118ms	2066ms	2048vs	17.52	17.25	27	
I_3Ge-$Co(CO)_4$	2113s	2062ms	2042vs	17.44	17.18	26	
$PhCl_2Ge$-$Co(CO)_4$	2112s	2056s	2038vs, 2027vs	17.36	17.09	27	
Ph_2ClGe-$Co(CO)_4$	2101s	2043s	2026vs, 2010vs	17.14	16.86	28	
Ph_3Ge-$Co(CO)_4$	2091s	2030s	2006vs	16.96	16.65	31	
Cl_3Sn-$Co(CO)_4$	2120s	2068ms	2048vs	17.54	17.28	26	
I_3Sn-$Co(CO)_4$	2109s	2058m	2037vs	17.37	17.11	26	
Ph_3Sn-$Co(CO)_4$	2087ms	2027m	1999vs	16.88	16.57	31	
Me_3Sn-$Co(CO)_4$	2082s	2020ms	1988vs	16.74	16.49	25	
Ph_3Pb-$Co(CO)_4$	2081s	2022m	1997vs	16.80	16.52	28	

[a] Spectra measured in hydrocarbon solvent.
[b] Values in mdynes/Å.
[c] Gas phase.

k_a is affected predominantly by changes in π-bonding, and k_e by inductive changes. Comparisons have been made by considering their difference $(k_e - k_a)$, which is insensitive to the phase in which the spectra are measured. π-Bonding by the substituent will increase k_a more than k_e and hence decrease the difference between them. The fact that $(k_e - k_a)$ for the silicon complexes is about half that for methyl and fluorocarbon complexes strongly suggests that there is π-bonding in the Si—Co bond.

Related germanium, tin, and lead complexes (*207*) have similar infrared spectra, and the same assignments have been made in the carbonyl region. Calculations of the force constants for these compounds have been made (*253*) using Hagen and MacDiarmid's equations (*107*) and, although there is evidence (*207*) of appreciable coupling between the $A_{1(a)}$ and $A_{1(e)}$ modes, which has been ignored, similar results are obtained. The $(k_e - k_a)$ values lie between 0.24 and 0.30 for all R_3E derivatives (R = halogen, phenyl, methyl), which suggests that π-bonding occurs in all cases. If these differences fairly represent π-bonding capacity, then the general order is $Me_3E > X_3E > Ph_3E > (MeO)_3E$, which is different from the order generally accepted (*3*, *191*) when E is replaced by P, As, or Sb. The high value of $(k_e - k_a)$ for $(MeO)_3Si$ may well be the result of $(p \rightarrow d)$ π-bonding between silicon and oxygen (*58*, *90*) competing with the overlap of π orbitals in the metal-metal bond. The values for the halide and phenyl derivatives are probably also affected in the same way, although the relative extent of this effect is not known. Values for germanium and tin suggest that π-bonding with halogens falls off from chlorine to iodine with germanium and is absent with tin, but that in both cases π-bonding with phenyl is appreciable. Thus the observed order of π-accepting ability for Group IVB ligands is not a simple picture.

Values of k_a give the expected order $X_3E > Ph_3E > Me_3E$, but there is no universal order of π-bonding for metals E. Different orders are obtained depending on the nature of their attached atoms and whether $(k_e - k_a)$ or k_a values are considered. There are too many assumptions inherent in the calculations to allow this point to be resolved satisfactorily. Similar conclusions are found for the manganese pentacarbonyl complexes: $(k_2 - k_1)$ values are spread more widely but give the order $Me_3Sn > Ph_3Sn > X_3Sn$, while k_1 values give $X_3Sn > Ph_3Sn > Me_3Sn$.

The spectra of $R_3E\text{-}M(CO)_3Cp$ (M = Cr, Mo, W) derivatives show three strong terminal carbonyl stretching frequencies, as do the halogen compounds (*211*), and most probably have the same molecular symmetry as $EtMo(CO)_3Cp$ (*21*) and $[Mo(CO)_3Cp]_2$ (*248*) although the alkyl derivatives (*211*) have only two carbonyl bands. Qualitative considerations of the frequencies give an order of "effective electronegativity" based on mean carbonyl frequencies as $Cl_3Sn > X > \text{alkyl} > Me_2ClSn > Ph_3E$. The position of Cl_3Sn suggests that there is appreciable π-bonding in these complexes too, although without the separation of inductive and mesomeric effects no further conclusions can be drawn.

Similarly, $X_3Sn\text{-}Fe(CO)_2Cp$ complexes (*191*) have the same spectra as the alkyl (*211*) and halogen (*208*, *210*) compounds. The order of "effective electronegativity," $CN > X \sim X_3Sn > PhCl_2Sn > Ph > Me > Me_3Sn$, indicates that the probable π-bonding order is $CN > Cl_3Sn > Cl$, which is in agreement with a more quantitative assessment (*158*). The *cis* configuration of $(R_3E)_2Fe(CO)_4$ has been proved from infrared data. D_{4h} symmetry of the *trans* isomer would give only one infrared-active mode (E_v), whereas four are expected (A_1, A_2, B_1, B_2) for the *cis* isomer (C_{2v} symmetry), as observed (*132*). This was confirmed by dipole moment measurements.

Disubstituted compounds are more difficult to analyze. Compounds of the type $R_2Sn[Co(CO)_3L]_2$ (*28*) often show more carbonyl bands than are required for local symmetry of the cobalt atoms but less than are required for total symmetry. Spectra measured in chlorinated solvents indicate that L is *trans* to the R_3Sn group, but in nonpolar solvents a greater number of bands is observed. A partial assignment of bands has been made (*207*) for the germanium complexes. An assignment can be made (*133*) for $[R_2E\text{-}Fe(CO)_4]_2$ on the basis of D_{2h} symmetry. Carbonyl frequencies increase in the order Pn < Sn < Ge.

An interpretation of the spectra for $R_2E[Fe(CO)_2Cp]_2$ considered (*94*) three distinct structures of C_{3v}, C_s, and C_1 symmetries, which all predict the observed number of carbonyl frequencies. From analysis of relative intensities, the alkyl derivatives were assigned C_s symmetry and the halogen compounds C_1. However, a recent structure determination (*41*) of $Cl_2GeFe(CO)_2Cp_2$ shows it to have C_2 symmetry in the crystal; but this case was not considered in the infrared analysis, although it will give rise to the same number of carbonyl bands that are observed.

2. *Metal-Halogen Stretching Frequencies*

Platinum-cholorine stretching frequencies have been used by Adams *et al.* (*2*) as a measure of the *trans* effect of Y in the series *trans*-L_2PtYCl, since ν(Pt—Cl) is insensitive to the nature of L. If Y is a ligand with a strong inductive *trans* effect, then a large decrease in ν(Pt—Cl) overshadows any effects from changes in the electronegativity of Y. Table IX shows that silicon and germanium ligands have very strong inductive *trans* effects, considerably greater than alkyls or aryls, while Ph_3Sn and Ph_3Pb are comparable to the hydride ion. ν(Pt—Cl) for the trichlorostannato ion seems abnormally high in view of the high *trans* effect found from n.m.r. data (*158*). But the mesomeric origin of this effect can actually lead to a strengthening of the Pt—Cl bond, as appears to be the case for $(COD)PtCl_2$, and also allows a greater electronegativity effect (*2*). It has been found (*18*) that *cis*- and *trans*-$(Ph_3P)_2PtCl(SnCl_3)$ have the same infrared spectra, with the ν(Pt—Cl) appearing as a shoulder at 315 cm^{-1} on the tin-chlorine stretching frequencies. This suggests that Ph_3P and Cl_3Sn have similar *trans* effects, and that the *trans* ligand may have little effect on ν(Sn—Cl).

In trichlorostannato complexes, the tin-chlorine stretching frequencies (Table X) show a considerable increase in frequency upon coordination. Frequencies in the boron halide adducts (*131*), where there is only σ-bonding, are similar to those of free $SnCl_3^-$. In transition metal complexes, where π-bonding is possible, the tin-chlorine stretching frequencies have values intermediate between those for divalent and tetravalent tin chlorides. The changes in frequency have been related (*222a*) to the electron affinities of the transition metal atoms by consideration of electronic changes at the tin atom. However, the π-acceptor properties of the $SnCl_3$ group were ignored, and there is a rough correlation between ν(Sn—Cl) values and the number of other π-bonding ligands attached to the central metal atom. It has been argued (*1*) that the far-infrared spectrum for $[Pt(SnCl_3)_5]^{3-}$ supports the trigonal bipyramidal structure (*74*) by the absence of platinum-chlorine stretching frequencies. However, Table IX shows that ν(Pt—Cl) would be expected at similar frequencies to ν(Sn—Cl) in *trans*-$[PtCl_2(SnCl_3)_2]^{2-}$, if $SnCl_3$ has a similar *trans* effect to triphenylphosphine. In view of the poor resolution reported (*1*), the datum does not distinguish unequivocally between the two compounds. The spectra of authentic *cis*- and *trans*-$[PtCl_2(SnCl_3)_2]^{2-}$ have not been reported, but, because good resolution of bands is not achieved (*222a*) in other compounds containing metal chlorine bands, the problem may not be easily resolved.

TABLE IX

PLATINUM-CHLORINE STRETCHING FREQUENCIES IN THE COMPLEXES *trans*-L_2PtClY

L	Y	ν(Pt—Cl) (cm^{-1})	Reference
Et_3P	Cl	340	(*2, 75*)
Ph_3P	Cl	345	(*18*)
Ph_3P	$SnCl_3$	315	
Ph_3P	$SnPh_3$	298	
Ph_3P	$PbPh_3$	286	
Ph_3P	H	287	
$PhMe_2P$	H	282	(*51*)
Et_3P	H	269	(*2*)
Et_3P	Me	274	
Et_3P	Ph	270	
$PhMe_2P$	$GeMePh_2$	248	(*51*)
$PhMe_2P$	$SiMePh_2$	242	

TABLE X

TIN-CHLORINE STRETCHING FREQUENCIES OF $SnCl_3$ IN TRANSITION METAL COMPLEXES

<table>
<tr><th rowspan="2">Complex</th><th colspan="2">ν(Sn—Cl) (cm^{-1})</th><th rowspan="2">Ref.</th></tr>
<tr><th>Asymmetric</th><th>Symmetric</th></tr>
<tr><td>$SnCl_3^-$</td><td>297</td><td>256</td><td>(*251*)</td></tr>
<tr><td>$(Ph_4As)SnCl_3$</td><td>289</td><td>252</td><td>(*131*)</td></tr>
<tr><td>$(Ph_4As)SnCl_3 \cdot BCl_3$</td><td>284</td><td>255</td><td></td></tr>
<tr><td>$(Ph_4As)SnCl_3 \cdot BF_3$</td><td>294</td><td>267</td><td></td></tr>
<tr><td>$(NBD)_2RhSnCl_3$</td><td>307</td><td>284</td><td>(*222a*)</td></tr>
<tr><td>$(Ph_3P)_3CuSnCl_3$</td><td>309</td><td>286</td><td>(*86*)</td></tr>
<tr><td>$(Ph_3P)_3AgSnCl_3$</td><td>313</td><td>288</td><td></td></tr>
<tr><td>$(Ph_3P)_3AuSnCl_3$</td><td>315</td><td>288</td><td></td></tr>
<tr><td>$(COD)_2IrSnCl_3$[a]</td><td>317</td><td>300, 290</td><td>(*222a*)</td></tr>
<tr><td>$(Ph_3P)_3RhSnCl_3$</td><td>327</td><td>302</td><td></td></tr>
<tr><td>$(Ph_3P)_2PtH(SnCl_3)$</td><td>331</td><td>309</td><td>(*18*)</td></tr>
<tr><td>$(Ph_3P)_2PtCl(SnCl_3)$</td><td>341</td><td>325</td><td></td></tr>
<tr><td>$(Ph_3P)_2PtPh(SnCl_3)$</td><td>341</td><td>318</td><td>(*198*)</td></tr>
<tr><td>$(Me_4N)_4[Rh_2Cl_2(SnCl_3)_4]$[b]</td><td>339</td><td>323</td><td>(*222a*)</td></tr>
<tr><td></td><td>362</td><td>335</td><td>(*1*)</td></tr>
<tr><td>$(Et_4N)_3[Pt(SnCl_3)_5]$</td><td colspan="2">ca. 337</td><td></td></tr>
<tr><td>$(Me_4N)_2[RuCl_2(SnCl_3)_2]$</td><td colspan="2">329</td><td>(*222a*)</td></tr>
<tr><td>$(Ph_3P)_2(CO)IrHCl(SnCl_3)$</td><td>339</td><td>320</td><td></td></tr>
<tr><td>$(Me_4N)_4[Ir_2Cl_6(SnCl_3)_4]$</td><td colspan="2">ca. 340</td><td></td></tr>
<tr><td>$MeSnCl_3$</td><td>384</td><td>366</td><td>(*233*)</td></tr>
</table>

[a] Assignment not unequivocal.

[b] Different assignments made by different workers.

3. *Metal-Metal Stretching Frequencies*

A large number of metal-metal frequencies have been measured (*1, 45*) but little can be said at present about their significance.

4. *Metal-Hydrogen Stretching Frequencies*

The metal-hydrogen stretching frequencies in the series *trans*-$(Et_3P)_2PtHY$ (Table XI) have been correlated with the *trans* effect of ligand Y (*55*), as have the chemical shifts of the hydrogen atoms in n.m.r. spectra. The *trans*-effect series on this basis, X < SCN < $SnCl_3$ < $SiPh_3$ < CN < $GePh_3$ < H, is in only fair agreement with that obtained from ν(Pt—Cl) values. The overall trends are similar, however, and confirm the high mesomeric effect of $SnCl_3$ and the strong inductive effects of Ph_3E.

TABLE XI

Trans EFFECT SEQUENCE FOR LIGANDS IN THE SERIES *trans*-$(Et_3P)_2PtHY$

Y	NO_3	Cl	Br	I	NCS	$SnCl_3$	$SiPh_3$	CN	$GePh_3$	H
ν(Pt—H) cm^{-1}[a]	2242	2183[b]	2178	2156[c]	2112	2105[d]	2056[e]	2041	1957[f]	1731[g]
δ(Pt—H) τ[h]	33.1	26.9	25.6	22.7	23.2	19.2[d]	—	17.8	—	—

[a] Chatt *et al.* (*50*), hexane solution.

[b] Cf. $(Pr_3P)_2PtHCl$, 2183 cm^{-1}; $(Ph_2EtP)_2PtHCl$, 2206 cm^{-1}; $(Ph_3P)_2PtHCl$, 2220 cm^{-1} (*50*).

[c] Cf. $(Ph_3P)_2PtHI$, 2186 cm^{-1} (*50*).

[d] Lindsey *et al.* (*158*). Cf. $(Ph_3P)_2PtHSnCl_3$, 2056 cm^{-1} (*18*).

[e] Baird (*18*).

[f] Value for $(Pr_3P)_2PtH(GePh_3)$ (*75*).

[g] Value assigned to $(Pr_3P)_2PtH_2$ (*75*). Cf. $(Ph_3P)_2PtH_2$, 1620 cm^{-1} (*164*).

[h] Chatt and Shaw (*55*), benzene solution.

C. N.M.R. SPECTRA

The n.m.r. spectra of methyltin derivatives have been studied (*130*, *203*) and some results are given in Table XII. It has been shown (*36*) that the methyl resonances shift to lower fields as the methyl groups in tetramethyltin are replaced by chlorine atoms. It has been suggested that this may not be due solely to the inductive withdrawal of shielding electron density, since chemical shifts are less (*36*, *243*) when ($p \rightarrow d$) π-bonding between metal and chlorine is favorable. A similar trend is observed (*130*, *200*) when the methyl groups are replaced by transition metal groups and the observed chemical shifts are smaller than those in the methyltin chlorides, which may be the result of π-bonding between the two metals.

The tin-proton coupling constants $J(^{119}Sn—Me)$ for the methyl groups also decrease with successive replacements of the methyl groups by transition metals (*64*, *130*, *199*, *200*, *206*). The coupling has been related (*95*, *123*) to the *s* character of the tin-methyl bonds, and the values for the transition metal derivatives, which are lower than that for tetramethyltin, imply a higher degree of *s* character (about 30% in the metal-metal bonds) than is expected for pure sp^3 hybridization. These findings are corroborated by structure determinations, which show deviations from regular tetrahedral bond angles that are larger in the disubstituted complexes. Correlations have been made (*37*) between $J(^{119}Sn—Me)$ values and Sn—C stretching frequencies, and it is interesting to note that there is a close similarity (*61*, *130*) between the coupling constants and

ν(Sn—C) in Me_6Sn_2 and $Me_3Sn\text{-}Mn(CO)_5$. Similar trends exist in the methyllead compounds (*95*) and their related transition metal complexes (*130, 200*).

Parshall (*197, 198*) has used intramolecular ^{19}F shielding to estimate the relative σ and π contributions in a metal ligand bond in square planar complexes of platinum. The chemical shift of the fluorine atom in *trans*-$(Et_3P)_2PtX$(*m*-fluorophenyl) is affected only by inductive effects in the Pt—X bond, while the chemical shift in the *p*-fluorophenyl analog is a measure of both the σ and π contributions. Thus the two effects can be separated and have been measured (*158, 197, 198*) for a variety of ligands. Results show that the trichlorostannato ion is a weak σ-donor but a strong π-acceptor ligand comparable to the cyanide ion and should thus have a high *trans* effect. This prediction is confirmed by infrared data.

TABLE XII

N.M.R. SPECTRA OF METHYLTIN CHLORIDES AND SOME TRANSITION METAL COMPLEXES

Compound	τ_{Me}	$J(^{119}Sn—Me)$ (cps)	Reference
Me_6Sn_2	9.78	48.4	(*36, 37*)
Me_4Sn	9.93	54.0	(*36, 37, 199*)
Me_3SnCl	9.37	59.7	(*36, 123*)
Me_2SnCl_2	8.84	71.0	
Me_3SnCl	8.35	100.0	
$Me_3Sn\text{-}Mo(CO)_3Cp$	9.52	49.0	(*200*)
$Me_3Sn\text{-}Mn(CO)_5$	9.54	48.3	(*61, 130*)
$Me_3Sn\text{-}W(CO)_3Cp$	9.40	48.7	(*200*)
$Me_3Sn\text{-}Re(CO)_5$	9.58	46.7	(*130*)
$Me_3Sn\text{-}Fe(CO)_2Cp$	9.55	49.0	(*199*)
$Me_3Sn\text{-}Ir(CO)_3(Ph_3P)$	—	49.0	(*64*)
$Me_2ClSn\text{-}Mo(CO)_3Cp$	9.02	47.7	(*200*)
$Me_2ClSn\text{-}Mn(CO)_5$	9.00	45.3	(*130*)
$Me_2Sn[Mo(CO)_3Cp]_2$	9.15	37.4	(*200*)
$Me_2Sn[Mn(CO)_5]_2$	9.17	36.7	(*130*)
$Me_2Sn[Mo(CO)_3Cp][Mn(CO)_5]$	9.20	36.9	(*199*)
$Me_3Sn\text{-}Co(CO)_4$	9.37	52.6	(*202*)
$Me_2Sn[Co(CO)_4]_2$	8.88	49.7	
$MeSn[Co(CO)_4]_3$	8.98	33	

VII. Conclusions

A. THE NATURE OF THE METAL–METAL BOND

1. *Multiple Bonding*

Chemical and physical evidence points toward considerable π-bonding in the E—M bonds resulting from overlap of *d* orbitals. All R_3E complexes are very much more stable than their methyl analogs, although they are still sensitive to oxidation. In general, stability is in the order $X_3E > Ph_3E > Me_3E$ and is enhanced by the introduction of a phosphine molecule into the coordination sphere. Disubstituted complexes are less stable than their monosubstituted analogs.

The metal-metal bonds show widely different reactivities depending on the nature of R_3E and the transition metal atoms. Thus for the phenyl derivatives, Sn—Mn and Ge—Re bonds are remarkably stable toward halogens; Sn—Re and Ge—Mn bonds are less so, and Sn—Fe, Pb—Mn, and Si—Co bonds are readily broken. Disubstituted derivatives are more reactive and at least one metal-metal bond is broken by the action of halogens. However, insufficient detail is at present known about the chemical behavior of Group IVB complexes in general.

Metal-metal bond distances and infrared and n.m.r. data support $(d \rightarrow d)$ π-bonding, but again there is a lack of comprehensive data. Many competing factors must be considered such as inductive effects, π-bonding between E and its other substituents, and hybridization changes. Therefore it is not instructive to make specific predictions about the relative π-acceptor abilities of the Group IVB metals, since they are sensitive to the nature of the transition metal ion and their substituent atoms. Further work is clearly needed to clarify the role of π-bonding in these complexes.

2. *Divalent and Tetravalent Compounds*

The divalent halides EX_2 react readily with transition metal compounds to form two classes of compounds. With the platinum metals, tin(II) chloride forms $SnCl_3$ complexes whose chemical behavior suggests that tin remains formally divalent. With other transition metals, particularly those of the first row and earlier periodic groups, the mono- and disubstituted complexes behave as tin(IV) compounds. In both cases the $SnCl_3$ group behaves as a strong π-acceptor so that the difference in behavior must lie in the σ-component of the bonding. If the overlap of *d* orbitals between tin and the platinum metals is favorable, it is possible that the coordinate link is predominantly a π-bond, with the electron pair from the tin atom that is responsible for initiating the bonding remaining close to its parent atom. With first-row transition metals where overlap is less favorable, or where there are less *d* electrons, a stronger, less polar σ-link may be required to draw the atoms close together for strong π-bonding. Reactions of the metal-metal bond would then favor the tin atom retaining its electron pair in the former case, but tend to split the bond homolytically in the latter.

These distinctions do not seem to exist in the alkyl or aryl derivatives, which can be prepared from R_3ELi, although there is evidence (*18*) that $(Ph_3P)_2PtCl(EPh_3)$ ($E = Sn$, Pb) decomposes to give diphenyltin and diphenyllead. This is to be expected from the lower stability of divalent organo compounds. Reactions of iron(II) (*13*, *171*) and molybdenum(V) or (VI) (*14*) with tin(II) chloride in the presence of dimethylglyoxime may be exceptions to the above generalization, although the structure of these complexes is not known. It is possible that the two metals can be linked by a dimethylglyoxime molecule without a direct metal-metal bond.

B. COMPOUND TYPES

All the Group IVB elements readily form monosubstituted complexes with a variety of transition metals. At present the range is greatest with tin and germanium, which is a reflection of their general stability; the lack of silicon and lead complexes is probably a result of less experimental effort, and in the next few years many more compounds will probably be synthesized.

To date only germanium and tin have been found to form disubstituted complexes and, when this review was begun, tri- and tetrasubstituted complexes were almost entirely confined to tin. However, more recently (*70*, *71*, *132*, *133*) the metal cluster compounds between tin and $Fe(CO)_4$ have been extended to germanium and lead. Otherwise, tetrasubstituted complexes have been confined almost entirely to iron compounds with Fe—Fe bonds present only when it is necessary to maintain a rare gas configuration. Apart from $Sn[Fe(CO)_2Cp]_2[Mo(CO)_3Cp]_2$ (*85*), no tetrasubstituted compounds with other transition metals are known. Attempts to prepare $Sn[Re(CO)_5]_4$ gave only $Sn_2[Re(CO)_5]_6$ (*181*) and $X_{4-n}Sn[Co(CO)_4]_n$ with all but $n = 4$ being known.

The silicon complex $RSiCo_3(CO)_9$ probably contains three $Co(CO)_3$ groups held together by Co—Co bonds as in the carbon complexes (*231*). It has been suggested (*144*) that the compound forms by spontaneous loss of carbon monoxide from intermediate $RSi[Co(CO)_4]_3$. The tin compounds $RSn[Co(CO)_4]_3$ show no tendency to lose carbon monoxide, although the mass spectra (*205*) of these compounds do not give the $RSnCo_3(CO)_{12}^+$ ion but a moderately high abundance of $RSnCo_3(CO)_{11}^+$. However, the intensity of the $RSnCo_3(CO)_9^+$ is low so that the condensed system of this sort is probably not very stable. It may be noted that $Ph_3Sn\text{-}Mn(CO)_5$ does not show this stepwise loss of carbonyl groups in its mass spectrum (*153*). It is possible that multiple bond character in the Sn—Co bonds is sufficient to outweigh any gain in bonding energy that might result from forming the tetrameric structure. The behavior of germanium and lead in this respect has not been reported.

A metal-metal bond is postulated in $(Acac)_2SnCo_2(CO)_7$, and a crystal structure determination of this compound would be of considerable interest. The compound is considered to arise from the spontaneous loss of a carbonyl group (*207*) from $(Acac)_2Sn[Co(CO)_4]_2$ because of constraint in the Co—Sn—Co bond angle arising from octahedral coordination of the tin atom. But electronic factors may also be important, since the mass spectrum of $Cl_2Sn[Co(CO)_4]_2$ (*205*) indicates that there is preferential loss of one carbonyl group in this complex also.

C. SYNTHETIC METHODS

The most common preparative method for all classes of compounds is the reaction of organohalides with the transition metal anions in nucleophilic substitution reactions. Thus one can use R_3EX, R_2EX_2, REX_3, and EX_4 to give mono-, di-, tri-, or tetrasubstituted derivatives, respectively, although behavior is not always systematic. Thus $SnCl_4$ gives $Sn[ML_n]_4$, while $GeCl_4$ gives $Cl_3Ge\text{-}ML_n$; R_2EX_2 and REX_3 frequently give R_2XE— and RX_2E— derivatives, respectively. Often higher substituted compounds can be formed by further nucleophilic substitution on mixed organohalogen derivatives. This method is particularly useful for preparing mixed metal complexes.

The reverse substitution on transition metal halides by R_3E^- or X_3E^- has been commonly used, particularly with the platinum metals. In a series of papers (*80–84*), Dessey and his co-workers have reported important polarographic studies on the formation of metal-metal bonds. They show that reactions between two metal species are dependent on the nucleophilicity of the relevant metal ion and the path of the reaction. $Ph_3E\text{-}Fe(CO)_2Cp$ ($E = Sn, Pb$) can be formed by reaction of either Ph_3E^- or $Fe(CO)_2Cp^-$ with the chloride of the other metal group and these reactions are said to commute (*82*). The systems $Ph_3Sn/Mo(CO)_3Cp$ and $Ph_3Pb/Mn(CO)_5$ do not commute. Direct nucleophilic substitution is observed in the reactions of Ph_3SnCl with $Mo(CO)_3Cp^-$ and Ph_3Pb (acetate) with $Mn(CO)_5^-$; but their commutative reactions give products suggesting that either metal-halogen interchange is taking place,

$$\begin{aligned} Ph_3E^- + XML_n &\rightarrow ML_n^- + Ph_3EX \\ Ph_3E^- + Ph_3EX &\rightarrow Ph_6E_2 + X^- \end{aligned} \tag{56}$$

or the intermediate $Ph_3E\text{-}ML_n$ complex is broken down through the elimination of ML_n^- (*83*) by the stronger nucleophile Ph_3E^- (*81*),

$$Ph_3E^- + Ph_3E\text{-}ML_n \rightarrow Ph_6E_2 + ML_n^- \tag{57}$$

On the other hand, reactions in the noncommutative set $Ph_3Sn/Mn(CO)_5$ seem to involve a one-electron transfer to give radicals that can take part in random or selective coupling.

These results are of considerable importance to the synthetic chemist since they enable predictions to be made on the success of reaction routes. For instance, Ph_3Pb^- can be used to prepare $Ph_3Pb\text{-}Fe(CO)_2Cp$ but not the $Mn(CO)_5$ or $Mo(CO)_3Cp$ complexes. Also $Sn[Fe(CO)_2Cp]_2\text{-}[Mo(CO)_3Cp]_2$ is the predicted product in the reaction between $Cl_2Sn[Fe(CO)_2Cp]_2$ and $Mo(CO)_3Cp^-$, as has been found (*85*), but the commutative reaction should give $Sn[Fe(CO)_2Cp]_4$ since $Mo(CO)_3Cp^-$ is the weaker nucleophile.

Other related synthetic procedures involve the elimination of a neutral molecule, as in the reaction of R_3EX with HML_n ($X = NR_2$, NO_3, H) or R_3EH with $ClML_n$.

An important reaction is the addition of divalent halides to metal-halogen bonds in X^1ML_n to give $X_2X^1E\text{-}ML_n$, or to metal-metal bonds to give $X_2E[ML_n]_2$. The mechanism of this reaction remains uncertain. It is possible that it involves nucleophilic attack through the donor properties of the lone pair of electrons on EX_2. Support for this idea is found in the ready reaction of compounds that can accept a donor molecule (e.g., $IFe(CO)_2Cp$), whereas $IMo(CO)_3Cp$, which has a higher coordination number and must increase this further, does not react. Alternatively, EX_2 might behave as a carbenoid entity (*28*, *28a*, *178*). The increase in reactivity of $[Co(CO)_3PR_3]_2$ with $SnCl_2$ (*28*) as the π-accepting ability of the phosphines decreases is in line with electrophilic attack of this type. It is interesting that the reverse reaction, involving attack by the carbenoid entity $(Ph_3P)_2Pt$ on R_3SnX, has been used (*150*) to prepare platinum-tin complexes.

D. CONCLUDING REMARKS

A large number of recent papers have increased severalfold our knowledge in this field. There is little doubt that, by the time this review is published, much more information will be available, but it has been the present aim to provide a comprehensive survey of the topic as it stood in mid-1967. It is clear that more work remains to be done in the synthetic structural, spectral, and chemical reactivity aspects, and it must be left to the reader to judge how far this has been achieved in the intervening time. The study of these complexes is providing useful information on metal-metal bonding, and emphasizes the link between transition and nontransition metals as equal partners in inorganic chemistry.

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