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Derivatives of Metal Carbonyls Containing a Bond between Atoms of Transition Metals and Group IVB Elements

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This review considers the methods of preparation, properties, and structure of organopolymetallic compounds containing elements of Group IVB connected with a metal carbonyl residue. Compounds of this type are interesting from the point of view of investigating metal-metal interaction, that is, from the theoretical point of view. Their practical use in various fields of chemistry and technology is possible. 176 references.

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I. INTRODUCTION

The intensive development of investigations in the field of the chemistry of carbonyl complexes of transition metals led to the preparation of a large number of compounds containing a direct bond between two metal atoms. Despite the fact that the existence of metal–metal bonds in organic derivatives of non-transition metals and in inorganic crystals is generally known, before 1957 no serious attention was paid to the possibility of the formation of a strong covalent bond between the atoms of transition metals in their organic derivatives—the carbonyls. It has now been found [1,2] that a metal–metal bond can be formed by all the transition metals capable of σ-bonding with carbon.

From 1962 onwards chemists have paid special attention to derivatives of metal carbonyls containing two or more covalently bonded atoms of different metals, both transition and non-transition. The present review examines the methods of preparation and properties of organopolymetallic compounds containing Group IVB elements bonded with a metal carbonyl residue. The investigation of metal–metal interaction in compounds of this type is of considerable interest both from the standpoint of the theory of the chemical bond and in view of their possible practical application.

In published reviews [1-5] dealing with the formation of covalent bonds between metal atoms, derivatives of metal carbonyls containing bonds between various transition and non-transition metals were either not considered or the consideration was limited owing to the absence of sufficient facts at the time these reviews were written.

II. STRUCTURES OF COMPOUNDS CONTAINING A BOND BETWEEN ATOMS OF TRANSITION AND NON-TRANSITION METALS

The possibility of the existence of a covalent bond between transition metal atoms was first shown in 1957 in an investigation of the structures of polynuclear metal carbonyls. Before then the only complexes (including carbonyls) known were those in which in addition to the metal–metal bond there were bridging atoms or groups between the metal atoms. The first complexes studied with metal–metal σ-bond structures were dimeric carbonyls of manganese and rhenium [6,7], or technetium [8] and molybdenum π-cyclopentadienylcarbonyl [9].

The ability of transition metals to form σ-bonds with Group IVB elements was observed [10] in 1956. Many series of compounds with chains of several covalently bound metal atoms, which can be classified as "clusters", have now been studied. According to Cotton's definition [4] "clusters" are compounds in which metal atoms are bound to one another exclusively by metal–metal bonds; this definition also includes those compounds in which not all the metals are identical. Several non-metal atoms can also be bound to the "cluster".

Since one or more $M'(CO)_5$ groups enter into most of the best studied clusters we will deal in greater detail with the molecular and electronic structure of this group.

1. Molecular Structure of the $M'(CO)_5$ Group, where M' = Mn, Tc, or Re

The structure of the $M'(CO)_5$ group was first found [6,7] in determining the structure of the dinuclear manganese carbonyl. Subsequent X-ray diffraction investigations showed that the characteristic peculiarities of this group are also kept in other compounds irrespective of the nature of the atoms or groups with which they are connected.

The metal atom in the $M'(CO)_5$ group has an octahedral configuration; five of the vertices of the octahedron are occupied by carbonyl groups and at the sixth there is a substituent X connected with the metal atom by a σ-bond. The C_{4V} symmetry of the $M'(CO)_5$ group is somewhat distorted owing to the non-linearity of the M'–C–O chains and displacement of the four equatorial CO groups to the side of the X substituent. For $Mn(CO)_5$ this displacement averages 3.8°. A possible reason for the departure from coplanarity of the equatorial CO groups is the mutual repulsion between the electrons of the axial and equatorial carbonyl groups. Another reason for the distortion of the molecule could be the intermolecular interaction due to the requirement for compact packing in the crystal lattice.

However, an electron diffraction study of the $Mn_2(CO)_{10}$ molecule showed [11] that the non-linearity of the Mn–C–O groups is also retained in the gas phase, and the oxygen atoms alternately depart to the right and left of the plane formed by the carbon atoms. Finally, rehybridisation of the d^2sp^3 orbitals of the metal atom, leading to release of energy and the strengthening of the bonds in the molecule, can be responsible for the decrease in symmetry [12].

The bonds between the metal atom and the carbonyl groups are not equivalent. In the manganese carbonyl molecule the $Mn-CO_{ax}$ distance is appreciably shorter than the bonds with the equatorial groups [11]. An analogous shortening of the M′–C bond and lengthening of the C–O bond for an axial group in comparison with the equatorial ones was observed in the molecules of $Tc_2(CO)_{10}$, [8] $HMn(CO)_5$, [13,14] $HCF{=}CFMn(CO)_5$, [15] and $HMnRe_2(CO)_{14}$. [16] Evidently this is connected with the reduction of symmetry of the electron shell along the X–M′–C–O axis, owing to the presence of substituent X (other than CO) in the trans-position to CO.

The structure of the $M'(CO)_5$ group is shown in Fig. 1. Table 1 gives the mean interatomic distances and angles between the bonds for M′ = Mn, Tc, and Re.

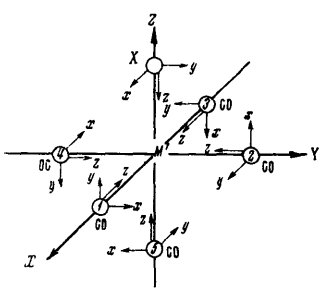


Figure 1. Structure and system of coordinates of the molecules of $XM'(CO)_5$ type.

2. Electronic Structure of Derivatives of the $XM'(CO)_5$ Type

A satisfactory description of the electronic structure of transition metal complexes is at present possible only within the framework of the LCAO-MO method. Unfortunately, there is only one theoretical investigation [17] of the nature of the bonds in the carbonyl complexes of the transition metals of Group VII and this did not include an analysis of the organopolymetallic compounds with direct metal–metal bonds.

The carbonyls of the Group VII metals are stable complexes of metals in the zerovalent state of oxidation with carbon monoxide. All the CO groups are unidentate ligands coordinated with the metal atom through carbon. Coordination by the lone pair of electrons of the carbon is preferable to that due to electrons of the oxygen atom, owing to the high electronegativity of the latter. Derivatives of metal carbonyls of the type $XM'(CO)_5$ obey Sidgwick's rule, which is reflected in the diamagnetism of compounds of this class. The metal atom acquires an inert-gas 18-electron shell by the addition to its 7 valence electrons of 10 electrons from the CO groups and the formation of an M′–X covalent bond.

As already noted above, the metal atom in the $M'(CO)_5$ group which enters into the composition of both the dimeric carbonyl and its derivatives retains the somewhat distorted octahedral configuration. According to the structural data given above and also spectroscopic [18] and kinetic investigations [19–21] the axial carbonyl group $CO_{(5)}$ (see Fig. 1) is bound to the metal atom much more strongly than each of the four equatorial groups $CO_{(1-4)}$. This shows the extensive π-bonding of the metal atom with $CO_{(5)}$. It is therefore necessary to consider three types of bond formed by the central atom with (a) the axial CO group, (b) the equatorial CO groups, (c) the ligand X.

Table 1. Mean bond lengths and valence angles in $M'(CO)_5$ groups.

Parameters of the molecules	Mn [7]	Tc [8]	Re [16]
Bond length Å			
$M'-C_{axial}$	1.792	1.899	1.86
$M'-C_{eq}$	1.840	2.000	2.005
$C-O_{axial}$	1.151	1.205	1.26
$C-O_{eq}$	1.154	1.121	1.125
Valence angles, degrees			
$M'-C-O_{axial}$	177.0±1.6	175.1±1.4	178.5±2.5
$M'-C-O_{eq}$	177.3±1.2	177.7±1.2	170.5±3.0
$C_{axial}-M-C_{eq}$	93.8±0.6	93.8±0.4	92.5±1.8
$cis\text{-}C_{eq}-M'-C_{eq}$	89.8±0.6	89.8±0.4	89.9±1.4
$trans\text{-}C_{eq}-M'-C_{eq}$	172.3±0.6	172.4±0.4	174.8±1.4

The scheme of the energy levels of the molecular orbitals for the $XM'(CO)_5$ compounds is shown in Fig. 2. [17]

(a) The bond between the metal atom and $CO_{(5)}$ has the character of σ- and π-interaction. The stable σ-bond $M'-C_{(5)}$ is the result of the combination of the s-, p_Z-, and d_{Z^2}-orbitals of the metal and the $2s$- and $2p$-AO's of the carbon. The π-bonding between the M′ atom and $CO_{(5)}$ is mainly effected by the interaction of the d_{XZ}- and d_{YZ}-orbitals of the metal with the bonding (π) and antibonding (π*) orbitals of the CO. The p_X- and p_Y-orbitals of the metal can also participate to some extent in π-bonding, but they are mainly used for σ-bonding with $CO_{(1-4)}$. Hence the $M'-CO_{(5)}$ π-interaction consists of one strong bonding, one mainly non-bonding, and two antibonding MO's.

(b) The four σ-bonds of the metal with the groups $CO_{(1-4)}$ situated in the xy plane are formed as a result of the combination of the s-, d_{Z^2}-, $d_{X^2-Y^2}$-, p_X-, and p_Y-orbitals of the metal and the $2s$- and $2p$-orbitals of carbon. Only the d_{XY}-orbital of the metal is favourable for π-bonding and the other orbitals, which have a symmetry suitable for π-bonding with $CO_{(1-4)}$ participate either, as stated above, in stronger π-bonding with $CO_{(5)}$, or in σ-bonding.

(c) The σ-bond of a metal atom with the X substituent is formed by the s-, p_Z-, and partly the d_{Z^2}-orbitals of the metal and the corresponding X orbitals. In addition π-bonding can also be effected between the d_{XZ}- and d_{YZ}-AO's of the metal and the π-orbitals of similar symmetry on substituent X. Two alternatives can be considered here: the π-donation of electrons from X to the metal atom and the dative interaction of the filled d_π-orbitals of the metal with vacant orbitals of X. In the first instance the energy of the non-bonding π-MO in the $M'-CO_{(5)}$ system is

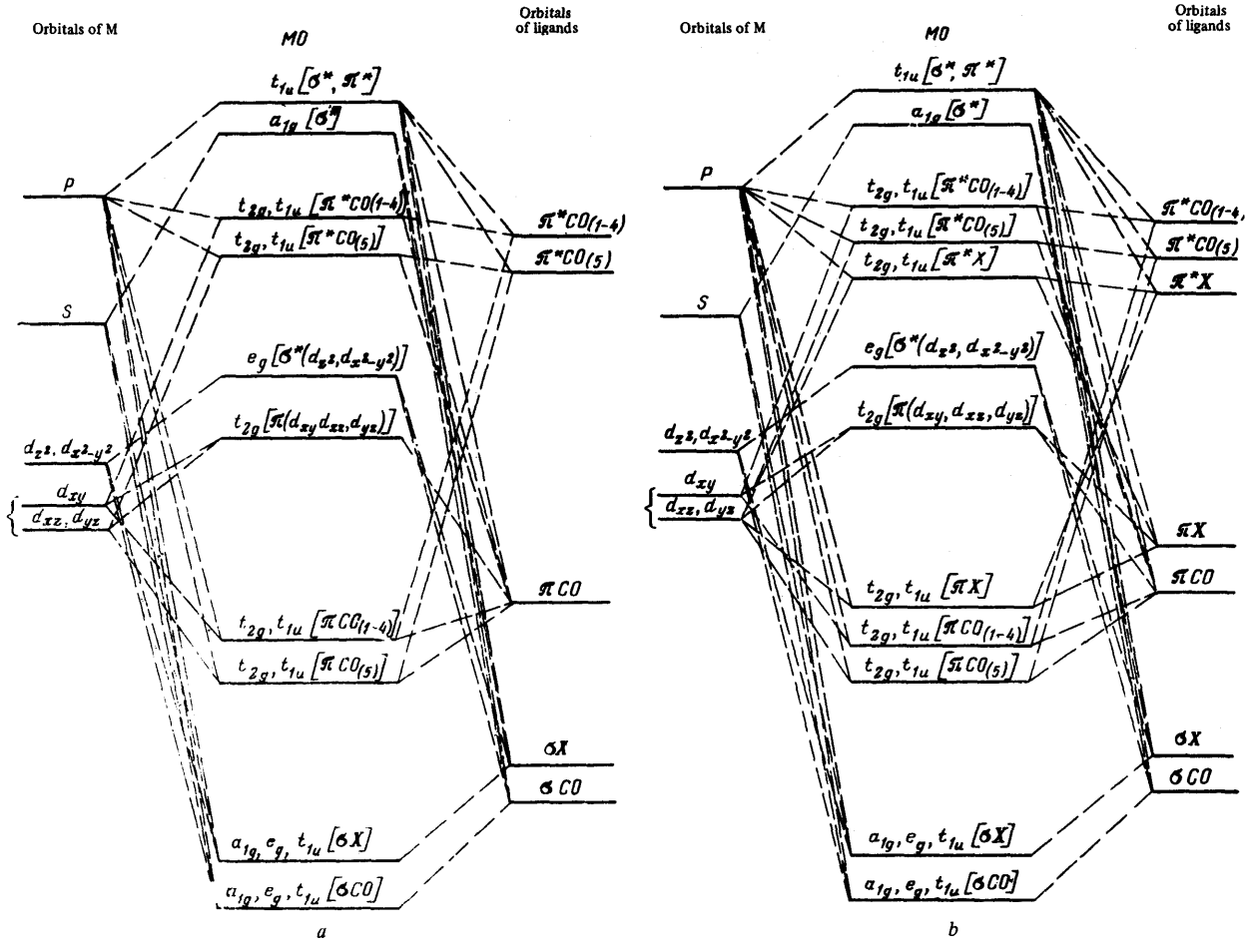


Figure 2. Scheme of energy levels for compounds of the $XM'(CO)_5$ type. *a*) X does not exhibit π-acceptor properties; *b*) X is a π-acceptor.

increased, whereas the energy of the π-orbitals of substituent X is reduced. As a result of this type of interaction additional strengthening of the $M'-CO_{(5)}$ bond should result. On the other hand, in dative π-interaction of M'–X there is competition between the π-orbitals of the ligands X and $CO_{(5)}$ for the electrons with the d_π-orbitals of the metal which should strengthen the M'–X bond and simultaneously weaken the $M'-CO_{(5)}$ bond. The scheme of the energy levels for the latter instance is shown in Fig. 2*b*.

In the diagrams the levels of the coulomb energies of the orbitals are arranged in the following order: $\sigma(CO, X) < \pi(CO) < \pi(X) < (n-1)d < ns < \pi^*(CO_{(5)}) < \pi^*(CO_{(1-4)}) < np$ in accordance with spectroscopic and kinetic results. To simplify the diagrams all the π- and π^*-orbitals of the equatorial CO-groups are shown together.

3. Structures of the Organopolymetallic Derivatives of Metal Carbonyls Containing a Metal–Metal Bond with a Group IVB Element

For the first metal carbonyl derivatives containing a Group IVB element (Si, Ge, Sn, or Pb) to be obtained it was assumed, without proof, that the two metal-containing fragments of the molecule are connected by a covalent metal–metal bond [10,22–24]. Direct proof of the covalent bonding between the atoms of the transition metal and the Group IVB element was obtained in 1964 as a result of X-ray diffraction investigation of organotin derivatives of manganese carbonyl [25,26] and it was found that in these compounds the metal–metal distance is even less than the sum of the so-called "covalent metallic radii" which is taken as the length of a single covalent bond [27].

An analysis of the compound $Ph_3SnMn(CO)_4PPh_3$ [25,28] showed that the covalently bound Sn, Mn, and P atoms are situated in a straight line, which is the principal axis of the distorted octahedron with the Mn atom at the centre; four of the vertices of the octahedron are occupied by CO groups and the other two by the tin and phosphorus atoms with approximately tetrahedral configurations. The phenyl groups at the tin and phosphorus atoms are in an eclipsed configuration relative to one another (Fig. 3). All the CO groups are somewhat displaced towards the tin atom. Table 2 gives the main parameters of the molecule.

The structures of several other derivatives of manganese carbonyl containing an Sn–Mn bond have been studied: $Ph_3SnMn(CO)_5$, [29] $Me_3SnMn(CO)_5$, [30,31] $Ph_2Sn[Mn(CO)_5]_2$, [26] $ClSn[Mn(CO)_5]_3$ [32,33] (Fig. 4*a*), and also the cluster $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$, [34–36] which contains the chain Mn–Sn–CO (Fig. 4*b*). In all these molecules retention of approximately octahedral configuration of the manganese

atom and of the tetrahedral configuration of tin is observed. A comparison of the Sn–Mn internuclear distances (see Table 2) shows how sensitive the length of the metal–metal bond is to the nature of the ligands attached. One of the possible reasons for the appreciable differences in the lengths of the Sn–Mn bond could be the thermal anisotropy of the metal atoms [28]. However, the main reasons for these differences are undoubtedly of an electronic nature.

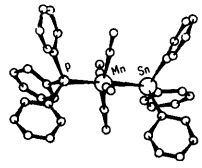


Figure 3. Structure of the $Ph_3SnMn(CO)_4PPh_3$ molecule.

In addition, purely steric factors play a large part. Thus in the series $Ph_3SnMn(CO)_5$, $Ph_2Sn[Mn(CO)_5]_2$, and $ClSn[Mn(CO)_5]_3$ as the number of $Mn(CO)_5$ groups bound to the tin atom is increased a tendency to an increase in the Sn–Mn distance is noted and the valence angles at the tin atom become increasingly distorted in comparison with the tetrahedral angles. As a result of the increase in steric hindrance the configuration of the tin atom gradually changes from tetrahedral to trigonal pyramidal.

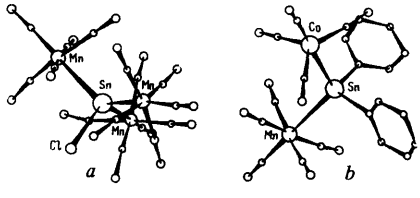


Figure 4. *a*) Structure of the $ClSn[Mn(CO)_5]_3$ molecule; *b*) structure of the $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$ molecule.

The X-ray structural investigation of clusters with Sn–Fe bonds is of considerable interest both for studying the lengths of metal–metal bonds and the coordination of the metal atoms, and also for investigating the nature of the metal–ligand bonds [39–46]. It was found that in these compounds the tin atom also has approximately tetrahedral coordination with different degrees of distortion. In derivatives of iron [39–43,47,48,55] and molybdenum [43] bonded with a π-cyclopentadienyl ring the coordination of the transition metal atoms is of the "piano-stool" type characteristic of the half-sandwich compounds (Fig. 5).

The change in the nature of the metal–metal bond with the nature of the substituent at the non-transition element atom and the transfer of the electronic effects of the substituents along the metal–metal bonds can be readily traced in the series of trinuclear derivatives of the $X_2Sn[Fe(CO)_2.Cp]_2$. [39–41] As the electronegativity of X increase in the series Me < ONO < Cl there is some increase in the multiplicity of the C–O bonds, appreciable strengthening of the Sn–Fe bonds and also successive increase in the Fe–Sn–Fe angles.

Table 2. Principal structural parameters of the molecules of the carbonyl derivatives with metal–metal bonds.

Compound	M–M′ bond	Bond length, Å	Sum of "covalent" radii, Å	Mean angle between bonds, deg		Reference
$Cl_3SiCo(CO_4)$	Si—Co	2.254	2.33	Co—Si—Cl	113.3	52
				Cl—Si—Cl	105.4	
$Ph_3GeMn(CO)_5$	Ge—Mn	2.54	2.57			53
		2.60				54
$Ph_3GeRe(CO)_5$	Ge—Re	2.69	2.58			54
$Cl_3Ge[Fe(CO)_2Cp^*]_2$	Ge—Fe	2.36	2.46	Fe—Ge—Fe	128.0	47, 48
				Cl—Ge—Cl	96.0	
$Ph_3SnCr(CO)_3Cp$	Sn—Cr	2.85	2.65			54
$Ph_3SnMo(CO)_3Cp$	Sn—Mo	2.87	2.77			54
$Ph_2Sn[Mo(CO)_3Cp]_2$	Sn—Mo	2.89	2.77	Mo—Sn—Mo	116.0	54
$Ph_2Sn[W(CO)_3Cp]_2$	Sn—W	2.81	2.78	W—Sn—W	121.0	54
$Me_3SnMn(CO)_5$	Sn—Mn	2.674	2.78	Mn—Sn—C	112.2	30, 31
				C—Sn—C	107.4	
$Ph_3SnMn(CO)_5$	Sn—Mn	2.674	2.78	Mn—Sn—C	112.7	29
				C—Sn—C	106.0	
$Ph_3SnMn(CO)_4PPh_3$	Sn—Mn	2.627	2.78	Mn—Sn—C	114.2	25, 28
				C—Sn—C	104.3	
$Ph_2Sn[Mn(CO)_5]_2$	Sn—Mn	2.70	2.78	Mn—Sn—Mn	117.0	26
				C—Sn—C	101.5	
$ClSn[Mn(CO)_5]_3$	Sn—Mn	2.737	2.78	Mn—Sn—Mn	116.5	32, 33
				Mn—Sn—Cl	101.5	
$Ph_2Sn\langle^{Mn(CO)_5}_{Co(CO)_4}$	Sn—Mn	2.73	2.78	Mn—Sn—Co	114.0	34–36
	Sn—Co	2.66	2.65	C—Sn—C	107.5	
$Ph_3SnRe(CO)_5$	Sn—Re	2.74	2.78			54
$Ph_3SnFe(CO)_2Cp$	Sn—Fe	2.536	2.67	Fe—Sn—C	113.4	42
				C—Sn—C	105.2	
$Me_2Sn[Fe(CO)_2Cp]_2$	Sn—Fe	2.64	2.67	Fe—Sn—Fe	124.0	39, 40
				C—Sn—C	96.0	
$(ONO)_2Sn[Fe(CO)_2Cp]_2$	Sn—Fe	2.56	2.67	Fe—Sn—Fe	126.0	39, 40
				O—Sn—O	67.4	
$Cl_2Sn[Fe(CO)_2Cp]_2$	Sn—Fe	2.43	2.67	Fe—Sn—Fe	128.6	41
				Cl—Sn—Cl	94.1	
$ClSn\langle^{Mo(CO)_3Cp}_{[Fe(CO)_2Cp]_2}$	Sn—Mo	2.89	2.77	Fe—Sn—Mo	116.9	43
	Sn—Fe	2.59	2.67	Fe—Sn—Fe	115.6	
				Fe—Sn—Cl	102.3	44
$Me_4Sn_3[Fe(CO)_4]_4$	Sn—Fe	2.62	2.67	Sn—Fe—Sn	77.9	
	Sn—Fe	2.75	2.67	Fe—Sn—Fe	98.0	
				Fe—Sn—Fe	116.0	
$n[Fe(CO)_4]_4$	Sn—Fe	2.54	2.67	Fe—Sn—Fe	68.9	45, 46
				Fe—Sn—Fe	133.0	
$Ph_3PbMo(CO)_3Cp$	Pb—Mo	2.90	3.11			54
$Ph_3PbRe(CO)_5$	Pb—Re	2.77	3.12			54
$Me_2Pb[Fe(CO)_2Cp]_2$	Pb—Fe	2.71	2.72	Fe—Pb—Fe	123.8	55
				C—Pb—C	102.0	

*Cp = π-cyclopentadienyl.

This effect agrees with the tendency to an increase in the *s*-character of the hybridised orbitals of the tin atom participating in the Sn–Fe bond (Bent's rule [37,38]). The changes examined can be explained on the basis of hypotheses concerning the existence of d_π–d_π-interaction between the completed $3d_\pi$ orbitals of iron and the vacant $5d_\pi$ orbitals of the tin atom, which is intensified when the π-acceptor ability of the SnX_2 group increases as a result of an increase in the electronegativity of substituent X. As will be shown subsequently, this explanation agrees well with the spectroscopic results and chemical properties of the organopolymetallic derivatives of metal carbonyls.

There is special interest in another class of derivatives of iron carbonyl containing the $Fe(CO)_4$ group. The iron atom in this group is capable of forming two covalent bonds with the atoms of Group IVB elements. On the basis of a measurement of molecular weights [49] and investigations of

infrared spectra[50,51] structures (I)–(IV) (Fig. 6) are proposed for several such clusters. Structures (III) and (IV) were confirmed by X-ray diffraction for the molecules $Me_4Sn_3[Fe(CO)_4]_4$[44] and $Sn[Fe(CO)_4]_4$[45,46] respectively.

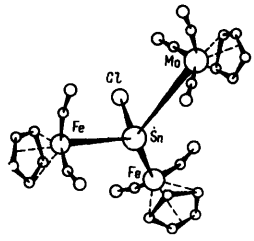


Figure 5. Geometry of the $ClSn[Fe(CO)_2Cp]_2$. $[Mo(CO)_3Cp]$ molecule.

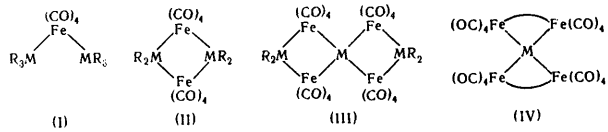


Figure 6. Structure of derivatives of iron tetracarbonyl containing an Fe–M bond where M = Ge, Sn, or Pb.

Table 2 gives the principal structural parameters of the compounds which contain a metal–metal bond between a transition metal atom and a Group IVB atom.

III. METHODS OF FORMATION OF COVALENT BONDS BETWEEN ATOMS OF TRANSITION METALS AND ELEMENTS OF GROUP IVB

This chapter considers the methods of preparation of compounds containing from one to four metal carbonyl groups bound to an atom of a Group IVB element. Such reactions of these compounds will be discussed in the following chapter.

Method I. Replacement of Halogen Atoms in Compounds of the $R_{4-n}MHal_n$ Type by Metal Carbonyl Groups

The most general method for the formation of metal–metal bonds is reaction between halogen derivatives of the Group IVB elements and the sodium derivatives of metal carbonyls. This method was first used (in a more general form) by Hein and coworkers[56–59] for the formation of a Pb–Fe bond in the reaction of R_3PbBr or R_3PbOH with $CaFe(CO)_4$.

Exchange reactions have been used to obtain most of the known organopolymetallic derivatives of the carbonyls of chromium, molybdenum, and tungsten[60–62], manganese[22,32,33,62–70], rhenium[62,66,67,71,72], iron[10,22,63,73–75], and cobalt[62,70,76–81]. Depending on the nature and ratio of the reagents and on the reaction conditions there is partial or complete replacement of halogen atoms by metal carbonyl groups:

$$R_{4-n}MX_n + nNaM'(CO)_xL \xrightarrow{THF} R_{4-n}M[M'(CO)_xL]_n + n\,NaX$$

$$R_{4-n}MX_n + m\,NaM'(CO)_xL \xrightarrow{THF} R_{4-n}X_{n-m}M[M'(CO)_xL]_m + m\,NaX$$

where M = Si, Ge, Sn, Pb; $M'(CO)_XL$ = $Cr(CO)_3Cp$, $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2Cp$, $Co(CO)_4$; R = H, alkyl, aryl; X = Cl, Br, I; n = 1–4; and m = 1–3.

The complexes which contain the $Fe(CO)_4$ group and have structures (I) and (II) (see Fig. 6) are obtained[50,82–84] by the following reactions:

$$2R_3MCl + Na_2Fe(CO)_4 \rightarrow (R_3M)_2Fe(CO)_4 + 2NaCl$$

$$2R_2MCl_2 + 2Na_2Fe(CO)_4 \rightarrow [R_2MFe(CO)_4]_2 + 4NaCl$$

where M = Ge, Sn, Pb; R = Me, Et, n-Bu, similar to the method used earlier by Hein.

Compounds with Sn–Ir bonds were synthesised with the aid of exchange reactions[85]:

$$R_{4-n}SnCl_n + n\,Na[Ir(CO)_3PPh_3] \rightarrow R_{4-n}Sn[Ir(CO)_3PPh_3]_n + n\,NaCl$$

where R = Me or Ph, and n = 1 or 2, as were compounds with Sn–Rh bonds[85]:

$$Me_3SnCl + Na[Rh(CO)_2(PPh_3)_2] \rightarrow Me_3SnRh(CO)_2(PPh_3)_2I + NaCl\ .$$

When the sodium derivatives of metal carbonyls react with polyhalide compounds of Group IVB elements mixtures of products with different degrees of substitution[64,65] are often formed, for example:

$$GeCl_4 + NaMn(CO)_5 \rightarrow Cl_3GeMn(CO)_5 + Cl_2Ge[Mn(CO)_5]_2 + [(OC)_5MnGeCl_2]\ .$$

By starting from halogen-containing organopolymetallic compounds, derivatives with a greater number of M–M′ bonds can be obtained, including those with different metal carbonyl groups[86,87]:

$$R_2ClSnMn(CO)_5 + NaM'(CO)_xL \rightarrow R_2Sn[Mn(CO)_5][M'(CO)_xL] + NaCl$$

where $M'(CO)_XL$ = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Re(CO)_5$, or $Co(CO)_4$; R = Me or Ph.

By the replacement of the chlorine atoms in $Cl_2Sn[Fe(CO)_2Cp]_2$ by metal carbonyl groups clusters containing three different metals were obtained:

$ClSn[Mo(CO)_3Cp][Fe(CO)_2Cp]_2$[43,88], $Sn[Mo(CO)_3Cp]_2[Fe(CO)_2Cp]_2$[88], $ClSn[Mn(CO)_5][Fe(CO)_2Cp]_2$[73] and $ClSn[Re(CO)_5][Fe(CO)_2Cp]_2$[73].

Steric factors have a considerable effect on the nature of the products formed in reactions of this type. For example, compounds with four $M'(CO)_5$ groups (M′ = Mn or Re) at germanium or tin atoms could not be obtained since distannanes are formed instead of the expected products[62,71]:

$$X_{4-n}Sn[M'(CO)_5]_n + NaM'(CO)_5 \rightarrow \begin{matrix}(OC)_5M' & & & & M'(CO)_5\\ & \diagdown & & \diagup & \\ & & (OC)_5M'-Sn-Sn-M'(CO)_5 & & \\ & \diagup & & \diagdown & \\ (OC)_5M' & & & & M'(CO)_5\end{matrix}$$

where n = 1 or 3; M′ = Mn or Re; X = Cl or Br. This is evidently explained by the large volume of the metal pentacarbonyl groups. Whereas many tin derivatives of the $XSn[M'(CO)_5]_3$ type have been obtained, where M′ = Mn or Re and X = Me, Ph, Cl, Br, I, etc.[32,33,62,66], only one analogous germanium compound is known, $ClGe[Mn(CO)_5]_3$.[65] Instead of the corresponding bromo- and phenyl derivatives digermanes were obtained, for example:

$$2PhBr_2GeMn(CO)_5 + 4NaMn(CO)_5 \rightarrow \begin{matrix}(OC)_5Mn & & & & Mn(CO)_5\\ & \diagdown & & \diagup & \\ & & Ph-Ge-Ge-Ph & & \\ & \diagup & & \diagdown & \\ (OC)_5Mn & & & & Mn(CO)_5\end{matrix}\ .$$

The existence of the compounds $Sn[Fe(CO)_2Cp]_4$ [73] and $Sn[Mo(CO)_3Cp]_2.[Fe(CO)_2Cp]_2$ [88] shows that the steric hindrance produced by the $Mo(CO)_3Cp$ and $Fe(CO)_2Cp$ groups is much less than that due to the steric effects of the $Mn(CO)_5$ and $Re(CO)_5$ groups.

This type of method for the formation of M–M′ bonds includes the reaction of the halogen derivatives of Group IVB elements with the $[Co(CO)_4]^-$ anion [80,81] formed during the dissolution of cobalt carbonyl in nucleophilic solvents [89]:

$$3Co_2(CO)_8 + 12CH_3OH \rightarrow 2[Co(CH_3OH)_6]^{2+}[Co(CO)_4]_2^- + 8CO$$

$$R_{4-n}MCl_n + m[Co(CO)_4]^- \xrightarrow{CH_3OH} R_{4-n}Cl_{n-m}M[Co(CO)_4]_m$$

where M = Ge, Sn, or Pb; R = Me, n-Bu, or Ph; n = 1–3; m = 1–3.

Method 2. The Insertion of Ge^{II} and Sn^{II} Halides at Metal–Metal, Metal–Carbon, and Metal–Halogen Bonds

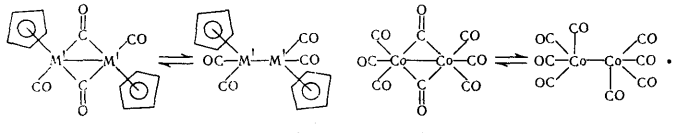
Several compounds which contain a bond between a Group IVB element and iron [24,74,90], cobalt [90–92], nickel [90], or ruthenium [93] atoms have been obtained as a result of the reaction of germanium(II) or tin(II) halides with dimeric carbonyls of the corresponding metals:

$$MX_2 + [M'(CO)_xL]_2 \rightarrow L(OC)_xM'–MX_2–M'(CO)_xL$$

where $M'(CO)_XL$ = $Fe(CO)_2Cp$, $Co(CO)_4$, $Co(CO)_3PR_3$, $Ni(CO)Cp$, $Ru(CO)_2Cp$; M = Ge or Sn; and X = Cl, Br, or I.

Reactions of this type are undergone both by the dihydrates of bivalent metal halides and by the anhydrous MX_2 in solutions in methanol, acetone, benzene or tetrahydrofuran (THF).

The reaction for the insertion of the MX_2 "carbenoids" at metal–metal bonds in dimeric carbonyls is based on the ability of Ge^{II} and Sn^{II} atoms to increase their covalency to four. As the experimental results show, this reaction is quite specific. They proceed comparatively readily with compounds which contain Fe–Fe, Co–Co, Ni–Ni, or Ru–Ru bonds, in the molecules of which in the crystalline state the metal–metal bonds are "maintained" by bridging carbonyl groups [94–96]. However, as the infrared spectra showed, in solutions the bridging forms $[M'(CO)_2Cp]_2$ (where M′ = Fe [97] or Ru [98]) and $Co_2(CO)_8$ [99–102] are in equilibrium with isomeric forms which do not contain bridging CO groups:



A rise in temperature shifts the equilibrium to the right.

The decrease in the coordination number of the metal atoms on going from the bridging form to the non-bridging form facilitates the approach of the MX_2 "carbenoids" to the M′–M′ bonds, which facilitates the insertion. In addition, the dissociation of $[Fe(CO)_2Cp]_2$ into $[Cp(CO)_2Fe]^{\cdot}$ radicals can be assumed to take place in nucleophilic solvents [103], and with $Co_2(CO)_8$ it is found that both $[(CO)_4Co]^{\cdot}$ radicals [104] and $[Co(CO)_4]^-$ anions [89,105] can be formed.

The insertion of $SnCl_2$ into phosphine derivatives of cobalt carbonyl free from bridging carbonyl groups has been effected [90–92]:

$$SnCl_2 + [Co(CO)_3PR_3]_2 \rightarrow Cl_2Sn[Co(CO)_3PR_3]_2$$

where R = n-Bu, Ph, or PhO. These reactions require more severe conditions and a much longer time than for $Co_2(CO)_8$. The insertion is hindered by increase in the π-acceptor capability of the ligands in the order: Bu_3P < < Ph_3P < $(PhO)_3P$.

Until recently insertions at metal–metal bonds in dinuclear carbonyls of molybdenum, tungsten, manganese, and rhenium, the fragments of which are bonded either in the crystalline state [6,7,9] or in solutions (according to the infrared spectra [106,107]) solely by an M′–M′ bond had not been effected. The reaction of $[Mo(CO)_3Cp]_2$ with $SnCl_2$ leads to the formation of $Cl_3SnMo(CO)_3Cp$. [24] The dimeric derivative of manganese carbonyl containing the 1,2-bis-diphenylphosphinoethane ligand reacts with $SnCl_2$ but the insertion product is again not obtained [108]:

$$[Mn(CO)_3L]_2 + SnX_2 \xrightarrow{\text{Acetone}} X_3SnMn(CO)_xL_y$$

where L = $Ph_2PCH_2CH_2PPh_2$; X = Cl, Br; x = 3 for y = 1; x = 1 for y = 2.

Manganese and rhenium carbonyls do not react with MX_2, [24,108] even on boiling in THF for three weeks [90]. It was recently observed [109] that to introduce MX_2 "carbenoids" at Mn–Mn and Re–Re bonds either elevated temperature or ultraviolet radiation, leading to the homolytic fission of these bonds, is necessary.

Hence the possibility of effecting insertion at M′–M′ bonds is determined by the stability of these bonds under the reaction conditions.

The insertion of "carbenoid" systems at transition metal–carbon bonds was first achieved at C–Fe bonds [110]:

$$MeFe(CO)_2Cp + GeCl_2\cdot C_4H_8O_2 \xrightarrow{\text{(dioxan)}} MeCl_2GeFe(CO)_2Cp$$

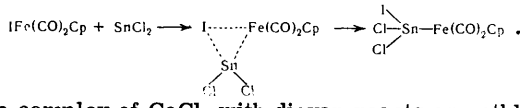
whereas with the C–W bond reaction with $SnCl_2$ led to the replacement of a methyl group by $SnCl_3$: [24]

$$MeW(CO)_3Cp + SnCl_2 \xrightarrow{\text{(acetone)}} Cl_3SnW(CO)_3Cp\ .$$

The reactions of halogen derivatives of metal carbonyls with germanium(II) and tin(II) halides were studied. $SnCl_2$ reacts with $ClFe(CO)_2Cp$ in methanol as follows [24]:

$$ClFe(CO)_2Cp + SnCl_2\cdot 2H_2O \rightarrow Cl_3SnFe(CO)_2Cp\ .$$

The reaction may proceed either by the insertion of $SnCl_2$ at the Fe–Cl bond or by the replacement of a chlorine atom in $ClFe(CO)_2Cp$ by $[SnCl_3]^-$ by an S_N1 or S_N2 mechanism. To find the mechanism $IFe(CO)_2Cp$ was treated with a tenfold excess of $SnCl_2$ as a result of which the complex $CH_3OH.ICl_2SnFe(CO)_2Cp$ was obtained [111]. Evidently the insertion of a "carbenoid" really does occur here, possibly proceeding with preliminary coordination of Cl_2Sn to the iron and iodine atoms and subsequent intramolecular migration of the iodine atom:



The complex of $GeCl_2$ with dioxan reacts smoothly with $ClFe(CO)_2Cp$ with the formation of $Cl_3GeFe(CO)_2Cp$. [112] In the reaction of this same complex with $IFe(CO)_2Cp$ a mixture of products is formed, in which $Cl_3GeFe(CO)_2Cp$ and $I_3GeFe(CO)_2Cp$ are present, as a comparison of the chemical shifts of the protons of the cyclopentadienyl ring shows. This can be due to the ready disproportionation of the compound expected:

$$5\ ICl_2GeFe(CO)_2Cp \rightarrow 3\ Cl_3GeFe(CO)_2Cp + I_2ClGeFe(CO)_2Cp + I_3GeFe(CO)_2Cp\ .$$

By analogy with the reactions of $GeCl_2$ and $MeFe(CO)_2Cp$ [110] it can be assumed that the reaction between the MX_2 halides and compounds with Fe–Hal bonds also proceeds by the insertion mechanism.

Method 3. Reaction of Trichlorogermane with Halogen Derivatives of Metal Carbonyls

The possibility of the formation of metal–metal bonds by reactions of this type was first demonstrated by the condensation of trichlorogermane with pentacarbonylmanganese chloride [113]:

$$Cl_3GeH + ClMn(CO)_5 \xrightarrow{(THF)} Cl_3GeMn(CO)_5 + HCl \ .$$

The compounds $Cl_3GeMo(CO)_3Cp$, $Cl_3GeW(CO)_3Cp$, [114] and $Cl_3GeFe(CO)_2Cp$ [115] were obtained by the same method. Reactions of this type take place in THF solutions or in ether–dioxan mixtures.

It is known [116] that in $HGeCl_3$ there is an equilibrium between the bivalent and quadrivalent forms of germanium, and the presence of ethers facilitates the protonic dissociation of the germyl hydrogen:

$$HGeCl_3 \rightleftarrows H^+ + GeCl_3^- \rightleftarrows H^+ + Cl^- + GeCl_2$$

and the formation of ether addition compounds of the type $[R_2O \rightarrow H \leftarrow OR_2]^+GeCl_3^-$. In dioxan the dissociation goes even further and the complex $Cl_2Ge.C_4H_8O_2$ is formed. As shown above, this complex reacts with $ClFe(CO)_2Cp$, most probably by insertion at the Fe–Cl bond. In the reaction of $HGeCl_3$ with $[Fe(CO)_2Cp]_2$ in THF, $Cl_2Ge[Fe(CO)_2Cp]_2$ formed in additon to $Cl_3GeFe(CO)_2Cp$. [115]

It can be assumed that the reaction of metal halogenocarbonyls with $HGeCl_3$ proceeds either by the insertion of $GeCl_2$ at the M′–Cl bond or by an ionic mechanism with participation of the $GeCl_3^-$ anion by analogy with the reactions of alkyl halides with trichlorogermane leading to compounds of the $RGeCl_3$ type [116]. Possibly both these mechanisms compete but they have not yet been distinguished.

Method 4. Replacement of the Mercury Atom in Mercury Derivatives of Metal Carbonyls by Tin(II) Halides

Sn–M′ bonds are formed in the reaction of SnX_2 with $XHgM'(CO)_xL$ or $Hg[M'(CO)_xL]_2$ in acetone or ethyl acetate [91,117]:

$$RHgR' + SnX_2 \rightarrow X_2SnRR' + Hg \quad (1)$$
$$RHgX + SnX_2 \rightarrow X_2SnR + Hg \quad (2)$$

where R and R′ = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Fe(CO)_2Cp$, $Co(CO)_4$, $Co(CO)_3PBu_3$; X = Cl or Br. The initial stage of reaction (1) may be the introduction of "carbenoid" groups: $R–Hg–R–SnX_2 \rightarrow [R–Hg–SnX_2–R]$. The intermediate compound is unstable owing to the low strength of the Hg–Sn bond and readily decomposes:

$$[R—Hg—SnX_2—R] \rightarrow Hg + X_2SnR_2.$$

Reaction (2) evidently proceeds by another mechanism. Unlike the electrophilic insertion of SnX_2 mentioned above here nucleophilic attack by SnX_3^- formed in the solution on the RHg^+ or $RHg[(Solv)]^+$ cation is possible:

$$R—Hg—X + SnX_3^- \xrightarrow{(Solv)} [RHgSnX_3] \rightarrow X_2SnR + Hg \ .$$

Method 5. Reaction of Silanes with Dimers of Metal Carbonyls

In the reaction of silanes with cobalt carbonyl a compound with a Si–Co bond is formed readily [118]. The reaction of silanes with dinuclear metal carbonyls serves as a preparative method for the synthesis of various silyl derivatives of molybdenum [119], manganese and rhenium [67, 70,119], iron [119], cobalt [50,70,120,121], and nickel [119]:

$$2R_3SiH + [M'(CO)_xL]_2 \rightarrow 2R_3SiM'(CO)_xL + H_2$$

where $M'(CO)_xL$ = $Mo(CO)_3Cp$, $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2Cp$, $Co(CO)_4$, $Ni(CO)Cp$; R = H, alkyl, aryl, halogen. It should be noted that the reaction with cobalt carbonyl is very fast even at room temperature, whereas very severe conditions are necessary with manganese and rhenium carbonyls.

Probably the initial stage in these reactions is the formation of $HM'(CO)_xL$, which then reacts with the silane:

$$R_3SiH + HM'(CO)_xL \rightarrow R_3SiM'(CO)_xL + H_2 \ .$$

Confirmation of this mechanism is given by the quantitative formation of compounds of the type $R_3SiCo(CO)_4$ in the reaction of silanes with either cobalt carbonyl or $HCo(CO)_4$. [121]

The reaction of $HSiCl_3$ with $Fe_3(CO)_{12}$ gives a compound with two terminal Cl_3Si groups at the iron atom, $(Cl_3Si)_2Fe(CO)_4$, and in reaction with $Fe(CO)_5$ in addition to this compound the cluster $[Cl_2SiFe(CO)_4]_2$ with two bridging silicon atoms is obtained [119].

Evidently the reaction of alkylgermanes [50,120] and alkylstannanes [51] with metal carbonyls can be classified among this type of reaction:

$$Et_3GeH + Co_2(CO)_8 \rightarrow Et_3GeCo(CO)_4$$
$$2Me_3SnH + Fe(CO)_5 \rightarrow (Me_3Sn)_2Fe(CO)_4 + H_2 + CO$$
$$2Me_2SnH_2 + 2Fe(CO)_5 \rightarrow [Me_2SnFe(CO)_4]_2 + 2H_2 + 2CO \ .$$

Apart from the general methods for the formation of M–M′ bonds considered above, there are specific methods applicable for the synthesis of individual organopolymetallic derivatives of metal carbonyls.

Compounds with Si–Mo or Si–W bonds were obtained by the reaction [122]:

$$HM'(CO)_3Cp + Me_2SiNMe_2 \xrightarrow{(THF)} Me_2SiM'(CO)_3Cp + Me_2NH.$$

Metal–metal bonds are formed by the photolytic reaction [123]:

$$Ph_4AsMCl_3 + M'(CO)_6 \xrightarrow{(CH_2Cl_2)} Cl_3MM'(CO)_5AsPh_4 + CO$$

where M = Ge or Sn; M′ = Cr, Mo, W.

Compounds of the $Cl_3MFe(CO)_4AsPh_4$ type were obtained [123] by a similar method from $Fe(CO)_5$. The formation of products with two metal–metal bonds of the $(Cl_3M)_2M'(CO)_4(AsPh_4)_2$ type, where M = Ge or Sn and M′ = Cr, Mo, or W, is also possible.

Compounds with M–M′ bonds were obtained [124] by reactions with oxidative eliminations, for example:

$$(bipy)Mo(CO)_4 + MeSnCl_3 \rightarrow MeCl_2SnMoCl(CO)_3(bipy) + CO \ .$$

The formation of a Ge–Mn bond was possible as a result of the reaction:

$$GeH_4 + 2HMn(CO)_5 \xrightarrow{(THF)} H_3Ge[Mn(CO)_5]_3 + 2H_2 \ .$$

In this even traces of $H_3GeMn(CO)_5$ or $HGe[Mn(CO)_5]_3$ were not observed although they might have been formed by the simple replacement of hydrogen atoms in the germane by the $Mn(CO)_5$ group. It is assumed that this reaction proceeds by the reduction of GeH_4 by the manganese carbonyl to GeH_2, which then adds two $Mn(CO)_5$ radicals. Traces of $H_2Ge[Mn(CO)_5]_2$ were observed in the reaction of GeH_4 with $Mn_2(CO)_{10}$. However, neither GeH_4 nor H_3GeK react with $ClMn(CO)_5$ or $BrMn(CO)_5$. [125].

Most of the compounds which contain the $Fe(CO)_4$ group were obtained as a result of specific reactions. Thus, compounds of the type $R_nSnR'_{4-n}$, where R = alkyl and R′ = vinyl or phenyl, react with $Fe(CO)_5$ to form clusters

of the $[R_2SnFe(CO)_4]_2$ type [49]. It is characteristic that these reactions are possible only for such compounds in which organic groups bound to the tin atom through sp^3 and sp^2 hybridised carbon atoms are present, for example, Me_2SnPh_2 or $Bu_2Sn(CH=CH_2)_2$; the groups bound to tin by the sp^2 carbon atom are more readily detached. Evidently the initial stage of the reaction is the formation of an unstable π-complex with participation of an iron atom.

The reaction

$$Bu_3SnCl + Fe(CO)_5 \rightarrow [Bu_2SnFe(CO)_4]_2 + Bu_4Sn_2[Fe(CO)_4]_4 + Sn[Fe(CO)_4]_4$$

was studied in detail [46,51]. It was suggested that initially a compound with structure (I) (Fig. 6) is formed:

$$2Bu_3SnCl + Fe(CO)_5 \rightarrow (Bu_3Sn)_2Fe(CO)_4 + CO,$$

which then disproportionates:

$$2(Bu_3Sn)_2Fe(CO)_4 \rightarrow [Bu_3SnFe(CO)_4]_2 + 2Bu_4Sn\ .$$

The composition of the mixture of products depends greatly on the reaction conditions. Thus after intensive boiling for 70 h only $Sn[Fe(CO)_4]_4$ is isolated. This compound can also be obtained by other methods:

$$Bu_6Sn_2 + Fe(CO)_5 \rightarrow Sn[Fe(CO)_4]_4 \leftarrow SnCl_2 + Fe(CO)_5\ .$$

Compounds having structure (II) (Fig. 6) are also formed by the reaction [126,127]:

$$R_2Sn(C{\equiv}CR')_2 + Fe_3(CO)_{12} \rightarrow [R_2SnFe(CO)_4]_2\ .$$

Oxidative elimination leads to compounds with structure (I), for example [124]:

$$SnX_4 + Fe(CO)_5 \rightarrow X_3SnFeX(CO)_4 \rightarrow (X_3Sn)_2Fe(CO)_4.$$

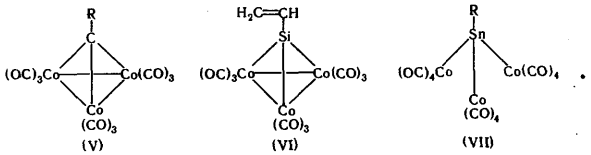
A series of specific methods for the formation of M–Co bonds are known. The direct reaction of MX_4 with cobalt carbonyl [77-81] can give halogen derivatives with from one to three $Co(CO)_4$ groups:

$$GeCl_4 + Co_2(CO)_8 \rightarrow Cl_{4-n}Ge[Co(CO)_4]_n + CoCl_2 + CO$$
$$4SnX_4 + 9Co_2(CO)_8 \rightarrow 4XSn[Co(CO)_4]_3 + 2CoX_2 + 24CO$$

where X = Cl, Br, or I and n = 1 or 2. It is thought that in these reactions after the Co–Co bond is broken unstable carbonylcobalt halides are formed, which then decompose. The rate of these reactions decreases considerably with drop in the nucleophilic nature of the solvent in the series: THF > benzene > heptane [77]. It is not ruled out that reaction in THF is greatly facilitated by the reaction of $Co_2(CO)_8$ with the solvent, leading to the formation of the $[Co(CO)_4]^-$ anion. Clusters with an $RSnCo_3$ skeleton were obtained [79,80,102] by a similar method:

$$RSnCl_3 + Co_2(CO)_8 \rightarrow RSn[Co(CO)_4]_3 \text{ (where R=Me, Bu)}\ .$$

Compounds of the type $RC[Co(CO)_3]_3$ with structure (V) are formed [128,129] in the reaction of organic trihalogenoderivatives with $Co_2(CO)_8$:



(V) (VI) (VII)

Kettle and Khan [130] obtained a compound with Si–Co bonds for which the structure (VI) is proposed:

$$(CH_2{=}CH)_4Si + Co_2(CO)_8 \rightarrow CH_2{=}CHSi[Co(CO)_3]_3\ .$$

Tris(tetracarbonylcobalt) derivatives of tin (VII) do not contain Co–Co bonds, unlike the tris(tricarbonylcobalt) derivatives of carbon and silicon (V) and (VI) formed in similar reactions. It is interesting that the products of the reaction of tetravinylstannane with $Co_2(CO)_8$ differ depending upon the solvent: $(CH_2{=}CH)_2Sn[Co(CO)_4]_2$ is formed in pentane whereas in THF $MeC[Co(CO)_3]_3$ is formed. The formation of the latter is evidently explained by the conversion of the vinyl group into an ethylidene group during the reaction. The reasons for the difference in the structure of the complexes with an $RMCo_3$ skeleton, where M = C, Si, or Sn are still unexplained.

When tin(II) acetate reacts with $Co_2(CO)_8$ a mixture of $(CH_3CO_2)_2Sn[Co(CO)_4]_2$ and $CH_3CO_2Sn[Co(CO)_4]_3$ is formed [131].

As a result of the reaction of bis-(2,4-pentadionato)$SnCl_2$ with $[Co(CO)_4]^-$ compounds with a 6-coordinated tin atom are obtained [132]:

$$(C_5H_7O_2)_2SnCo_2(CO)_7,\quad (C_5H_7O_2)_2Sn[Co(CO)_4]_2 \text{ and } (C_5H_7O_2)_2ClSnCo(CO)_4.$$

IV. PROPERTIES OF ORGANOPOLYMETALLIC COMPOUNDS

Derivatives of Group IVB elements and metal carbonyls which contain metal–metal bonds are usually crystalline substances soluble in the usual organic solvents and insoluble in water. These compounds decompose comparatively readily in solution. In the solid state they are rather stable to the action of heat, light, oxygen, and atmospheric moisture. The stability of the compounds which differ in the transition metal atom increases considerably with increase in the atomic number of the metal within each group, for example, in the series Cr < Mo < W. With increase in the number of metal carbonyl groups the stability of the compounds falls slightly. In the series of compounds which differ only in the atoms of the Group IVB elements the stability of the lead derivatives is much less than that of its group analogues. Usually, with increase in the electronegativity of the substituent at the non-transition element the stability of the compounds increases.

The following reaction modes are characteristic for the compounds of the $X_{4-n}M[M'(CO)_xL]_n$ type: (1) substitution of M for X at the Group IVB element; (2) reactions at the M–M' bonds, and (3) replacement of the carbonyl groups at the transition metal atoms by other ligands. Furthermore, some of these compounds are capable of forming addition products with electron-donating reagents.

1. Replacements at the Group IVB Element

It is known [133,134] that halogenogermanes and halogenostannanes with organic groups readily exchange halogen atoms for other substituents. Halogen derivatives of germanium and tin containing metal carbonyl groups are also capable of exchanging halogen atoms for other atoms or groups whilst retaining the metal–metal bonds. Thus the chlorine atoms in $Cl_3GeFe(CO)_2Cp$ are replaced by acetoxy-groups [112]:

$$Cl_3GeFe(CO)_2Cp + 3CH_3COOK \rightarrow (CH_3COO)_3GeFe(CO)_2Cp + 3KCl\ .$$

Compounds are obtained with different functional groups at the germanium or tin atoms bound to two metal carbonyl groups:

$$Cl_2M[M'(CO)_xL]_2 + 2Y^- \rightarrow Y_2M[M'(CO)_xL]_2 + 2Cl^-\ ,$$

where $M'(CO)_xL$ = $Mo(CO)_3Cp$, $W(CO)_3Cp$; M=Sn[135], Mn $(CO)_5$; M=Ge[136]; $Fe(CO)_2Cp$, M = Ge, Sn[79,137]; Y=CH_3COO, MeO, EtS, SCN, OH, S, ONO, NO_3.

In the reaction with organic derivatives of lithium, sodium, or magnesium replacement of halogen atoms by organic groups occurs[73,74,135,137,138], for example:

$$I_2Ge[Fe(CO)_2Cp]_2 + 2MeLi \rightarrow Me_2Ge[Fe(CO)_2Cp]_2 + 2LiI$$

$$Cl_2Sn[Mo(CO)_3Cp]_2 + 2C_5H_5Na \rightarrow (C_5H_5)_2Sn[Mo(CO)_3Cp]_2 + 2NaCl$$

$$Br_3GeMn(CO)_5 + 3PhMgBr \rightarrow Ph_3GeMn(CO)_5 + 3MgBr_2 .$$

On passing gaseous HBr through solutions of $Cl_3GeMn(CO)_5$ or $Cl_2Ge[Mn(CO)_5]_2$ chlorine atoms are quantitatively replaced by bromine[138].

It was noted above that in the reaction of compounds of Group IVB elements containing several halogen atoms with the sodium derivatives of metal carbonyl mixtures of products with different degrees of substitution are obtained. A convenient method for the synthesis of individual halogen-containing compounds is the exchange of acetoxy-groups for halogen atoms:

$$(CH_3COO)_nGe[M'(CO)_xL]_{4-n} + nHX \rightarrow X_nGe[M'(CO)_xL]_{4-n} + nCH_3COOH$$

where $M'(CO)_xL = Mn(CO)_5$,[136] $Fe(CO)_2Cp$,[112,137] X = F, Cl, Br, I; $n = 2$ or 3.

Compounds with Ge–Fe bonds have been reduced[74]:

$$Cl_2Ge[Fe(CO)_2Cp]_2 + 2NaBH_4 \rightarrow H_2Ge[Fe(CO)_2Cp]_2$$

but attempts to obtain similar compounds with M–Mn or M–Re bonds were unsuccessful since reaction with $LiAlH_4$ or $NaBH_4$ is accompanied by the breaking of M–M′ bonds. Alkylation of compounds with Sn–Mo or Sn–W bonds could not be brought about with Grignard reagents[135]. These facts show the decrease in the stability of the M–M′ bonds under the conditions of these reactions is in the order M–Fe > M–Re ≃ M–Mn > M–W ≃ M–Mo, where M = Ge or Sn.

Carbonyl derivatives of the type $R_{4-n}M[M'(Cl)_xL]_n$, where R is an organic radical, react with halogens or hydrogen halides in two (sometimes competing) directions: either with partial or complete replacement of R or with breaking of the M–M′ bond. The direction of the reaction is determined primarily by the nature of the reactants and also by the quantitative ratio of the reagents and the reaction conditions.

$H_3SiMn(CO)_5$ was rather inert to the action of HCl;[69] gradual replacement of hydrogen atoms takes place only at 75°, and the Si–Mn bond is retained:

$$H_3SiMn(CO)_5 + nHCl \rightarrow H_{3-n}Cl_nSiMn(CO)_5 + nH_2$$

where $n = 1$–3. The considerable differences in the reactivity of the germanium and tin derivatives of the corresponding metal carbonyls is connected on the one hand with the lesser stability of the C–Sn bond in comparison with C–Ge. On the other hand an analysis of the reactions given below suggests that the stability of the Sn–M′ bonds is much greater than that of the Ge–M′ bonds. The triphenylgermyl derivatives of manganese and rhenium carbonyls do not react with HCl,[64,72] unlike the corresponding tin derivatives, which react with hydrogen halides with partial or complete replacement at the tin atom[22,71]. The Ph_3Sn derivatives of molybdenum, tungsten[60,135], iron[73], and cobalt[77] carbonyls behave similarly:

$$Ph_3SnM'(CO)_xL + nHX \rightarrow Ph_{3-n}X_nSnM'(CO)_xL + nC_6H_6$$

where X = Cl, Br, I and $n = 1$–3. Diphenylstannanes containing two metal carbonyl groups react with hydrogen halides, usually with retention of the Sn–M′ bonds[72,73,86,135]:

$$Ph_2Sn[M'(CO)_xL]_2 + 2HX \rightarrow X_2Sn[M'(CO)_xL]_2 + 2C_6H_6 .$$

It is characteristic that $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$ reacts with HCl with replacement of only one phenyl group[86] but $Ph_2Sn[Co(CO)_4]_2$ does not undergo this reaction at all[77]. Evidently, the Sn–C bond is stabilised as a result of the addition of the electronegative $Co(CO)_4$ group to the tin atom. $Ph_2Ge[Re(CO)_5]_2$ reacts with HCl with the loss of one metal carbonyl group and not a phenyl group[72].

In the reaction of halogens with Ph_3Sn derivatives of manganese and rhenium carbonyls, depending on the ratio of the reagents mono-, di-, or tri-halogeno-derivatives are formed with retention of the Sn–M′ bonds[22,71,72]:

$$Ph_3SnM'(CO)_5 + nX_2 \rightarrow Ph_{3-n}X_nSnM'(CO)_5 + nPhX .$$

The action of halogens on $Ph_2Sn[Re(CO)_5]_2$ leads to the replacement of one of the two phenyl groups (depending on the ratio of the reagents)[71], whereas the analogous manganese compound reacts with the breaking of both C–Sn bonds and one Sn–Mn bond[22].

The reaction of $Ph_3GeMn(CO)_5$ and its rhenium analogue with chlorine or bromine at room temperature leads to breaking of the Ge–M′ bonds without replacement of the phenyl groups at the germanium atom. On the other hand, at temperatures above 70°, irrespective of the ratio of the reactants, all three phenyl groups are replaced by halogen atoms with retention of the Ge–M′ bond[64,72]:

$$Ph_3GeM'(CO)_5 + 3X_2 \rightarrow X_3GeM'(CO)_5 + 3PhX .$$

The direct action of halogens does not bring about replacement of three phenyl groups in Ph_4Ge or Ph_3GeX, or even one in Ph_2GeX_2, where X = Cl, Br, or I. The capability for ready and simultaneous replacement of three phenyl groups in $Ph_3GeM'(CO)_5$ shows the greater electron-donating ability of the $Mn(CO)_5$ and $Re(CO)_5$ groups in comparison with the phenyl groups.

The introduction of halogen atoms into phenylgermyl derivatives has been shown[65] to greatly strengthen Ge–Mn bond and to some extent the Ge–C bond, in comparison with the corresponding bonds in $Ph_3GeMn(CO)_5$. Thus at room temperature $Ph_2BrGeMn(CO)_5$ does not react with bromine, and at 72° one phenyl group is readily replaced by bromine, but $PhBr_2GeMn(CO)_5$ reacts very slowly with an excess of bromine at 72° to form $Br_3GeMn(CO)_5$.

Hence it can be taken as proved that the Ge–C bond in the germyl derivatives of the Group VII metal carbonyls is broken under the action of halogens much more readily than in ordinary organogermanium compounds.

Unlike the rearrangements[133]:

$$Ph_2GeX_2 + GeX_4 \rightarrow 2PhGeX_3$$

where X = Cl, Br, or I, which take place at high temperature in the presence of catalysts, the rearrangement of germanes which contain an $Mn(CO)_5$ group proceeds without a catalyst at a temperature not much above the melting point of the mixture of reagents[64]:

$$Ph_2BrGeMn(CO)_5 + Br_3GeMn(CO)_5 \rightarrow 2PhBr_2GeMn(CO)_5 .$$

Reactions with rearrangement at the tin atom are used[22] as a convenient method for making monohalogeno-derivatives:

$$PhBr_2SnMn(CO)_5 + Ph_3SnMn(CO)_5 \rightarrow 2Ph_2BrSnMn(CO)_5 .$$

The possibility of the rearrangement of atoms of different halogens in germyl derivatives of iron carbonyl has been demonstrated[112]:

$$Cl_3GeFe(CO)_2Cp + I_3GeFe(CO)_2Cp \rightarrow Cl_2IGeFe(CO)_2Cp + ClI_2GeFe(CO)_2Cp .$$

With derivatives of metal carbonyls which contain lead replacement at the lead atom is not observed although the

Pb–C bond is the weakest in the series of organometallic derivatives of the Group IVB elements [134]; the Pb–M′ bond is broken first.

2. Reaction of Compounds of the $X_{4-n}M[M'(CO)_xL]_n$ type at M–M′ Bonds

A. Breaking of the metal–metal bond. Unlike $H_3SiMn(CO)_5$ its addition product with pyridine reacts rapidly with HCl with quantitative breaking of the Si–Mn bond [69]:

$$H_3SiMn(CO)_5 \cdot 2C_5H_5N + 3HCl \rightarrow H_3SiCl + HMn(CO)_5 + 2C_5H_5N \cdot HCl .$$

$H_3SiCo(CO)_4$ is broken by HCl or water with the formation of cobalt carbonyl hydride [76]:

$$H_3SiCo(CO)_4 + HX \rightarrow H_3SiX + HCo(CO)_4$$

where X = Cl or OH. As noted above, the action of hydrogen halides does not break the M–M′ bond in germanium and tin derivatives of the $Ph_3MM'(CO)_xL$ type or in $Ph_2Sn[M'(CO)_xL]_2$, [22,60,64,72,73,77,135] but one of the Sn–Fe bonds in $PhSn[Fe(CO)_2Cp]_3$ is broken under the action of HCl:[73]

$$PhSn[Fe(CO)_2Cp]_3 + 3HCl \rightarrow Cl_2Sn[Fe(CO)_2Cp]_2 + ClFe(CO)_2Cp .$$

This shows that the M–M′ bond is weakened with increase in the number of metal carbonyl groups at the non-transition element atom. $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$ reacts in a different manner with HCl and HBr: under the action of HCl only one phenyl group is replaced [86] whereas reaction with HBr under these conditions leads to the replacement of both phenyl groups and breaking of the Sn–Co bond [77]:

$$Ph_2Sn[Mn(CO)_5][Co(CO)_4] + HBr \rightarrow Br_2SnMn(CO)_5 .$$

Differences in the reactivity of metal–metal bonds in relation to the action of halogens are more noticeable. For example, in compounds of the $Ph_3MM'(CO)_5$ type (M′ = Mn or Re) the Sn–M′ bond is not broken by halogens at either room or elevated temperature. Whereas Ge–Mn or Ge–Re bonds are stable to the action of halogens at temperatures above 70° they are broken at room temperature [64,72]:

$$Ph_3GeM'(CO)_5 + X_2 \rightarrow Ph_3GeX + XM'(CO)_5 .$$

Probably the reaction of $Ph_3GeM'(CO)_5$ with halogens proceeds by different mechanisms at different temperatures in accordance with a change in the relative strength of the Ge–C and Ge–M′ bonds. Above 70° the rapid homolytic breaking of the Ge–C bond becomes possible [134] and at 20°C the Ge–Mn and Ge–Re bonds become less resistant to the action of halogens and are broken more rapidly than the Ge–C bonds, which are relatively more stable under these conditions. The breaking of Ge–M′ bonds at low temperature can proceed heterolytically, although the possibility of a homolytic process is not excluded.

Under the action of halogens the M–M′ bonds in $Ph_3SnFe(CO)_2Cp$, [22] $Ph_3MM'(CO)_3Cp$ (M = Sn or Pb), and $Ph_2Sn[M'(CO)_3Cp]_2$ (M′ = Cr, Mo, W) [135] are broken. Bromine detaches one metal carbonyl group from $Ph_2Ge[M'(CO)_5]_2$, where M′ = Mn or Re:[64,71,72]

$$Ph_2Ge[M'(CO)_5]_2 + Br_2 \rightarrow Ph_2BrGeM'(CO)_5 + BrM'(CO)_5 .$$

An excess of chlorine splits not only both the Sn–C bonds in $Ph_2Sn[Mn(CO)_5]_2$ but also one of the Sn–Mn bonds, $Cl_3SnMn(CO)_5$ being formed [22]. In the analogous rhenium compound both the Sn–Re bonds are retained under the action of chlorine [71], which shows that the Sn–Re bond is stronger than the Sn–Mn bond.

The bonds of transition metal atoms with lead are less stable. Reaction of $Ph_3PbMn(CO)_5$, $Et_2Pb[Mn(CO)_5]_2$, [22] and $Ph_3PbRe(CO)_5$ [60] with halogens and HCl leads to the complete decomposition of the molecule.

Apart from the breaking of the M–M′ bond under the action of halogens and hydrogen halides, some reactions of this type with other agents are known. The Si–Mn bond is readily broken by ammonia [69]:

$$2H_3SiMn(CO)_5 + NH_3 \rightarrow 2HMn(CO)_5 + (H_3Si)_2NH .$$

A similar reaction was observed for $H_3SiCo(CO)_4$ with the difference that here disilazane was decomposed to SiH_4, $(H_3Si)_3N$, and polymeric products, probably owing to the greater acidity of $HCo(CO)_4$ compared with that of $HMn(CO)_5$.

The reaction of $H_3SiCo(CO)_4$ with mercury(II) iodide is [76]:

$$2H_3SiCo(CO)_4 + HgI_2 \rightleftarrows 2H_3SiI + Hg[Co(CO)_4]_2$$

and the equilibrium is greatly displaced to the right.

Reactions with redistribution at the atoms of the non-transition elements which use the M–M′ bond are also known, for example [24]:

$$Cl_2Sn[Fe(CO)_2Cp]_2 + SnCl_4 \rightarrow 2Cl_3SnFe(CO)_2Cp$$

and also reactions with substitution at the cobalt atom, as a result of which the Si–Co bond is broken and a Ge–Co bond is formed [121]:

$$Me_3SiCo(CO)_4 + GeF_4 \rightarrow F_3GeCo(CO)_4 + Me_3SiF .$$

B. Insertion at Metal–Metal Bonds. In the reaction of perfluoroethylene with $Me_3SnMn(CO)_5$, $Me_3GeMn(CO)_5$, or $Me_3SnCo(CO)_4$ under ultraviolet radiation in pentane compounds containing M–C–C–M′ chains, where M = Ge or Sn and M′ = Mn or Co are obtained [139–142]. Whereas only one $CF_2{=}CF_2$ molecule is inserted per Sn–Mn bond, several perfluoroethylene molecules can be inserted at a Ge–Mn bond with formation of compounds of the $Me_3Ge(C_2F_4)_nMn(CO)_5$ type. As well as insertion products a mixture of fluorinated derivatives is formed in these reactions: Me_3MF, $C_5F_9Mn(CO)_5$, and other organofluorine derivatives of manganese carbonyls.

The reaction mechanism for the introduction of perfluoroethylene at M–M′ bonds has not been explained. Despite the fact that the reaction proceeds only under conditions favourable to free-radical processes, the products characteristic of reactions of Me_3M' radicals with perfluoroalkenes are not observed. The appearance in the reaction mixture of the fluoro-derivatives of germanium, of tin, and of manganese carbonyl can be explained by the decomposition of the insertion products as follows:

$$Me_3M{-}Mn(CO)_5 + CF_2{=}CF_2 \xrightarrow{h\nu} Me_3M{-}CF_2{-}CF_2{-}Mn(CO)_5$$

$$Me_3MCF_2CF_2Mn(CO)_5 \rightarrow CF_2{=}CF{-}Mn(CO)_5 + Me_3MF$$

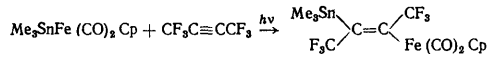
$$CF_2{=}CF{-}Mn(CO)_5 \xrightarrow{-2CO} [CF_2{=}CFMn(CO)_4]_2$$

$$CF_2{=}CF{-}Mn(CO)_5 \xrightarrow{+CO} CF_2{=}CF{-}\underset{\underset{O}{\|}}{C}{-}Mn(CO)_5 .$$

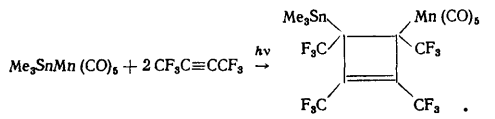
Evidently $Me_3GeC_2F_4Mn(CO)_5$ is more stable than the analogous tin compound.

Unlike perfluoroethylene, $CF_2{=}CFCl$ and $CF_2{=}CFH$ react with $Me_3MMn(CO)_5$ and $Me_3SnCo(CO)_4$ to form not insertion products but mixtures of different fluorinated organometallic compounds. Perfluoropropene also does not form an addition product with $Me_3GeMn(CO)_5$. [139]

The introduction of acetylene compounds at the M–M′ bond has also been studied [143]. Thus the photochemical reaction of perfluorobut-2-yne with $Me_3SnFe(CO)_2Cp$ in pentane leads to the formation of a 1 : 1 addition product:

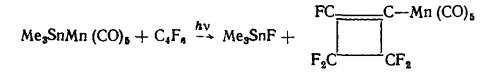


A similar reaction with $Me_3SnMn(CO)_5$ gives a cyclic insertion product:



The reaction of $Ph_3SnMn(CO)_5$ with perfluorobutyne proceeds with much greater difficulty and leads to the formation of a compound in very low yield, evidently also a 1 : 2 addition product.

The reaction of $Me_3SnMn(CO)_5$ with perfluorocyclobutene involves breaking of the Sn–Mn bond:



3. Replacement of Carbonyl Groups by Other Ligands

Derivatives of metal carbonyls containing a metal–Group IVB element bond can react with some nucleophilic reagents with the replacement of one or more CO groups.

Triphenylphosphine reacts with a Ge–Mo complex [123]:

$$Cl_3GeMo(CO)_5AsPh_4 + Ph_3P \xrightarrow[-CO]{} Cl_3GeMo(CO)_4(PPh_3)AsPh_4 \xrightarrow{+PPh_3} \rightarrow \textit{цис}\text{-}Mo(CO)_4(PPh_3)_2 + Cl_3GeAsPh_4$$

whereas $Cl_3SnMo(CO)_5AsPh_4$ reacts with Ph_3P with the simultaneous replacement of CO by phosphine and breaking of the Sn–Mo bond. The analogous derivatives of chromium and tungsten do not react with phosphine.

At elevated temperature replacement of CO groups in compounds of the $Ph_3MM'(CO)_5$ type (M = Ge or Sn, M′ = Mn or Re) by triphenyl-phosphine, -arsine, and -stibine takes place with the retention of the metal–metal bonds [22, 64, 71, 72] for example,

$$Ph_3MMn(CO)_5 + Ph_3P \rightarrow Ph_3MMn(CO)_4PPh_3 + CO .$$

The reaction rate decreases slightly in accordance with the nature of the M–M′ bonds: Ge–Mn > Sn–Mn ≳ Ge–Re > Sn–Re. It is characteristic that the replacement of CO groups in compounds with a heteroatomic M–M′ bond proceeds more readily than in the corresponding dimeric carbonyls [144, 145].

Ethylene, unlike perfluoroethylene is capable of displacing CO from $Me_3SnMn(CO)_5$ with the formation of a π-complex [140]:

$$Me_3SnMn(CO)_5 + C_2H_4 \rightarrow Me_3SnMn(CO)_4(\pi\text{-}C_2H_4) + CO .$$

The germyl analogue does not react with ethylene [141]

The derivatives of iron carbonyl of the $[R_2SnFe(CO)_4]_2$ type react smoothly with PR'_3 under ultraviolet radiation, with formation [126–7] of a compound of the type $[R_2SnFe(CO)_3PR'_3]_2$. Depending on the ratio of the reagents both di- and mono-substituted products can be obtained [50, 84]:

$$[Bu_2SnFe(CO)_4]_2 + 2\,Et_3P \rightarrow [Bu_2SnFe(CO)_3PEt_3]_2 + 2\,CO$$
$$[R_2MFe(CO)_4]_2 + PR'_3 \rightarrow (OC)_4Fe{-}MR_2{-}Fe(CO)_3PR'_3 + CO$$

where M = Sn or Pb; R = Et or Bu; and R′ = Et, Ph, or OMe.

The organopolymetallic derivatives of cobalt carbonyl are also capable of replacement of the CO groups. Phosphines react in heptane with the silicon and lead derivatives even at 25–50°C: [50, 69]

$$R_3MCo(CO)_4 + PR'_3 \rightarrow R_3MCo(CO)_3PR'_3 + CO$$

where M = Si or Pb; R = H, Et, or Cl; and R′ = Et or Ph.

When $Cl_2Sn[Co(CO)_4]_2$ is boiled with PPh_3 in THF a disubstituted product, $Cl_2Sn[Co(CO)_3PPh_3]_2$, is formed irrespective of the ratio of the initial reagents [90]. An analogous derivative of germanium was obtained [78] in THF at room temperature and also on boiling in hexane. At room temperature in hexane monosubstituted products of the type:

$$Cl_2M[Co(CO)_4][Co(CO)_3PPh_3],$$

where M = Ge or Sn, are formed.

Hence all the organopolymetallic derivatives of metal carbonyls react with nucleophilic reagents with release of CO, unlike the alkyl derivatives of manganese, rhenium, and cobalt carbonyls $R{-}M'(CO)_X$ which in analogous reactions [146, 147] form acyl compounds of the $R{-}\overset{\overset{O}{\|}}{C}{-}M'(CO)_{X-1}L$ type. It has been found that [69] the introduction of CO at the M–M′ bond does not take place even at high carbon monoxide pressure. Evidently this phenomenon is connected with an increase in the strength of the M–M′ bonds owing to $d_\pi{-}d_\pi$ interaction between the metal atoms [51, 81, 148]. This interaction can be represented schematically as a large contribution from resonance structure (IX):

$$\underset{\text{(VIII)}}{X_3M{-}M'{=}C{=}O} \leftrightarrow \underset{\text{(IX)}}{X_3M{=}M'{-}C{\equiv}O} .$$

Evidently the increased strength of the M–M′ bond in comparison with the C–M′ bond hinders the migration of the X_3M radical to the carbonyl group, as occurs with alkyl derivatives [149].

The fact that the replacement of CO groups in $Ph_3SnMn(CO)_5$ and $Ph_3GeMn(CO)_5$ leads to derivatives in which the phosphinic group is in the trans-position to the Ph_3M group [28, 150], whereas the corresponding organic derivatives of manganese and rhenium carbonyls have the *cis*-configuration [151, 152], mentoattention. Evidently apart from the steric factors electronic effects also play a part here. Possibly the presence of $d_\pi{-}d_\pi$ interaction between the manganese and germanium or tin atoms, that is, the high contribution of structure (IX), determines the low strength of the bond of the axial carbonyl group with the metal in comparison with the equatorial ones.

Additional confirmation of the $d_\pi{-}d_\pi$ metal–metal interaction can be seen in the increase in the rate of exchange of the CO groups for PPh_3 in compounds of the $X_2M[Co(CO)_4]_2$ type (where M = Ge or Sn) with increase in the electronegativity of X in the order Me < Ph < Cl. The introduction of substituents of greater electronegativity favours an increase in the electron-accepting power of the tin or germanium atoms leading to an increase in the multiplicity of the M–Co bonds and the weakening of the $d_\pi{-}\pi^*$ Co–CO bonding.

V. PHYSICAL METHODS OF INVESTIGATION OF DERIVATIVES OF METAL CARBONYLS CONTAINING A METAL–METAL BOND

Physical methods of investigating compounds containing bonds between Group IVB elements and transition metals,

are used not only for finding or confirming the hypothetical structure of the molecules, but also give valuable information about the nature of the bonds in these compounds, which often cannot be obtained by purely chemical methods. The results of the X-ray structural investigation of the molecules of organopolymetallic compounds are given in Chapter II. The present chapter deals with the use of optical methods, radio and mass spectroscopy, and also the electrochemical investigation of compounds with M–M′ bonds.

1. Infrared Spectroscopy

The literature now contains information about the infrared spectra of most of the derivatives of metal carbonyls containing a bond between the transition metals and Group IVB elements.

The low-frequency range of the infrared spectra (700 to 100 cm^{-1}) of these compounds has been studied comparatively little and a precise assignment of the bands of the M–M′ and M′–CO stretching vibrations and M′–C–O deformation vibrations, which appear in this range, has not yet been made. In an analysis of the spectra of compounds of type $X_3GeMn(CO)_5$ and $X_2Ge[Mn(CO)_5]_2$ [150] the intense band at 470–450 cm^{-1} is assigned to ν^3_{Mn-C}, and the band in the 660–640 cm^{-1} range to δ_{CO}, by analogy with the assignment of the bands in the infrared spectra of $Mn_2(CO)_{10}$ [106,107] and $XMn(CO)_5$ (X = Cl, Br, I). [153] With increase in the electronegativity of X in the Ge–Mn compounds there is a decrease in the ν_{Mn-C} frequency. In the $Ph_3GeMn(CO)_4PPh_3$ spectrum there is a more significant increase in the ν_{Mn-C} frequency (by 55 cm^{-1}) and a decrease in the frequency of the C–O stretching vibrations, in comparison with the corresponding frequencies in the spectrum of the unsubstituted derivative, which confirms the close relation between the degree of $d_\pi - p^*_\pi$ bonding of M′–CO and of the π-bonding of the C–O groups.

Several papers [154–156] deal with the determination of the frequencies of the M–M′ stretching vibrations. It has been shown that the change in the $\nu_{M-M'}$ frequencies which appears in the 220–160 cm^{-1} range can be correlated with the corresponding changes in the frequencies of the C–O stretching vibrations. Usually, with an increase in the electronegativity of the substituent X in the compounds of type $X_{4-n}M[M'(CO)_xL]_n$, there is an increase in the $\nu_{M-M'}$ frequency which is consistent with increase in the $d_\pi - d_\pi$ interaction between the metal atoms.

The absorption range of the stretching vibrations of the CO groups (2200–1800 cm^{-1}) has been investigated most completely. X-ray diffraction investigations have shown that irrespective of the symmetry of the molecule as a whole in most of the compounds of the $X_{4-n}M[M'(CO)_xL]_n$ type a certain local symmetry of the metal carbonyl groups, found also for the corresponding derivatives of $XM'(CO)_xL$ type, where X is an organic radical or halogen atom, is mainly retained. It must therefore be expected that the infrared spectra of the derivatives or carbonyls which contain an M–M′ bond will be analogous to the spectra of the organohalogen derivatives of the corresponding metal carbonyls. Table 3 gives the theoretical and observable number of bands, ν_{CO}, for the organopolymetallic carbonyl compounds with various symmetries.

As Table 3 shows, the number of ν_{CO} bands in compounds which contain one $M'(CO)_xL$ group corresponds to the theoretical for the local symmetry of this group independently of the general symmetry of the molecule.

However, for compounds which contain several metal carbonyl groups there is always a greater number of bands. The appearance of additional bands in the spectra of these compounds can be connected with the interaction of the individual $M'(CO)_xL$ groups with one another. Furthermore allowance must be made for the decrease in the total symmetry of the molecules $X_{4-n}M[M'(CO)_xL]_n$ where $n > 1$ in comparison with the molecules of the compounds $X_3MM'(CO)_xL$.

Table 3. Number of bands of the stretching vibrations of the CO groups and their assignment in the infrared spectra of organopolymetallic derivatives of metal carbonyls.

Type of compound	Symmetry point group	Assignment of bands	Number of bands: theoretical	Number of bands: observed	Reference
Group VI					
$X_3MM'(CO)_3Cp$	C_{3v}	A_1+E	2	3	61, 135
$X_2M[M'(CO)_3Cp]_2$	C_{2v}		5		
	C_2, C_s, C_1		6	5–6	61, 135
Group VII					
$X_5MM'(CO)_5$	C_{4v}	$2A_1+E(+B_1)$	3–4	2–4	67, 150, 157
$X_2M[M'(CO)_5]_2$	C_{2v}	$3A_1+3B_1+B_2$	7	4–8	66, 150, 157
$XM[M'(CO)_5]_3$	C_{3v}	$3A_1+4E$	7	6–9	65, 66
Group VIII					
a. Iron derivatives					
$X_3MFe(CO)_2Cp$	C_{3v}	A_1+B_1	2	2	158, 159
$X_2M[Fe(CO)_2Cp]_2$	C_2	$2A+2B$	4	4	158, 159
	C_s	$2A'+2A''$	4	4	74, 158
	C_1	$4A$	4	4	
$(X_3M)_2Fe(CO)_4$	C_{2v}	$2A_1+B_1+B_2$	4	3	51
$[X_2MFe(CO)_4]_2$	D_{2h}	$B_{1u}+2B_{2u}+B_{3u}$	4	4	51
$X_4M_3[Fe(CO)_4]_4$	D_{2d}	$3B_2+4E$	7	4	51
$M[Fe(CO)_4]_4$	D_{2d}	$3B_2+4E$	7	4	51
b. Cobalt derivatives					
$X_3MCo(CO)_4$	C_{3v}	$2A_1+E$	3	3–4	81
	C_s	A_1+3A'	4	4	
$X_2M[Co(CO)_4]_2$	C_{2v}	$3A_1+3B_1+B_2$	7	7	81
	C_s	$4A'+4A''$	8	8	
$XM[Co(CO)_4]_3$	C_{3v}		7	6–8	80

It was found [158,159] that in compounds of the type $X_2M[Fe(CO)_2Cp]_2$ (where M = Ge or Sn) the picture of the νCO bands can change significantly with the nature of substituent X. X-Ray structural analysis of compounds of this type [39–41,43,44] showed that in the crystalline state they have C_2 or C_1 molecular symmetry. In solutions where the molecules are in a less sterically hindered state some change in the geometric configuration can be expected. In a study of the infrared spectra it was suggested that owing to rotation around the Ge–Fe bond and Sn–Fe bonds rotational isomers can exist in solutions, having C_2, C_1, or C_S symmetry depending on the electronic features and the volume of substituent X. For the compound $MeCl_2GeFe(CO)_2Cp$ the assumption of the existence of rotational isomers by rotation around the Ge–Fe bond was confirmed [159] in studying the effect of the polarity of the solvent and the temperature on the ratio of the intensities of the absorption bands.

On the basis of the assignment of the bands according to vibrational type, an analysis of the displacement of the corresponding bands as a function of the Group IVB element and the X substituents bound to them becomes possible.

In studying the infrared spectra of derivatives of the type $X_nR_{3-n}GeCo(CO)_4$ it was found [81] that there is a linear relation between the frequencies of the ν_{CO} bands and the total electronegativity of the halogen atoms bonded with the germanium. A similar dependence for the main frequency ν_{CO} was observed [50,120] in compounds of the $X_3SiCo(CO)_4$ type, where X = Et, Ph, OMe, or Cl. The existence of such a relation shows the connection between the charge on the atom of the non-transition Group IV element and the frequency ν_{CO} in all the derivatives of this type.

The nature of the change in the frequencies in the series of cobalt derivatives with the nature of the Group IVB element has been explained [50]. In the spectra of the compounds $Et_3MCo(CO)_4$ there is an almost linear decrease in the mean frequency ν_{CO} in the series of M: C > Si > > Ge > Sn > Pb. Since the electronegativities of Si, Ge, Sn, and Pb are similar [27] it can be suggested that the σ-components of the M–Co bonds should also always be similar. If that is so the decrease in the mean frequency ν_{CO} can be the result of a decrease in the π-transfer from the d_π-orbitals of the cobalt atom to the vacant d_π-orbitals of the non-transition element in the order Si > Ge > Sn > > Pb. Charge transfer in the M–Co π-system is confirmed by a study of the dipole moments of the complexes $X_3MCo(CO)_4$ and agrees with the values of the overlap integrals in these compounds [50].

The most convenient subjects for an analysis of the electronic effects of substituents bound to a transition metal atom are derivatives of Group VII metal carbonyls of the type $X_3MM'(CO)_5$ where M' = Mn or Re. Group theory predicts that in the infrared spectra of these compounds (point group symmetry C_{4v}) there should be three permitted bands ν_{CO}: $2A_1 + E$ and that the B_1 band should be active in Raman spectra [18,160,161]. Fig. 7 shows the vibration types.

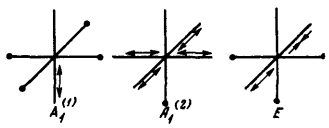


Figure 7. Types of vibrations of CO groups in $XM'(CO)_5$ and $X_3MM'(CO)_5$ (M' = Mn or Re) permitted in the infrared spectra. Only one component of the *E* vibrations is shown.

The band of type $A_1^{(1)}$, which has the lowest frequency, is assigned to the vibrations of the axial CO group. The most intense band of type *E* is assigned to the vibrations of the four equatorial groups. The bands of types $A_1^{(1)}$ and *E* often coincide. The $A_1^{(2)}$ vibrations are active in the infrared spectra only because of the non-coplanarity of the equatorial CO groups; this band of maximal frequency has low intensity and therefore is difficult to use in an analysis of the effects of substituents at the metal carbonyl group.

The study of the infrared spectra of the compounds $XMn(CO)_5$ showed that there is a linear relation between the position of the type *E* bands and the Taft inductive parameter σ* for substituent X in the order: Me, H, Ph, I, CF_3, Br, Cl. [162] A similar change in frequency with the electronegativity of the substituent $R_nX_{3-n}M$ was also observed in the series of derivatives of type $R_nX_{3-n}MM'(CO)_5$, where M = Ge, Sn; M' = Mn or Re; R = Me or Ph; X = Cl or Br; and $0 \leq n \leq 3$. [67,150]

On the basis of an LCAO-MO examination of the bonds in the $XM'(CO)_5$ molecules (Chapter II) it can be assumed that inductive transfer in the molecules of type $X_3MM'(CO)_5$ should be reflected in the position of all the absorption bands of the CO groups, whereas the mesomeric effect associated with the transfer of electrons from $(n-1)d_{XZ}$ and d_{YZ} orbitals of the transition metal to the vacant d_π orbitals of the Group IVB element will affect only the vibration frequency of the axial carbonyl group.

The analysis of the infrared spectra of several compounds containing an M–M' bond which was made on the basis of this assumption showed [163] that there is a considerable $d_\pi - d_\pi$ interaction between the atoms of the Group VII element and the Group IVB element. The degree of π-bonding increases with increase in the electronegativity of the substituent connected with the transition metal atom. It was found that the degree of π-bonding for germanium compounds is greater than for analogous tin derivatives.

The direction of the inductive effect of the substituents X_3M in compounds with an M–M' bond varies on going from X = alkyl or aryl to X = halogen. The substituents Me_3M and Ph_3M are stronger electron donors than Me (and Ph), whereas the Cl_3M and Br_3M groups are comparable in their electron-acceptor properties with halogen atoms. There is some additivity in the increase in σ-acceptor properties of the $R_nX_{3-n}M$ groups with successive increase in the number of halogen atoms bound to the Group IVB element (Table 4). [150,163]

Table 4. Change in the σ- and π-effects in the series of $Ph_nBr_{3-n}GeMn(CO)_5$ compounds.

Compound	Frequency ν_{CO}, cm^{-1}			σ*	Δσ*	π	Δπ
	$A_1^{(1)}$	*E*	$A_1^{(2)}$				
$Ph_3GeMn(CO)_5$	2004	2004	2094	−0.45	0.97	1.73	0.51
$Ph_2BrGeMn(CO)_5$	2019	2019	2108	0.52	0.90	2.24	0.43
$PhBr_2GeMn(CO)_5$	2033	2033	2117	1.42	0.84	2.67	0.39
$Br_3GeMn(CO)_5$	2046	2046	2136	2.26		3.06	

The effect of the nature of the transition metal on the vibration frequency of the CO groups is much greater than the effect of the Group IVB element. In the series of isostructural derivatives of carbonyls of Group VI metals there is an increase in the mean frequency ν_{CO} with increase in the atomic number of the metal, for example, for $Ph_3SnM'(CO)_3Cp$ [61] ν_{CO} is 1987, 1923, 1897 for M' = Cr; 2004, 1934, 1909 for M' = Mo; and 2014, 1927, 1902 cm^{-1} for M' = W. A similar increase in mean frequencies is observed also for derivatives of rhenium carbonyl compared with the corresponding manganese compounds [67,163].

The assignment of the ν_{CO} bands according to the types of vibrations in the spectra of the compounds which contain several metal carbonyl groups is difficult. Nevertheless, it has been shown [61,66,74,80,81,135,136,150,157–159] that with increase in the electron accepting ability of the substituents bound to the Group IVB element there is an increase in all the frequencies of the CO vibrations.

The literature contains information about the ultraviolet spectra of the carbonyl compounds containing an M–M′ bond, limited to the series of compounds $R_3MM'(CO)_3Cp$ (with M = Ge or Sn; M′ = Mo or W; R = Me or Ph),[61] but these results are too few and the observed picture too complex for a successful interpretation.

2. PMR Spectroscopy

As a result of the study of the PMR spectra of compounds of the $X_3SnM'(CO)_3Cp$ and $X_2Sn[M'(CO)_3Cp]_2$ type (M′ = Mo and W) [135] and also of $X_3MFe(CO)_2Cp$ and $X_2M[Fe(CO)_2Cp]_2$ [158,159] (M = Ge and Sn) it was found that the chemical shift of the protons of the cyclopentadienyl ring (in the τ-scale relative to Me_4Si) increases with decrease in the electronegativity of substituent X. In the series of $X_3GeFe(CO)_2Cp$ compounds [112] the value of τ increases with the change in X in the order: F < Cl < Br < I. These facts show the inductive transfer of the electronic effects of the substituents X through the M–M′ bond to the cyclopentadienyl ring.

For methylgermanes and methylstannanes of the $Me_{4-n}MX_n$ type there is a linear dependence of the quantity τ on the total Taft inductive parameter σ^*,[133,164] for example, τ_{CH_3} is 9.93 in Me_4Sn, 9.37 in Me_3SnCl, 8.84 in Me_2SnCl_2, and 8.35 in $MeSnCl_3$, which corresponds with an increase in the inductive withdrawal of electrons from methyl groups of the electron-accepting substituents at tin or germanium atoms. On the other hand, in the trimethylstannyl derivatives of metal carbonyls it is difficult to find any correspondence between the values of τ_{CH_3} and the nature of the metal carbonyl groups. A successive increase in the number of metal carbonyl groups in $Me_{4-n}Sn[M'(CO)_xL]_n$ molecules leads to a displacement of the signal of the methyl protons to the strong field side (see Table 5), which could be due to the electron-acceptor nature of the metal carbonyl groups.

In studying the change in the spin-spin coupling constants J(Sn–H) in compounds of the $Me_{4-n}SnX_n$ type with the electronegativity of X, the following hypothesis was used[165]: the Sn–H spin–spin coupling tends to be proportional to the s-character of the hybrid sp^3 orbitals of the tin used in the Sn–CH_3 bond and the s-character of the tin atom tends to be concentrated in orbitals directed towards electropositive substituents, according to Bent's rule [37,38]. Here it was also assumed that the change in substituent X only affects the electronic state of the tin atom whereas other parameters of the X–Sn–C–H system of bonds remain almost unchanged. In the $Me_{4-n}SnCl_n$ series with successive increase in the number of chlorine atoms the value of $J(^{119}Sn–H)$ gradually increases: Me_4Sn 54.0; Me_3SnCl 59.7; Me_2SnCl_2 71.0, $MeSnCl_3$ 100.0 Hz.[166] The successive replacement of the methyl groups by metal carbonyl groupings leads to a decrease in the value of J [61,66,67,87] (Table 5).

Proceeding from these assumptions the decrease in the value of J in Sn-metal carbonyl compounds in comparison with Me_4Sn can be treated as a decrease in the s-character of the tin orbitals in the Sn–CH_3 bonds and a corresponding increase in it in the bonds with the transition metal atoms. This serves as confirmation of the electron-donating nature of the metal carbonyl groups and of the considerable covalency of the Sn–M′ bonds in these compounds.

Table 5 shows that the value of J is much greater for compounds containing a $Co(CO)_4$ group. This can be explained by the somewhat greater electronegativity of the $Co(CO)_4$ group in comparison with that of the other metal carbonyl groups [66].

The conclusions drawn on the basis of the change in the constant J agree with the X-ray structural data (see Chapter II) which show the increase in the s-character of the Sn–M′ bonds (tendency $sp^3 \rightarrow sp^2$) with increase in the number of metal carbonyl groups in these compounds. Unfortunately there are few compounds for which both structural and PMR data are known.

Hence an analysis of the chemical shifts of the methyl protons and of the value of the spin-spin coupling constants J(Sn–CH_3) (Table 5) leads to directly contradictory results. However, since the interpretation of the change in the constants J agrees with the conclusions from a study of the infrared spectra, and with the X-ray structural data, this characteristic evidently more correctly reflects the properties of the metal carbonyl groups. The contradiction arising in the treatment of the chemical shifts can be connected with the considerable extent of the M′–Sn–C–H chain and also with several other factors which influence the screening of protons.

An example of the use of PMR spectra for determining the composition of compounds and of finding the mechanism of reaction of the metal carbonyl compounds is the work of Nesmeyanov and coworkers [112] where the analysis of the displacement of signals of protons and the change in their intensity in compounds of the type $X_3GeFe(CO)_2Cp$ (X = Br, I) demonstrated exchange between the halogen atoms bound to a germanium atom (see Chapters III and IV).

Table 5. PMR spectra of methylstannyl derivatives of metal carbonyls.

Compounds of the $Me_{3-n}Cl_nSnM'(CO)_xCp$ type	τ	J(Sn–H), Hz	Compounds of the $Me_{2-n}ClSn[M'(CO)_xCp]_2$ type	τ	J(Sn–H), Hz	Compounds of the $MeSn[M'(CO)_xCp]_3$ type	τ	J(Sn–H), Hz
$Me_3SnMo(CO)_3Cp$	9.52	49.0	$Me_2Sn[Mo(CO)_3Cp]_2$	9.15				
$Me_2ClSnMo(CO)_3Cp$	9.02	47.7	$Me_2Sn[Mo(CO)_3Cp][Mn(CO)_5]$		36.9			
$Me_2SnW(CO)_3Cp$		48.7	$Me_2Sn[W(CO)_3Cp][Mn(CO)_5]$		37.3			
$Me_2SnMn(CO)_5$	9.54	48.3	$Me_2Sn[Mn(CO)_5]_2$	9.17	36.7	$MeSn[Mn(CO)_5]_3$	8.62	~24
$Me_2ClSnMn(CO)_5$	9.06	45.8						
$Me_2SnRe(CO)_5$	9.58	46.7	$Me_2Sn[Re(CO)_5]_2$	9.14	36.7	$MeSn[Re(CO)_5]_3$	8.43	24.7
$Me_2SnFe(CO)_2Cp$	9.55	49						
$Me_2ClSnFe(CO)_2Cp$	8.55							
$Me_2SnCo(CO)_4$	9.37	45.8	$Me_2Sn[Co(CO)_4]_2$	8.88	45.7	$MeSn[Co(CO)_4]_3$	8.98	33.0
		52.6						
			$MeClSn[Co(CO)_4]_2$	8.48				

Values given for J ($^{119}Sn–CH_3$).

3. Nuclear Gamma Resonance

Confirmation of the electron donating nature of the metal carbonyl groups in compounds containing a bond between the tin and transition metal atoms was obtained from nuclear gamma resonance spectra (Mössbauer effect)[167-169].

Table 6. Chemical shift* of the resonance of ^{119}Sn in the compounds $Ph_{4-n}Sn[Re(CO)_5]_n$ and $Ph_{4-n}Sn[Fe(CO)_2Cp]_n$.[167,168]

Compound	Chemical shift, δ, mm s^{-1}	Compound	Chemical shift, δ, mm s^{-1}
Ph_4Sn	1.11	Ph_4Sn	1.11
$Ph_3SnRe(CO)_5$	1.45	$Ph_3SnFe(CO)_2Cp$	1.48
$Ph_2Sn[Re(CO)_5]_2$	1.70	$Ph_2Sn[Fe(CO)_2Cp]_2$	1.74
$PhSn[Re(CO)_5]_3$	1.75	$PhSn[Fe(CO)_2Cp]_3$	2.00
		$Sn[Fe(CO)_2Cp]_4$	2.14

*Relative to SnO_2.

In the nuclear gamma resonance spectra of the compounds of the $R_{4-n}Sn[M'(CO)_xL]_n$ type, where $M'(CO)_xL$ = $Mn(CO)_5$, $Re(CO)_5$, or $Fe(CO)_2Cp$, and R = alkyl or phenyl, quadrupole splitting of the ^{119}Sn signal is absent, which shows the high degree of covalency of the metal–metal bond. In compounds which contain the $Co(CO)_4$ group quadrupole splitting occurs but to a lesser extent than the splitting brought about by the introduction of halogen atoms at the tin atom. This is additional confirmation of the high electronegativity of $Co(CO)_4$ in comparison with the other metal carbonyl groups.

Table 7. Nuclear gamma resonance spectra of the compounds $X_2Sn[Fe(CO)_2Cp]_2$.

X	^{119}Sn		^{57}Fe	
	δ, mm s^{-1}	Δ, mm s^{-1}	δ, mm s^{-1}	Δ, mm s^{-1}
Et	1.74	0	0.373	1,88
Me	1.68	0	0.378	1,715
Cl	1.94	2.37	0,361	1,64

In the spectra of the compounds $X_{4-n}Sn[M'(CO)_xL]_n$ (where M' = Mn, Re, Fe, Co; and X = Me, Et, Ph, Cl, or Br) there is a gradual increase in the chemical shift of the δ resonance of ^{119}Sn with increase in the number of metal carbonyl groups (see Table 6), which can be regarded as the consequence of the decrease in the ionicity of the bond due to the electron-donating nature of the metal carbonyl groups.

A comparison of the results[171] from nuclear gamma resonance spectra of the $X_2Sn[Fe(CO)_2Cp]_2$ compounds relative to both ^{119}Sn and ^{57}Fe shows that the substituent X at the tin atom affects the electron density of both metal atoms (Table 7).

4. Mass Spectroscopy

Information about the comparative strength of metal–ligand bonds and about the energies necessary for breaking these bonds can be obtained from the mass spectra of organopolymetallic compounds.

In the fragmentation of metal carbonyl derivatives with M–M′ bonds competing processes can take place: removal of CO, loss of ligand containing a Group IVB element as an entity, and also the removal of a part of the ligand from the Group IVB atom and transfer of an atom or group of atoms from the ligand to the transition metal. For example, in the mass spectrum of $Ph_3SnMn(CO)_5$ peaks are observed which correspond with the ions: Ph_3SnMn^+, Ph_3Sn^+, $PhMn^+$, HMn^+, and Mn^+, and in the mass spectra of $PhBr_2SnMn(CO)_5$ there are peaks of $PhBr_2SnMn^+$, $PhSn^+$, $BrMn^+$, $PhMn^+$, HMn^+, and Mn^+.[170]

An investigation of the derivatives of molybdenum[171], manganese and rhenium[66,170,172], iron[172], and cobalt[79,80] carbonyls of the type $X_{4-n}M[M'(CO)_xL]_n$ showed that the fragmentation of these compounds occurs first with the successive removal of ligands (CO and Cp) from the transition metal atom. For compounds which contain several metal carbonyl groups fragmentation proceeds with gradual removal of these groups. The M–M′ bond is broken, usually last of all. Thus in the mass spectrum of $ClSn[Mn(CO)_5]_3$ peaks for the presence of $ClSnMn_3(CO)_x^+$ (x = 0, 3–6, 8–11, 15), $ClSnMn_2(CO)_x^+$ (x = 0, 3, 5, 9, 10), $SnMn(CO)_x^+$ (x = 0, 45) have been noted. Hence under the conditions for measuring the mass spectra the M–M′ bond exhibits greater stability than the M–X bond and still greater than the M′–CO or M′–Cp bonds. With increase in the number of metal carbonyl groups attached to the atom of the Group IVB element, the strength of the M–M′ bonds decreases which agrees with the chemical properties and with the increase in the length of these bonds observed in the structural investigations.

With the aid of mass spectroscopy it was shown that the structure of compounds of the $XSn[Co(CO)_4]_3$ type corresponds with structure (VII) (see Chapter III).[79,80] In the fragmentation of these compounds a considerable proportion of ions formed as a result of the breaking of the Sn–Co bonds was observed, which could mean that the $SnCo_3$ skeleton is weaker than that of $SnMn_3$.[66]

Mass spectroscopy is very valuable for finding the structure of the products formed by the introduction of perfluoroacetylenes at Sn–Mn and Sn–Fe bonds[143] (see Chapter IV).

5. Polarography

Polarographic reduction of a series of metal carbonyl derivatives with M–M′ bonds[173-176] allowed the relative polarisation of these bonds to be estimated. The reduction of compounds of this type is always accompanied by breaking of the M–M′ bond, which leads to the formation of anions containing a transition metal atom.

$$R_3M{-}M'(CO)_xL \begin{cases} \xrightarrow{+1e} R_3M^{\cdot} + [:M'(CO)_xL]^- & (A) \\ \xrightarrow{+2e} R_3M^-: + [:M'(CO)_xL]^- & (B) \end{cases}$$

When M = Sn and R = Me or Ph the reduction has a single-electron nature (scheme A), whereas phenyl derivatives are reduced at more negative potentials than the methyl derivatives. When M = Pb the reduction proceeds by scheme (B) with the formation of two anions.

The ease of reduction varies in the following sequence:

$$Sn{-}Co > Et_3Pb{-}Mn > Me_3Sn{-}Mn = Me_3Sn{-}Mo > Ph_3Pb{-}Mn = Ph_3Pb{-}Fe > Ph_3Pb{-}Mo > Ph_3Pb{-}Re = Ph_3Sn{-}Mo > Ph_3Sn{-}Mn = Ph_3Sn{-}Re > Ph_3Sn{-}Fe.$$

The reduction of the compounds $Me_2Sn[Mo(CO)_3Cp]_2$ and $Me_2Sn[Fe(CO)_2Cp]_2$ leads to the loss of both metal carbonyl groups as anions:

$$Me_2Sn[M'(CO)_xCp]_2 + 2e \rightarrow Me_2Sn + 2[:M'(CO)_xCp]^- .$$

The reduction potential of the compound with Sn–Fe bonds here is higher than for the Sn–Mo bond.

In the reduction of the compound

$$[Cp(OC)_3Mo]_2Sn[Fe(CO)_2Cp]_2$$

which contains different transition metal atoms, a more complex picture is observed. Evidently loss of the Mo fragment takes place first and then a system with an Fe–Sn–Sn–Fe chain is formed.

REFERENCES

1. J. Lewis and R. S. Nyholm, Sci. Progress, 52, 557 (1964).
2. J. Lewis, Pure a. Appl. Chem., 10, 11 (1965).
3. N. S. Vyazankin and O. A. Kruglaya, Uspekhi Khim., 35, 1388 (1966) [Russ. Chem. Rev., No. 8 (1966)].
4. F. A. Cotton, Uspekhi Khim., 36, 1799 (1967) [Translated from Quart. Rev., 20, 389 (1966)].
5. B. J. Bulkin and C. A. Rundell, Coord. Chem. Rev., 2, 371 (1967).
6. L. F. Dahl, E. Ishishi, and R. E. Rundle, J. Chem. Phys., 26, 1750 (1957).
7. L. F. Dahl and R. E. Rundle, Acta crystal., 16, 419 (1963).
8. M. F. Bailey and L. F. Dahl, Inorg. Chem., 4, 1140 (1965).
9. F. C. Wilson and D. P. Shoemaker, J. Chem. Phys., 27, 809 (1957).
10. T. S. Piper, D. Lemal, and G. Wilkinson, Naturwiss., 43, 129 (1956).
11. N. I. Gapotchenko, N. V. Alekseev, K. N. Anisimov, N. E. Kolobova, and I. A. Ronova, Zhur. Strukt. Khim., 9, 892 (1968).
12. M. J. Bennett and R. Mason, Nature, 205, 760 (1965).
13. S. J. La Placa, W. C. Hamilton, and J. A. Ibers, Inorg. Chem., 3, 1491 (1964).
14. S. J. La Placa, J. A. Ibers, and W. C. Hamilton, J. Amer. Chem. Soc., 86, 2288 (1967).
15. F. W. B. Einstein, H. Luth, and J. Trotter, J. Chem. Soc. (A), 89 (1967).
16. M. R. Churchill and R. Bau, Inorg. Chem., 6, 2086 (1967).
17. H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, Canad. J. Chem., 41, 1281 (1963).
18. L. E. Orgel, Inorg. Chem., 1, 25 (1962).
19. A. Wojcicki and F. Basolo, J. Amer. Chem. Soc., 83, 525 (1961).
20. W. Hieber and K. Wollmann, Chem. Ber., 95, 1552 (1962).
21. R. J. Angelici and F. Basolo, J. Amer. Chem. Soc., 84, 2495 (1962).
22. R. D. Gorsich, J. Amer. Chem. Soc., 84, 2486 (1962).
23. W. Hieber, J. Gruber, and F. Lux, Ztschr. anorg. allgem. Chem., 300, 275 (1959).
24. F. Bonati and G. Wilkinson, J. Chem. Soc., 179 (1964).
25. R. F. Bryan, Proc. Chem. Soc., 232 (1964).
26. B. T. Kilbourn and H. M. Powell, Chem. a. Ind., 1578 (1964).
27. L. Pauling, The Nature of the Chemical Bond, 3-d Ed., Cornell Univ. Press, Ithaca, New York, 1960.
28. R. F. Bryan, J. Chem. Soc., (A), 172 (1967).
29. H. P. Weber and R. F. Bryan, Chem. Commun., 443 (1966).
30. R. F. Bryan, Chem. Commun., 355 (1967).
31. R. F. Bryan, J. Chem. Soc. (A), 696 (1968).
32. J. H. Tsai, J. J. Flynn, and F. P. Boer, Chem. Commun., 702 (1967).
33. J. H. Tsai, F. P. Boer, and J. C. Tou, Proc. 10th Intern. Conf. on Coord. Chem., Tokyo, (1967), p. 226
34. B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, O. P. Osipova, and M. Ya. Zakharova, Chem. Commun., 749 (1967).
35. B. P. Biryukov, K. N. Anisimov, Yu. T. Struchkov, N. E. Kolobova, O. P. Osipova, and M. Ya. Zakharova, Zhur. Strukt. Khim., 8, 554 (1967).
36. B. P. Bir'yukov, O. P. Solodova, and Yu. T. Struchkov, Zhur. Strukt. Khim., 9, 233 (1968).
37. H. A. Bent, Canad. J. Chem., 38, 1235 (1960).
38. H. A. Bent, Chem. Rev., 61, 275 (1961).
39. B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, Chem. Commun., 750 (1967).
40. B. P. Bir'yukov, K. N. Anisimov, Yu. T. Struchkov, N. E. Kolobova, and V. V. Skripkin, Zhur. Strukt. Khim., 8, 556 (1967).
41. J. E. O'Connor and E. R. Corey, Inorg. Chem., 6, 968 (1967).
42. R. F. Bryan, J. Chem. Soc. (A), 192 (1967).
43. J. E. O'Connor and E. R. Corey, J. Amer. Chem. Soc., 89, 3930 (1967).
44. R. M. Sweet, C. J. Fritchie, and R. A. Schunn, Inorg. Chem., 6, 749 (1967).
45. P. F. Lindley and P. Woodward, J. Chem. Soc. (A), 382 (1967).
46. J. D. Cotton, J. Duckworth, S. A. R. Knox, R. F. Lindley, I. Paul, F. G. A. Stone, and P. Woodward, Chem. Commun., 253 (1966).
47. M. A. Bush and P. Woodward, Chem. Commun., 166 (1967).
48. M. A. Bush and P. Woodward, J. Chem. Soc. (A), 1833 (1967).
49. R. B. King and F. G. A. Stone, J. Amer. Chem. Soc., 82, 3833 (1960).
50. O. Kahn and M. Bigorgne, J. Organometal. Chem., 10, 137 (1967).
51. J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, J. Chem. Soc. (A), 264 (1967).
52. W. T. Robinson and J. A. Ibers, Inorg. Chem., 6, 1208 (1967).
53. B. T. Kilbourn, T. L. Blundell, and H. M. Powell, Chem. Commun., 444 (1965).
54. Yu. T. Struchkov, K. N. Anisimov, O. P. Osipova, N. E. Kolobova, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 172, 107 (1967).
55. B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, Zhur. Strukt. Khim., 9, 924 (1968).
56. F. Hein, H. Pobloth, and E. Heuser, Ztschr. anorg. allgem. Chem., 248, 84 (1941).
57. F. Hein, Ztschr. anorg. allgem. Chem., 249, 293
58. F. Hein and E. Heuser, Ztschr. anorg. allgem. Chem., 254, 138 (1947).
59. F. Hein and E. Heuser, Ztschr. anorg. allgem. Chem., 255, 125 (1947).

60. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and M. Ya. Zakharova, Dokl. Akad. Nauk SSSR, **156**, 612 (1964).
61. H. R. H. Patil and W. A. G. Graham, Inorg. Chem., **5**, 1401 (1966).
62. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, Izv. Akad. Nauk SSSR, Ser. Khim., 1395 (1967).
63. D. Seyferth, H. P. Hoffmann, R. Burton, and J. F. Helling, Inorg. Chem., 1, 227 (1962).
64. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, Izv. Akad. Nauk SSSR, Ser. Khim., 160 (1966).
65. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, Dokl. Akad. Nauk SSSR, **176**, 844 (1967).
66. J. A. J. Thompson and W. A. G. Graham, Inorg. Chem., **6**, 1365 (1967).
67. W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, Inorg. Chem., **5**, 2217 (1966).
68. B. J. Aylett and J. M. Campbell, Chem. Commun., 217 (1965).
69. B. J. Aylett and J. M. Campbell, Inorg. Nucl. Chem. Letters, 3, 137 (1967).
70. Y. L. Baay, A. Berry, S. K. Gonal, A. P. Hagen, and A. G. McDiarmid, 3-d, Intern. Symp. on Organometal. Chem., Münich, 1967, p. 110.
71. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, Dokl. Akad. Nauk SSSR, **156**, 383 (1964).
72. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, Izv. Akad. Nauk SSSR, Ser. Khim., 163 (1966).
73. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1290 (1966).
74. N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, J. Chem. Soc. (A), 1130 (1966).
75. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, Izv. Akad. Nauk SSSR, Ser. Khim., 2364 (1967).
76. B. J. Aylett and J. M. Campbell, Chem. Commun., 159 (1967).
77. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, A. B. Antonova, and V. N. Khandozhko, in "2-e Vses. Soveshch. po Khimii Kompleksnykh Soedinenii Kobal'ta, Nikelya, i Margantsa, Tbilisi, 1966, Tezisy Dokladov" (Second All-Union Conference on the Chemistry of Complex Compounds of Cobalt, Nickel, and Manganese, Tbilisi, 1966, Summaries of Papers Presented), p. 35.
78. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, Izv. Akad. Nauk SSSR, Ser. Khim., 1879 (1967).
79. D. J. Patmore, W. A. G. Graham, Inorg. Nucl. Chem. Letters, 2, 179 (1966).
80. D. J. Patmore and W. A. G. Graham, Inorg. Chem., **5** 2222 (1966).
81. D. J. Patmore and W. A. G. Graham, Inorg. Chem., **6**, 981 (1967).
82. W. Hieber and H. Breu, Chem. Ber., **90**, 1270 (1957).
83. O. Kahn and M. Bigorgne, Compt. rend., **261**, 2483 (1965).
84. O. Kahn and M. Bigorgne, Compt. rend., **262C**, 906 (1966).
85. J. P. Collman, F. D. Wastine, and W. R. Roper, J. Amer. Chem. Soc., **88**, 5035 (1966).
86. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and M. Ya. Zakharova, Izv. Akad. Nauk SSSR, Ser. Khim., 1122 (1965).
87. H. R. H. Patil and W. A. G. Graham, J. Amer. Chem. Soc., **87**, 673 (1965).
88. S. V. Dighe and M. Orchin, J. Amer. Chem. Soc., **87**, 1146 (1965).
89. I. Wender, H. W. Sternberg, and M. Orchin, J. Amer. Chem. Soc., **74**, 1216 (1952).
90. D. J. Patmore and W. A. G. Graham, Inorg. Chem., **5**, 1405 (1966).
91. F. Bonati, S. Cenini, D. Morelli, and R. Ugo, Inorg. Nucl. Chem. Letters, 1, 107 (1965).
92. F. Bonati, S. Cenini, D. Morelli, and R. Ugo, J. Chem. Soc. (A), 1052 (1966).
93. F. G. A. Stone, 3-d Intern. Sympos. on Organometal. Chem. Münich, 1967, p. 8.
94. O. S. Mills, Acta crystal., 11, 620 (1958).
95. L. Cavalca and J. W. Bassi, Ricerca sci., **23**, 1377 (1953).
96. J. F. Tilney-Bassett and O. S. Mills, J. Amer. Chem. Soc., **81**, 4757 (1959).
97. F. A. Cotton and G. Yagupsky, Inorg. Chem., **6**, 15 (1967).
98. A. R. Manning, J. Chem. Soc. (A), 1319 (1968).
99. K. Noack, Spectrochim. acta, **19**, 1925 (1963).
100. K. Noack, Helv. chim. acta, **47**, 1064 (1964).
101. K. Noack, Helv. chim. acta, **47**, 1555 (1964).
102. G. Bor, Spectrochim. acta, **19**, 2065 (1964).
103. L. I. Denisovich, Candidate's Thesis, Institute of Organoelemental Chemistry, Moscow, 1968.
104. H. J. Keller and H. Wawersik, Z. Naturforsch., **20b**, 938 (1965).
105. W. Hieber, Chem. Ber., **86**, 700 (1953).
106. N. Flitcroft, D. K. Huggins, and H. D. Kaesz, Inorg. Chem., 3, 1123 (1964).
107. A. N. Nesmeyanov, G. G. Dvoryantseva, Yu. N. Sheinker, N. E. Kolobova, and K. N. Anisimov, Dokl. Akad. Nauk SSSR, 169, 843 (1966).
108. F. Bonati and R. Ugo, Istituto Lombardo (Rend. Sci.), **A-98**, 607 (1964).
109. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, Izv. Akad. Nauk SSSR, Ser. Khim., 1950 (1969).
110. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1419 (1968).
111. A. R. Manning, Chem. Commun., 906 (1966).
112. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1520 (1969).
113. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, Izv. Akad. Nauk SSSR, Ser. Khim., 1319 (1965).
114. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and M. Ya. Zakharova, Izv. Akad. Nauk SSSR, Ser. Khim., 1880 (1967).
115. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 2246 (1966).
116. V. F. Mironov and T. K. Gar, "Organicheskie Soedineniya Germaniya" (Organic Compounds of Germanium), Izd. Nauka, Moscow, 1967.
117. F. Bonati, S. Cenini, and R. Ugo, J. Chem. Soc. (A), 932 (1967).
118. A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., 87, 1133 (1965).
119. W. Jetz and W. A. G. Graham, J. Amer. Chem. Soc., 89, 2773 (1967).

120. O. Kahn and M. Bigorgne, Compt. rend., 263C, 973 (1966).
121. Y. L. Baay and A. G. MacDiarmid, Inorg. Nucl. Chem. Letters, 3, 159 (1967).
122. D. J. Cardin, S. A. Keppie, B. M. Kingston, and M. F. Lappert, Chem. Commun., 1035 (1967).
123. J. K. Ruff, Inorg. Chem., 6, 1502 (1967).
124. R. Kummer and W. A. G. Graham, Inorg. Chem., 7, 310 (1968).
125. A. G. Massey, A. J. Park, and F. G. A. Stone, J. Amer. Chem. Soc., 85, 2021 (1963).
126. S. D. Iberkwe and M. J. Newlands, J. Chem. Soc. (A), 1783 (1967).
127. S. D. Iberkwe and M. J. Newlands, Chem. Commun., 115 (1965).
128. W. T. Dent, L. A. Duncanson, R. G. Guy, and H. W. B. Reed, Proc. Chem. Soc., 119 (1961).
129. G. Bor, L. Markô, and B. Markô, Chem. Ber., 95, 333 (1962).
130. S. F. A. Kettle and I. A. Khan, Proc. Chem. Soc., 82 (1962).
131. D. J. Patmore and W. A. G. Graham, Inorg. Chem., 7, 771 (1968).
132. D. J. Patmore and W. A. G. Graham, Chem. Commun., 7 (1967).
133. F. Glockling, Quart. Rev., 20, 45 (1966).
134. R. Ingram, S. Rozenberg, G. Gilman, and F. Rikens, "Organotin and Organogermanium Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1962.
135. A. N. Nesmeyanov, N. E. Kolobova, M. Ya. Zakharova, B. V. Lokshin, and K. N. Anisimov, Izv. Akad. Nauk SSSR, Ser. Khim., 529 (1969).
136. K. N. Anisimov, N. E. Kolobova, A. B. Antonova, and B. V. Bezborodov, Izv. Akad. Nauk SSSR, Ser. Khim., 202 (1968).
137. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 142 (1968).
138. K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, Izv. Akad. Nauk SSSR, Ser. Khim., 2664 (1968).
139. H. C. Clark and J. H. Tsai, Chem. Commun., 111 (1965).
140. H. C. Clark and J. H. Tsai, Inorg. Chem., 5, 1407 (1966).
141. H. C. Clark, J. D. Cotton, and J. H. Tsai, Inorg. Chem., 5, 1582 (1966).
142. A. D. Beveridge and H. C. Clark, Inorg. Nucl. Chem. Letters, 3, 95 (1967).
143. R. E. J. Bichler, M. R. Booth, and H. C. Clark, Inorg. Nucl. Chem. Letters, 3, 71 (1967).
144. W. Hieber and W. Freyer, Chem. Ber., 92, 1765 (1959).
145. W. Hieber and W. Freyer, Chem. Ber., 93, 462 (1960).
146. R. D. Closson, J. Kozikowski, and T. H. Coffield, J. Org. Chem., 22, 598 (1957).
147. R. F. Heck, Adv. Organometal. Chem., 4, 243 (1966).
148. A. P. Hagen and A. G. MacDiarmid, Inorg. Chem., 6, 686 (1967).
149. F. Basolo and R. G. Pearson, Adv. Inorg. Chem. a. Radiochem., 3, 3 (1961).
150. A. N. Nesmeyanov, G. G. Dvoryantseva, T. N. Ul'yanova, N. E. Kolobova, K. N. Anisimov, and A. B. Antonova, Izv. Akad. Nauk SSSR, Ser. Khim., 2241 (1967).
151. K. N. Anisimov, N. E. Kolobova, A. A. Ioganson, Izv. Akad. Nauk SSSR, Ser. Khim., 1749 (1969).
152. K. Noack, M. Ruch, and F. Calderazzo, Inorg. Chem., 7, 345 (1968).
153. M. A. Bennett and R. J. H. Clark, J. Chem. Soc., 5560 (1964).
154. H. M. Gager, J. Lewis, and M. J. Ware, Chem. Commun., 616 (1966).
155. N. A. D. Carey and H. C. Clark, Chem. Commun., 293 (1967).
156. N. A. D. Carey and H. C. Clark, Inorg. Chem., 7, 94 (1968).
157. R. Ugo, F. Cariati, F. Bonati, S. Cenini, and D. Morelli, Ricerca sci., 36, 253 (1966).
158. K. N. Anisimov, B. V. Lokshin, N. E. Kolobova, and V. V. Skripkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1024 (1968).
159. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, B. V. Lokshin, and F. S. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 758 (1969).
160. F. A. Cotton and C. S. Kraihanzel, J. Amer. Chem. Soc., 84, 4432 (1962).
161. M. A. El-Sayed and H. D. Kaesz, J. Mol. Spectroscopy, 9, 310 (1962).
162. B. V. Lokshin, K. N. Anisimov, N. E. Kolobova, A. A. Ioganson, and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Ser. Khim., 2447 (1968).
163. A. A. Ioganson, A. B. Antonova, B. V. Lokshin, N. E. Kolobova, K. N. Anisimov, and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1957 (1969).
164. M. P. Brawn and D. E. Webster, J. Phys. Chem., 64, 698 (1960).
165. N. Flitcroft and H. D. Kaesz, J. Amer. Chem. Soc., 85, 1377 (1963).
166. M. J. Maddox, S. J. Stafford, and H. D. Kaesz, Adv. Organometal. Chem., 3, 1 (1965).
167. A. N. Karasov, N. E. Kolobova, L. S. Polak, V. S. Shpinel', and K. N. Anisimov, Teoret. i Eksper. Khim., 2, 126 (1966).
168. V. I. Gol'danskii, B. V. Borshagovskii, E. F. Makarov, R. A. Stukan, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, Teoret. i Eksper. Khim., 3, 478 (1967).
169. R. N. Herber, Progress in Inorg. Chem., 8, 1 (1967).
170. M. J. Mays and R. N. F. Simpson, J. Chem. Soc.(A), 1936 (1967).
171. A. Carrik and F. Glockling, J. Chem. Soc. A, 40 (1967).
172. J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, J. Chem. son, J. Chem. Soc. A, 1663 (1966).
173. R. E. Dessy, P. M. Weissmann, and R. J. Pohl, J. Amer. Chem. Soc., 88, 5117 (1966).
174. R. E. Dessy, P. J. Pohl, and R. B. King, J. Amer. Chem. Soc., 88, 5121 (1966).
175. R. E. Dessy and P. M. Weissmann, J. Amer. Chem. Soc., 88, 5124 (1966).
176. R. E. Dessy and P. M. Weissmann, J. Amer. Chem. Soc., 88, 5129 (1966).

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