

Transition-Metal Complexes with Derivatives of Divalent Silicon, Germanium, Tin, and Lead as Ligands

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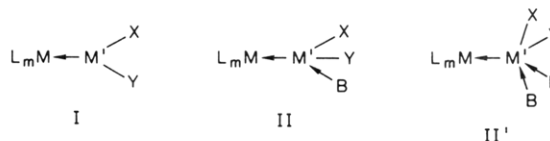
I. Introduction

The coordination chemistry of neutral donors has mainly been restricted to compounds of the group 15 and 16 elements, represented by amines, phosphines, ethers, ketones, and various sulfur-containing compounds, and to those of the soft carbon ligands such as carbon monoxide and isocyanides. The ability of these compounds to coordinate to transition metals is based on the presence of a stereochemically active lone pair of electrons available for the formation of a coordinative donor bond.¹ Since 1964 this type of chemistry has extended to include complexes of the nonisolable carbenes, in which the carbon atom only achieves an electron sextet and in recent years also to special compounds of the heavier group 14 elements in the divalent oxidation state.



Wolfgang Petz was born in Munich in 1940 and grew up in Augsburg, West Germany. He studied chemistry at the University of Munich where he received his Diplom-Chemiker degree in 1966 under the supervision of Professor Dr. H. Nöth. Continuing work with Prof. Nöth, he obtained his doctoral degree with a thesis about platinum- and iridium-boron compounds at the University of Marburg in 1969. Postdoctoral work followed, with G. Schmid at the same University. Between 1972 and 1978 he was Dozent at the University of Marburg and worked on chemical reactions of metal-coordinated carbon monoxide. In 1979 he completed his Habilitation in inorganic chemistry and received a 1-year fellowship of the Deutsche Forschungsgemeinschaft. His principle research interests include carbene complexes, the chemistry of thiocarbonyl compounds, stannylenes complexes, metal-assisted desulfurization reactions, and the coordination chemistry of organic thiocarbonyl derivatives. In 1982 he started as an author at the Gmelin-Institute of the Max-Planck-Society (directed by Prof. E. Fluck), working as author and editor. As Privatdozent he is teaching at the University of Marburg. When not involved with chemistry, he enjoys photography, wind surfing, and theater. He is married and has three children.

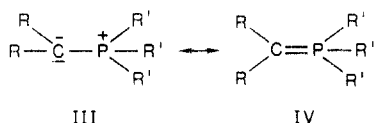
The explosive development of transition-metal carbene chemistry is summarized in various excellent review articles, but little attention has been focused on the silicon, germanium, tin, and lead homologues.² They were only mentioned briefly in some reviews concerning the general chemistry of divalent group 14 elements.³ This review is an attempt to summarize the chemical properties and the most important spectroscopic features of these complexes, which can roughly be divided into type I and type II classes:



In these arrangements, M' represents a group 14 element other than carbon, X and Y are σ -bonded substituents, and B stands for a neutral Lewis base molecule such as THF, pyridine, or related donors. The parts $M'XY$ in type I and $M'XY \leftarrow B$ in type II are neutral entities and coordinate with a lone pair of electrons to a transition metal M, which is surrounded by a set of ligands (abbreviated as L_m) to achieve the inert gas configuration. We will also include type II complexes containing more than one neutral donor molecule B and designate them type II' species.

Similar to the term "carbenes" for CR_2 moieties, the $M'XY$ entities will be called "silylenes", "germylenes", "stannylenes", and "plumbylenes"⁴ and considered as neutral species with the formal oxidation number 2+ at the respective main-group element M' .

The existence of type II complexes indicates that the $M'XY$ ligand still behaves as a Lewis acid even when coordinated to a transition-metal moiety and is able to add a variety of neutral donor molecules. The resulting ligands $M'XY \leftarrow B$, also known in the free state, may be regarded as ylides, in analogy to the Wittig compounds $R_2C=PR'_3$, whose versatile coordination chemistry has also been extended in recent years.⁵ Ylides can formally be considered as carbon(II) compounds stabilized by neutral Lewis base molecules, as outlined in resonance structure III. The expression "ylide" is also transferred in the literature to the monomeric base adducts of the heavier group 14 elements in the divalent oxidation state.



In a manner similar to carbene ligands, the ylene moiety $M'XY$ generally behaves as a "soft" donor and is coordinated mainly to transition-metal complexes in which the metal is in a low oxidation state.

The scope of this review will be restricted to compounds containing the $M'XY$ or $M'XY \leftarrow B$ ligands bonded in a terminal manner at the transition metal, while compounds with a bridging $M'XY$ species (μ - $M'XY$) are generally omitted. These latter complexes can also be described with the M' element in the tetravalent oxidation state.

The coordination chemistry of Ge(II) and Sn(II) ostensibly began in 1971 with the work of T. J. Marks,⁶ 7 years after publication of the first short note about carbene complexes by E. O. Fischer et al.⁷ But it may be that W. Hieber, the father of metal carbonyl chemistry, actually initiated work in this area without recognizing it as such. In 1957, he reported the synthesis of a novel iron-tin compound, $[(t-Bu)_2SnFe(CO)_4]_2$, and it is rather likely that he dissolved this compound in a polar solvent such as pyridine,⁸ a procedure that leads directly to a tin ylide complex as described recently.⁹

In general, the divalent group 14 element M' is represented by germanium and tin and to a lesser extent by lead. The resulting complexes are summarized in tables (Chapter IV) and arranged in order of the complexity of the $M'XY$ ligand.

Only a few papers deal with complexes in which ligands with formally divalent silicon are coordinated to neutral moieties containing iron, tungsten, or platinum.

These papers are summarized in a separate chapter.

Since the starting point of this chemistry, about 70 papers have been published over a period of 15 years. Contributions have come mainly from the research groups of T. J. Marks, P. Jutzi, M. F. Lappert, P. G. Harrison, and W.-W. duMont and deal with preparative, structural, and spectroscopic aspects, including Mössbauer spectroscopy in connection with iron and tin nuclei. It has now come to a point where a critical review of the existing material can be made with the intention that interest in this area will be stimulated and further studies and theoretical calculations will be performed.

II. Structure and Bonding

A. Type I Compounds

The structural data of 11 type I complexes are available at present, and selected parameters are summarized in Table 1.

The structures of type I complexes in the solid state consist of discrete molecules with no additional intermolecular contacts. The divalent element M' is found in an unsaturated three-coordinate environment, and coplanarity is achieved with the three adjacent atoms, thus indicating the sp^2 character of the Sn or Ge atoms. Among the ligands $M'XY$ involved, the base $Ge(Smes)_2$ (mes = mesityl) displays more similarity to nucleophilic carbenes than other ligands because the rotational position of the SGeS plane, bisecting the angle between the equatorial CO groups, corresponds exactly to that of the related carbene complexes.¹⁰ In contrast, the $CM'C$ plane of the more bulky $M'[CH(SiMe_3)_2]_2$ ligand is essentially coplanar with the plane formed by one set of meridial CO groups.^{11,12}

Noticeably shortened $M'-M$ distances relative to the corresponding single bonds (i.e., $Cr-Sn = 285$ pm) can be interpreted in terms of a change in the state of hybridization about the tin atom¹¹ but could also reflect a π interaction between the elements in the sense of a formal double bond. Thus, in $(CO)_5CrGe(Smes)_2$ a bond order of at least 1.5 is suggested.¹⁴ When one, however, considers the complexes $[CpMn(CO)_3Ge]$ or $[(CO)_5W]_3M'$, which contain one short and two longer $M'-M'$ distances at the sp^2 M' atom, the presence of an additional π bond between one transition metal and the group 14 element is more clearly established.^{15,16}

The $X-M'-Y$ angles at the ylene moieties are slightly smaller than those of similar carbene complexes,¹⁰ and although data for only a few type I complexes are available, a decrease going down the periodic table becomes apparent: C, 108–114°; Ge, 103°; Sn, 98°. This may be accounted for either by more s character in the $M'-M$ bond ($M = Cr$) or by decreasing steric hindrance down this series. Lower $X-M'-Y$ angles are found in compounds where the ylene unit represents a trimetallacyclopropane ring system (Figure 1).

An "internal" stabilization effect, similar to that operative in most carbene complexes¹⁸ by substituents with back-donating π capacity, is not a requirement here, and large groups are apparently sufficient to establish a three-coordinate geometry. The lack of internal stabilization is expressed by normal Ge-S single-bond distances in $(CO)_5CrGe(Smes)_2$, although the planar conformation of the germylene ligand may be

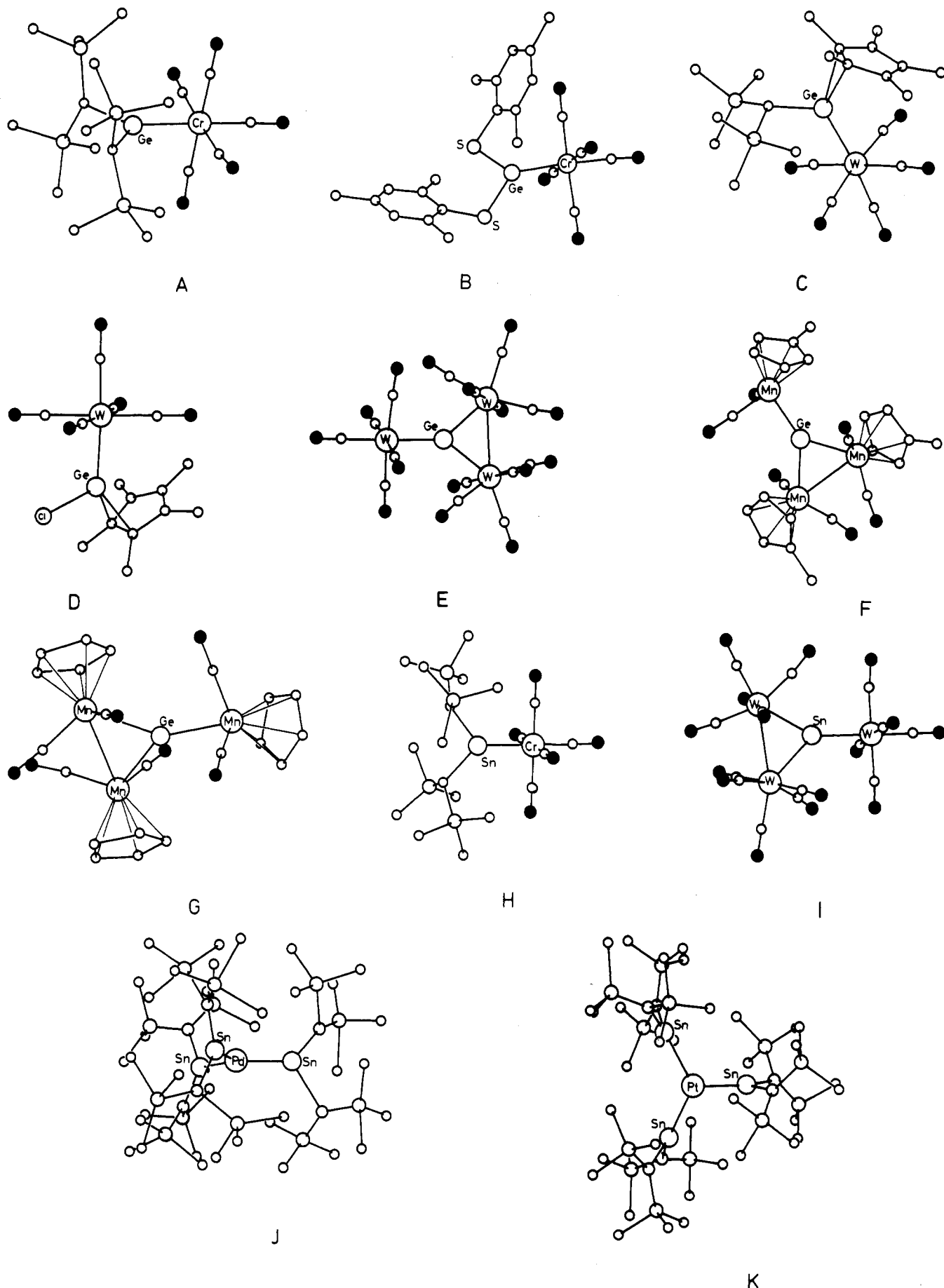
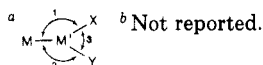


Figure 1. Structures of type I germylene and stannylene complexes. Reference key: $(\text{CO})_5\text{Cr}=\text{Ge}[\text{CH}(\text{SiMe}_3)_2]_2$ (A), 12; $(\text{CO})_5\text{Cr}=\text{Ge}(\text{SC}_9\text{H}_{11})_2$ (B), 14; $(\text{CO})_5\text{W}=\text{Ge}[\text{CH}(\text{SiMe}_3)_2](\text{C}_5\text{Me}_5)$ (C), 19; $(\text{CO})_5\text{W}=\text{GeCl}(\text{C}_5\text{Me}_5)$ (D), 20; $(\text{CO})_5\text{W}=\text{Ge}[\text{W}(\text{CO})_5]_2$ (E), 16; $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mn}=\text{Ge}[\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$ (F), 15; $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mn}=\text{Ge}[\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$ (G), 22; $(\text{CO})_5\text{Cr}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ (H), 11; $(\text{CO})_5\text{W}=\text{Sn}[\text{W}(\text{CO})_5]_2$ (I), 16; $\text{Pd}\{\text{=Sn}[\text{N}(\text{SiMe}_3)_2]_2\}_3$ (J), 17; $\text{Pt}\{\text{=Sn}[\text{N}(\text{SiMe}_3)_2]_2\}_3$ (K), 17.

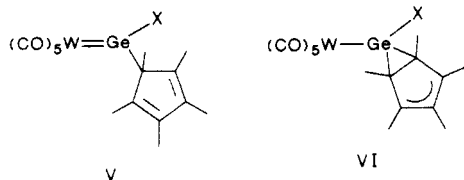
TABLE 1. X-ray Structural Data of Type I Germylene and Stannylene Complexes

compound	no. (Table 5 and 6)	$d(M=M')$, pm	angle, ^a deg	remarks	ref
(CO) ₅ Cr=Ge[CH(SiMe ₃) ₂] ₂ (A)	11	<i>b</i>	(1) 128.1 (1) (2) 128.4 (1) (3) 102.8 (2) Σ 359.3	coplanarity between GeC ₂ plane and plane defined by Cr and three eq CO gps	12
(CO) ₅ Cr=Ge(SC ₉ H ₁₁) ₂ (B)	43	236.7 (2)	(1) 137.5 (1) (2) 119.9 (1) (3) 102.4 (2) Σ 359.8	planar-trigonal geometry for Ge; cis-trans arrangement of mesityl gps; phenyl rings perpendicular to GeS ₂ plane that bisects the angle between the eq CO gps	14
(CO) ₅ W=Ge[CH(SiMe ₃) ₂](C ₅ Me ₅) (C)	14	263.2 (2)	(1) 126.1 (4) (2) <i>b</i> (3) <i>b</i>	crystallographic mirror symmetry through W, Ge, and bonded C at alkyl, bisecting pairs of eq CO bonds	19, 20
(CO) ₅ W=GeCl(C ₅ Me ₅) (D)	16	251.1 (1)	(1) 113.7 (1) (2) <i>b</i> (3) <i>b</i>	plane defined by Cl, W, and Ge bisecting the 90° angle between two eq CO gps	20
(CO) ₅ W=Ge[W(CO) ₅] ₂ (E)	91	250.5 (2)	(1) 139.7 (1) (2) 141.3 (1) (3) 78.8 (1) Σ 359.8	other W-Ge dist, 258.9 (1) and 257.9 (2) pm; GeW ₃ system essentially planar; W-W = 327.8 pm	16
C ₅ H ₄ Me(CO) ₂ Mn=Ge[Mn(C ₅ H ₄ Me(CO) ₂) ₂] (F)	89	226.0 (2)	(1) 142.3 (1) (2) 139.7 (1) (3) 78.0 (0) Σ 360.0	GeMn ₃ system essentially planar; other Ge-Mn single-bond distances, 235.9 (2) and 238.0 (1) pm; Mn-Mn distance (298.2 pm) slightly longer than in Mn ₂ (CO) ₁₀ (292 pm)	15
Cp(CO) ₂ Mn=Ge[Mn(Cp(CO) ₂) ₂] (G)	90	225.0	(1) 140.5 (1) (2) 140.8 (1) (3) 78.4 (1) Σ 359.7	Mn-Ge single bonds, 236.0 and 236.4 pm; isostructural with the C ₅ H ₄ Me derivative	22
(CO) ₅ Cr=Sn[CH(SiMe ₃) ₂] ₂ (H)	114	256.2 (2)	(1) 130 (2) 132 (3) 98 Σ 360	coplanarity similar to that in Ge derivative; surprisingly low CSnC angle (98°)	11
(CO) ₅ W=Sn[W(CO) ₅] ₂ (I)	180	270.2 (2)	(1) 134.9 (1) (2) 150.9 (1) (3) 74.1 (1) Σ 359.9	other W-Sn distances, 278.9 (2) and 277.6 (2) pm; analogue to the Ge complex but a longer W-W distance (335.4 pm)	16, 26
Pd[=Sn[N(SiMe ₃) ₂] ₂] ₃ (J)	140	253.3 (1) 254.0 (1) 251.7 (1)	(1) <i>b</i> (2) <i>b</i> (3) 107 (1)	atoms Pd, Sn, N all trigonal planar coordinated; PdSn ₂ angles 120°; SnN ₂ planes at 85° to PdSn ₃ plane	17
Pt[=Sn[N(SiMe ₃) ₂] ₂] ₃ (K)	141	247.0 (6) 248.7 (6) 250.4 (6)	(1) <i>b</i> (2) <i>b</i> (3) 104 (1)	isomorphous to Pd complex	17



advantageous for a Ge-S π interaction.¹⁴

In contrast, internal stabilization is discussed for complexes bearing the η²-bonded C₅Me₅ ligand at the M' atom. In these compounds the formal double bond is assumed to be localized not between germanium and the transition metal but between germanium and the cyclopentadienyl system, and the bonding properties of the complexes are better portrayed by VI rather than V.^{19,20} The W-Ge distances are 7-13 pm longer than the short one in [(CO)₅W]₃Ge and correspond to normal single bonds, thus supporting this bonding concept.²¹



The Cr-CO distances in all Cr(CO)₅ fragments are very similar, but a significant shortening in trans position to the ylene ligand is observed. This suggests an enhanced back-bonding from the transition metal to CO according to a higher σ-donor/π-acceptor ratio of the new ligand relative to CO similar to that operative in the Fischer-type carbene complexes.¹⁰ Similar results

were obtained on going to type II complexes bearing the Cr(CO)₅ fragment. The addition of a base molecule to the tin atom does not significantly alter the σ-donor/π-acceptor ratio of the ligand. No data of corresponding germanium complexes are known.

B. Type II Compounds

Structural information concerning type II complexes is limited to a few examples. In (CO)₅CrSn(Bu-*t*)₂py and (CO)₅CrSn(SCH₂CH₂)₂NBu-*t*, the common (CO)₅Cr-Sn-N unit allows a direct comparison of the environment at the tin atoms, which are further connected to carbon and sulfur atoms, respectively. The main distances and angles around the tin atom are shown in Figure 2.

The most striking feature is that in (CO)₅CrSn(SCH₂CH₂)₂NBu-*t* the Sn-N bond is tilted further away from the chromium atom (131.3 vs. 107.4°). This and the somewhat longer Sn-N distance may be a consequence of the chelating ethylene groups between the nitrogen and the sulfur atoms causing distortion by ring tension in the bicyclic ligand system. The crowding *tert*-butyl group is directed toward the Cr(CO)₅ group

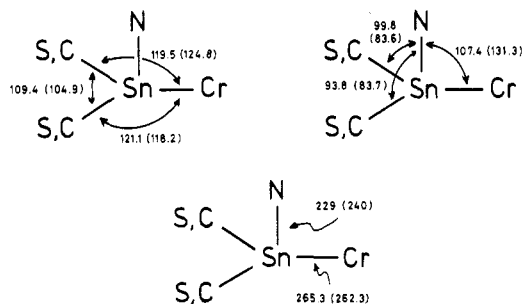


Figure 2. Comparison of the geometry at the tin atom of the tin ylide compounds $(\text{CO})_5\text{Cr}=\text{Sn}(\text{Bu}-t)_2\text{py}$ and $(\text{CO})_5\text{Cr}=\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{NBu}-t$ (distances and angles of the second compound given in brackets).

and probably enhances this effect.

It is surprising that the transition from a type I to a type II complex by addition of a base induces only a

slight deviation from planarity of the atoms X, Y (=X in this case), Sn, and Cr. Thus, in both compounds the tin atoms lie only 44 $[(\text{CO})_5\text{CrSn}(\text{Bu}-t)_2\text{py}]$ and 50 pm $[(\text{CO})_5\text{CrSn}(\text{SCH}_2\text{CH}_2)_2\text{NBu}-t]$ above the plane defined by the three others, resulting in a distorted tetrahedral coordination at the respective tin atom.^{23,24} A similar low deviation from the "stannylenic planarity" of about 40 pm is found in the unusual complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2\text{Sn}[\text{CH}(\text{SiMe}_3)_2]\text{COCH}(\text{SiMe}_3)_2$ where the stabilizing base represents an acyclic oxygen atom²⁵ (Figure 3).

The Cr-Sn distances are nearly identical (average 264 pm) in both compounds but are situated between that of the type I example $(\text{CO})_5\text{CrSn}[\text{CH}(\text{SiMe}_3)_2]_2$ containing a formal double bond (256 pm) and a Cr-Sn single bond with an sp^3 -hybridized tin atom (285 pm).¹³ This indicates that the π interaction between the transition metal and tin has decreased by the additional

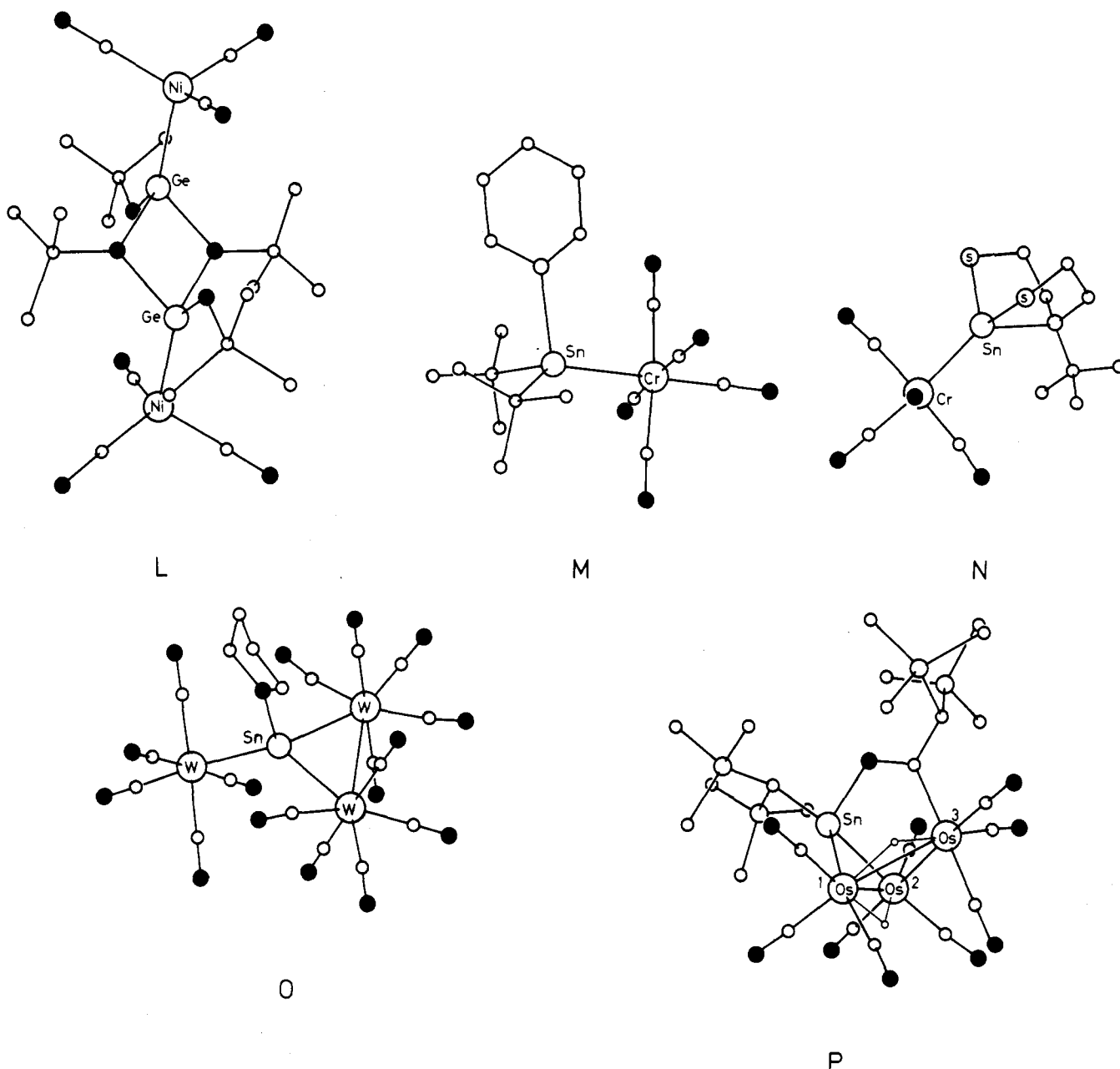


Figure 3. Structures of type II Ge and Sn ylide complexes. Reference key: $[(\text{CO})_3\text{Ni}=\text{Ge}(\text{OCMe}_3)_2]_2$ (L), 27; $(\text{CO})_5\text{Cr}=\text{Sn}(\text{Bu}-t)_2\text{py}$ (M), 23; $(\text{CO})_5\text{Cr}=\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{NBu}-t$ (N), 24; $(\text{CO})_5\text{W}=\text{Sn}[\text{W}(\text{CO})_5]_2\text{-THF}$ (O), 26; $\text{Os}_3\text{Sn}(\mu\text{-H})_2(\text{CO})_{10}[\text{CH}(\text{SiMe}_3)_2]_2$ (P), 25.

TABLE 2. X-ray Structural Data of Type II Germylene and Stannylene Ylide Complexes

compound	no. (Tables 5-7)	$d(M=M')$, pm	$d(M'-B)$, pm	remarks	ref
$[(CO)_3Ni=Ge(OCMe_3)_2]_2$ (L)	185	228.3 (2)	193.2 (6)	small OGeO angles (74.9, 95.5°) and all NiGeO angles >119°; Ge-Ni distances shorter than sum of covalence radii	27
$(CO)_5Cr=Sn(Bu-t)_2\leftarrow py$ (M)	99	265.3 (3)	229 (1)	normal Sn-N but unusually large Sn-C distances at 224 pm compared with those at 213 pm in $Me_3SnMn(CO)_5$; N coordination induced only small deviation from planarity of atoms Cr, C, C, Sn	23
$(CO)_5Cr=Sn(SCH_2CH_2)_2NBu-t$ (N)	151	262.2 (1)	240.0 (4)	normal Sn-S single bond distances of 242 pm; boat-boat conformation of eight-membered ring system	24
$(CO)_5W=Sn[W(CO)_5]_2\leftarrow THF$ (O)	181	271.3 (2)	229 (2)	other Sn-W distances, 279.0 (2) and 279.4 (2) pm	26
$Os_3Sn(\mu-H)_2(CO)_{10}[CH(SiMe_3)_2]_2$ (P)	182	265.8 (1)	211.7 (5)	tin atom viewed as a formal electron pair donor to Os(1) [or Os(2)]; Os(2)-Sn distance not reported	25

TABLE 3. X-ray Structural Data of Type II' Complexes

compound ^b	no. (Table 8)	$d(M=M')$, pm	$d(M'-B)$, pm	remarks	ref
$(CO)_4Fe=Sn(oep)$ (Q)	232	249.2 (1)	218.7 (3)	tin atom 81.8 (9) pm from plane of four N atoms; normal Fe-Sn bond distances	29
$(CO)_5MnHg(CO)_4Mn=Sn(tpp)$ (R)	228	255.4 (3)	218.3 (19)	tin ligand in cis position to nearly linear Mn-Hg-Mn chain (164.4°) with Sn-Mn-Hg angle of 94.5 (1)°; tin atom 85 pm above plane defined by four N atoms	31
$(PPh_3)_2Pt[Sn(pd)_2]_2$ (S)	227	255.8	<i>a</i>	ligands PPh_3 and $Sn(pd)_2$ distributed around central Pt atom in distorted-tetrahedral arrangement	32
$PEt_3HPtSnR_3(SnR_2OMe)_2SnR_2$ (R = C_6H_4Me-p ; T)	236	261.6 (1)	227.6 (7)	geometry around tin(II) atom that of distorted trigonal bipyramid with O atoms at apical positions; other Sn-O distances, 210 pm; other Sn-Pt distances vary between 258.5 (1) and 264.5 (1) pm	33

^a Not reported. ^b Key to ligands in Table 8.

N coordination but is still operative to some extent. The transition from the type I complex $(CO)_5WSn[W_2(CO)_{10}]$ to the type II species $(CO)_5WSn[W_2(CO)_{10}]\leftarrow THF$ induces a bond lengthening of only about 1 pm of all W-Sn bonds.²⁶

The X-ray analysis of $[(CO)_3NiGe(OBu-t)_2]_2$ establishes the dimeric nature of the complex, with a four-membered Ge-O-Ge-O ring for the "external" stabilization of the divalent group 14 element. The transition-metal moieties are found to be in trans position.²⁷ A similar arrangement has been postulated earlier for the transition-metal complexes of $[Sn(NMe_2)_2]_2$ on the basis of IR and NMR information.²⁸ The analysis confirms that the basic structure in this sort of free ligand remains unaltered upon complex formation (Table 2).

C. Type II' Compounds

The structures of four type II' compounds are known where formally divalent tin atoms attain the coordination number 5. In the majority of complexes the substituents X, Y, B¹, and B² of the neutral ligand M'(XYB¹B²) are the same and are represented by the nitrogen atoms of porphyrinato groups or oxygen atoms of acetylacetonato residues. The common structural feature of the porphyrinato complexes is the square-pyramidal array at the tin atoms, with the nitrogen atoms in the basal plane (Figure 4).

In $(CO)_4Fe-Sn(oep)$ the tin porphyrinato ligand (oep = octaethylporphyrinato) occupies an axial position in the trigonal-bipyramidal iron atom.²⁹ The Fe-Sn bond is not shortened in comparison with various Cp- $(CO)_2FeSnR_3$ compounds, where metal-metal bond distances between 246 and 256 pm have been measured.³⁰ Thus, the formulation of the complex with a partial double bond between iron and tin seems un-

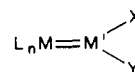
justified. In contrast, the Mn-Sn bond in $(CO)_5MnHg(CO)_4Mn-Sn(tpp)$ is one of the shortest such bonds yet observed (structure R in Figure 4; tpp = tetraphenylporphyrinato). An additional π interaction between Mn and Hg probably accounts for this bond shortening.³¹

The distorted tetrahedral arrangement of the ligands around the central Pt atom in $(PPh_3)_2Pt[Sn(acac)_2]_2$ is typical for Pt(0) and accounts for the divalent character for the tin nuclei.³²

In the complex $(PEt_3)(H)Pt(SnR_3)(SnR_2OMe)_2(SnR_2)$ the tin atom of the SnR_2 group (R = *p*- MeC_6H_4) can be formulated as subvalent with donor bonds from the two OMe groups of the neighboring SnR_2OMe ligands. This coordination induces a distorted bipyramidal arrangement of the ligands at the tin atom with the oxygen atoms at apical positions³³ (Table 3).

D. Conclusions

In summary, the significantly shortened M-M' distances in the type I compounds relative to authentic single bonds and the consequently realized trigonal-planar environments at the respective M' atom indicate the presence of a formal double bond and account for structural resemblances to carbene complexes:



If a donor molecule is added, resulting in an ylide complex, the M=M' bond is apparently only slightly influenced and the distances increase only to some extent. The addition of an additional base molecule to M' (usually realized with porphyrinato or acetylacetonato ligands at M') does not, however, continue this trend unambiguously, and the presence of at least

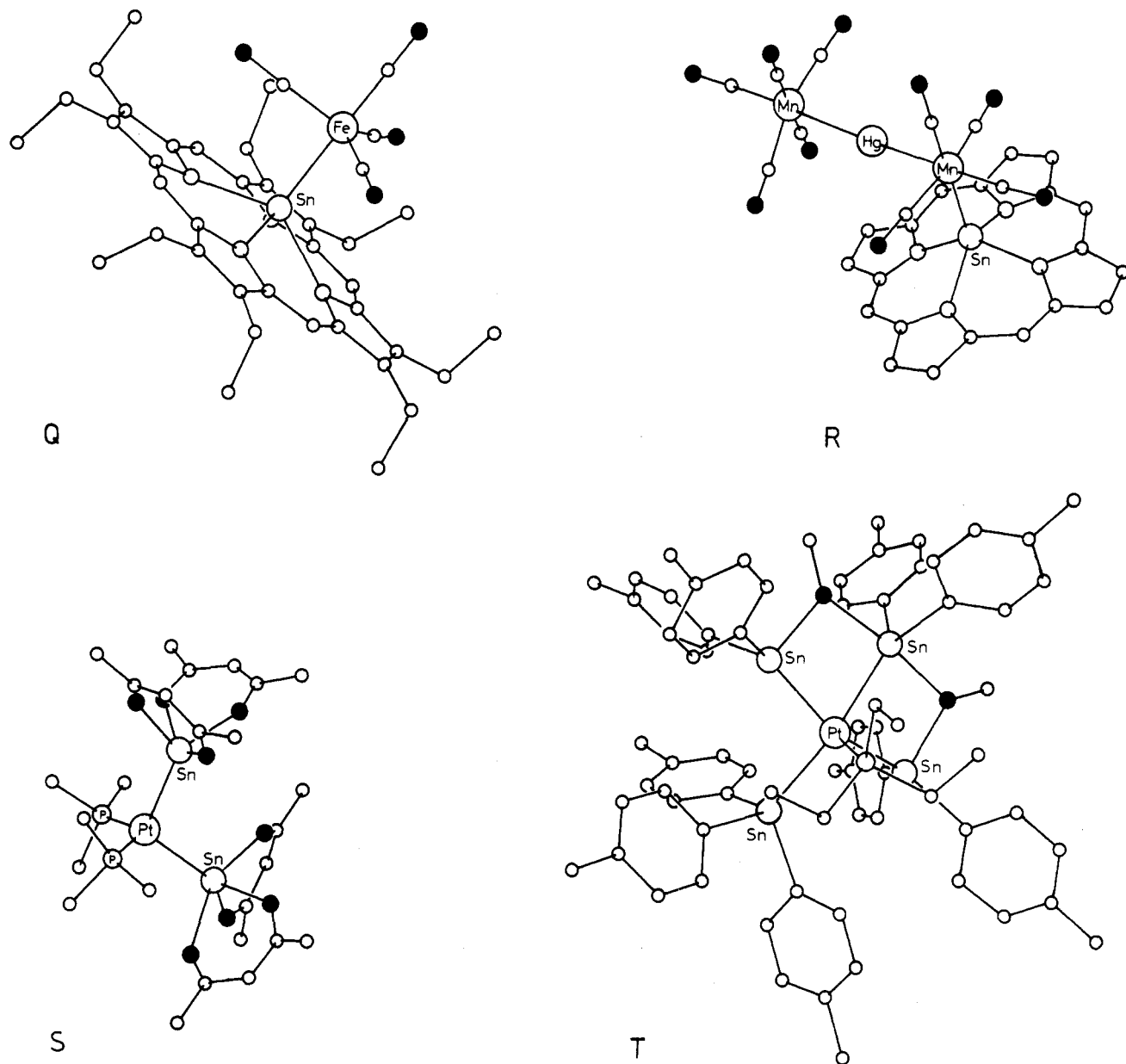


Figure 4. Structures of type II' compounds; phenyl groups of the tpp ligand in R omitted for clarity (tpp = tetraphenylporphyrinato). Reference key: $(\text{CO})_4\text{Fe}=\text{Sn}(\text{oep})$ (Q), 29; $(\text{CO})_5\text{MnHg}(\text{CO})_4\text{Mn}=\text{Sn}(\text{tpp})$ (R), 31; $(\text{PPh}_3)_2\text{Pt}[\text{Sn}(\text{pd})_2]_2$ (S); $\text{PtEt}_3\text{HPtSnR}_3(\text{SnR}_2\text{OMe})_2\text{SnR}_2$ (T) (R = $\text{C}_5\text{H}_4\text{Me-p}$).

partial double bonds may be discussed in some cases.

III. Syntheses of the Complexes

Several synthetic routes have been developed, resulting in about 200 complexes in which the elements Ge, Sn, and Pb serve as donor atoms. They may roughly be divided into six classes, which are discussed in this chapter.

In section A the starting material is a tetravalent group 14 compound of the general formula $\text{Y}_2\text{M}'\text{X}_2$ where X represents halogen ligands. The divalent group 14 species is formed by dehalogenation using a low-valent transition-metal complex. Parallels are found in the carbene chemistry; in some cases carbene complexes are available by dehalogenation of *gem*-dihalogenides.³⁴

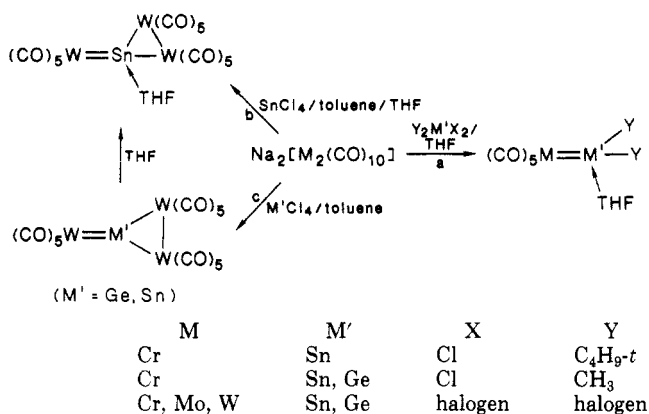
The pathway described in B resembles the procedure usually used in the preparation of complexes with so-called soft ligands like phosphines or arsines and soft Lewis acids like transition-metal carbonyl moieties.

This method is practical for all monomeric ylens containing the subvalent group 14 element or the corresponding ylide ligands forming type I and type II complexes, respectively.

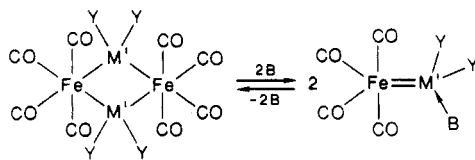
In section C base replacement reactions are described, and in D new type I and type II complexes are obtained by substitution of one or both σ -bonded X,Y ligands at a given complex $\text{L}_m\text{M}=\text{M}'\text{XY}$ or $\text{L}_m\text{M}=\text{M}'\text{XY}\leftarrow\text{B}$. The generation of type II complexes from an existing type I complex by simple addition of a base is treated in E, and miscellaneous syntheses are described in F.

A. Complex Formation upon Reduction of Tetravalent Group 14 Compounds

In coordinating solvents such as THF, the decarbonyldimetalates of the group 6 elements react with various dialkylgermanium or tin halides at low temperatures to produce type II complexes by incorporating one molecule of the solvent. No similar diarylstannylene or -germylene complexes are available via

SCHEME 1^a

^a Reference key: (a) 6, 35, 361; (b) 16; (c) 16.

SCHEME 2^a

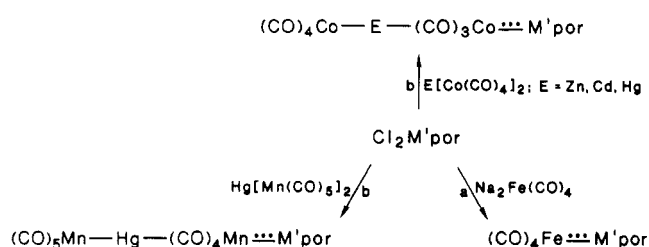
^a B = THF, py, CH₃CN, DMF, diethyl ether, acetone. Substituent key: M' = Ge, Y = CH₃, C₆H₅; M' = Sn, Y = CH₃, C₄H₉-t, C₆H₅; M' = Pb, Y = C₄H₉-n, C₆H₅. Reference 39.

this route.⁶ The tetrahalides M'X₄ afford the corresponding ylide complexes (CO)₅M=M'X₂←THF.³⁵

Earlier reports on base-free complexes with the SnY₂ or GeY₂ ligands (Y = halogen) prepared via this route were found to be erroneous; in each case a THF molecule was found to be coordinated at the group 14 element. It is not removable without decomposition of the complex.³⁶

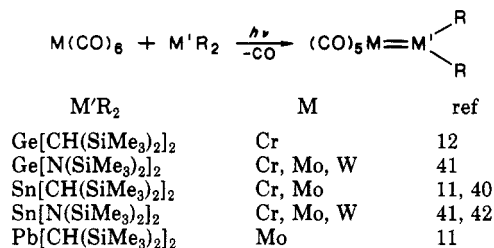
In earlier reports it was also mentioned that the reaction cannot be carried out in noncoordinating solvents.^{6,37} Recently, however, Huttner et al. have shown that in toluene solution total dehalogenation of the tetrahalides occurs by treatment with Na₂[W₂(CO)₁₀], resulting in the new type I complexes (CO)₅W=M'[W₂(CO)₁₀] in moderate yields. Small amounts of THF present from the preparation of the decacarbonyldimetalates also give the corresponding type II complex.¹⁶ The reactions are summarized in Scheme 1.

With Na₂[Fe(CO)₄] and Y₂M'X₂ compounds (Y = aryl, alkyl; X = halides), the stable dimeric complexes [(CO)₄FeM'(Y)₂]₂, containing a four-membered ring system, are generally available in high yields.³⁸ The structure persists in noncoordinating solvents, but in coordinating solvents an equilibrium between the dimer and the base-stabilized ylide complex is generated by homolytic cleavage of the metal-metal bonds. In several cases, especially by use of stronger bases such as pyridine, the monomeric adducts can be isolated; other complexes are only stable in the coordinating solvent B and identified by a dramatic change of the IR absorption in the ν(CO) region, thus indicating the appearance of a C_{3v}(CO)₄FeL molecule. Evaporation of the solvent regenerates the corresponding dimer; stronger bases need more vigorous conditions. The equilibrium (Scheme 2) is generally attained within 5–15 min. The equilibrium shifts increasingly to the right in the order of py > acetone > THF > diethyl ether.³⁹

SCHEME 3^a

^a Reference key: (a) 29; M' = Sn, Ge; por = octaethylporphyrinato (oep), *meso*-tetra-*p*-tolylporphyrinato (tptp); (b) 31; M' = Sn; por = tetraphenylporphyrinato (tpp).

SCHEME 4



The action of Na₂[Fe(CO)₄] on porphyrin complexes of tetravalent tin or germanium, (por)M'Cl₂ [por = octaethylporphyrinato (oep) or *meso*-tetra-*p*-tolylporphyrinato (tptp)], in THF solution affords monomeric complexes of type II' with the formal 0 oxidation state of the pentacoordinated iron atom. The rigid arrangement of the four nitrogen atoms in the bulky porphyrin ligand and the presence of two additional N atoms for the electronic saturation of the subvalent group 14 element probably prevent the molecule from dimerizing.²⁹

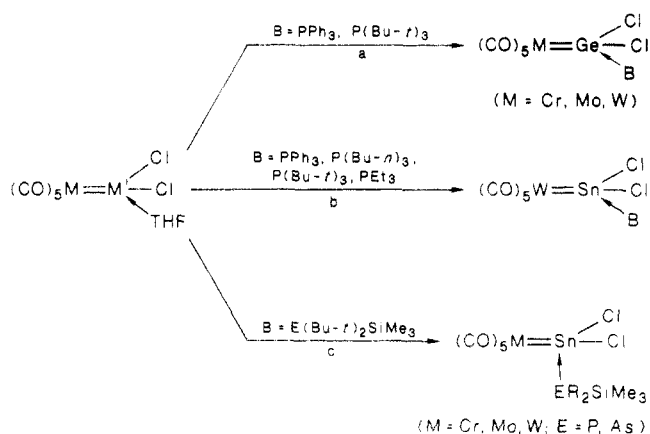
Unexpected results are obtained by the reaction of (tpp)SnCl₂ (tpp = tetraphenylporphyrinato) with Na[Mn(CO)₅] in the presence of metallic mercury or according to pathway b in Scheme 3. Both reactions lead to type II' complexes with a bent array of four metal atoms. Metallic mercury is considered to be the reducing agent for the tetravalent tin.³¹

B. Replacement of CO and Other Weakly Bonded Donor Ligands

UV irradiation of transition-metal carbonyl complexes in the presence of an appropriate soft ligand with a stereochemical active lone pair of electrons has proved to be a convenient method for CO replacement. The analogous procedure with M'R₂ compounds is, however, restricted to subvalent group 14 compounds with bulky ligands such as R = CH(SiMe₃)₂ or N(SiMe₃)₂, which are monomeric in solution and behave chemically as singlet stannylenes or germlynes^{11,12,40–42} (Scheme 4).

Small amounts of *trans*-disubstituted complexes are also formed upon UV irradiation but are prepared more conveniently from the corresponding tetracarbonyl-(norbondadiene)metal complexes.^{41,42} Only a small amount of the yellow plumblyene complex (CO)₅Mo=Pb[CH(SiMe₃)₂]₂ is obtained via this route because extensive decomposition of the ligand to metallic lead takes place upon UV irradiation.¹¹

All complexes containing the ligands M'[CH(SiMe₃)₂]₂ or M'[N(SiMe₃)₂]₂ are thermally stable up

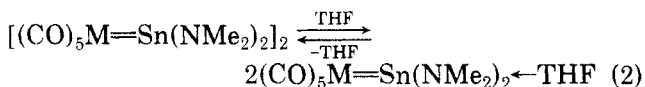
SCHEME 8^a

^a Reference key: (a) 48; (b) 49, 50; (c) 52-54.

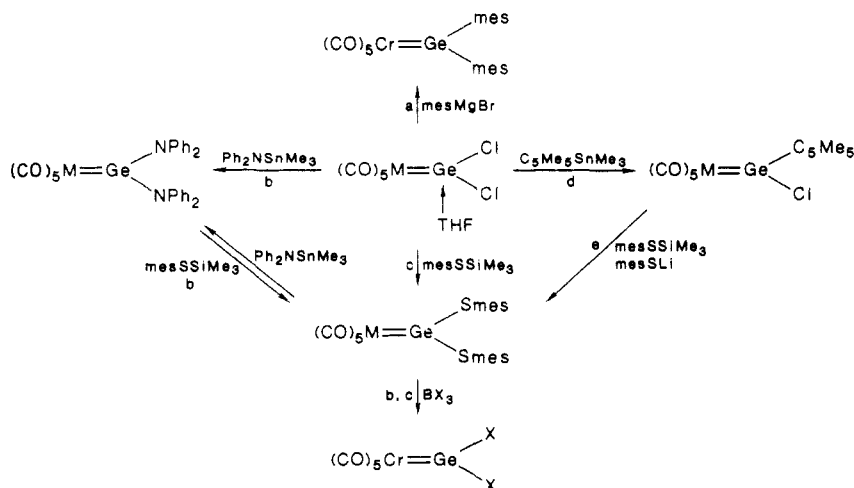
ported in the literature, and they are restricted to the exchange of THF by some phosphines (Scheme 8).⁴⁸⁻⁵⁰ The new ylide complexes are monomeric, like the starting THF adducts, and are comparable to ylide complexes obtained by addition of a phosphine ligand to an appropriate carbene complex.⁵¹ The resulting M'-P bond is very stable, and no exchange reactions are observed in the presence of THF.^{4c}

Ylide complexes with an Sn-P bond were also postulated to be formed as intermediates in the synthesis of polymeric type II complexes with silylphosphines or -arsines before elimination of Me₃SiCl occurs.^{49,52-54} Similarly, it was found that the paramagnetic base (C₄H₉-t)₂NO can successfully compete with THF for the Lewis acid (CO)₅Cr=Sn(C₄H₉-t)₂, giving the paramagnetic adduct (CO)₅Cr=Sn(C₄H₉-t)₂·ON(C₄H₉-t).⁵⁵

The reverse reaction, the substitution of an N base by THF, is observed when the dimeric type II complexes [(CO)₅M=Sn(NMe₂)₂]₂ (M = Cr, Mo, W) are dissolved in THF. The reaction is accompanied by a change of color from deep orange-yellow to pale yellow (eq 2).



Removal of the solvent in vacuo quantitatively regenerates the dimeric starting complexes.²⁸

SCHEME 9^a

^a M = Cr, W. X = Cl, Br, I. Reference key: (a) 59; (b) 56; (c) 57; (d) 20; (e) 19.

D. Nucleophilic Substitution

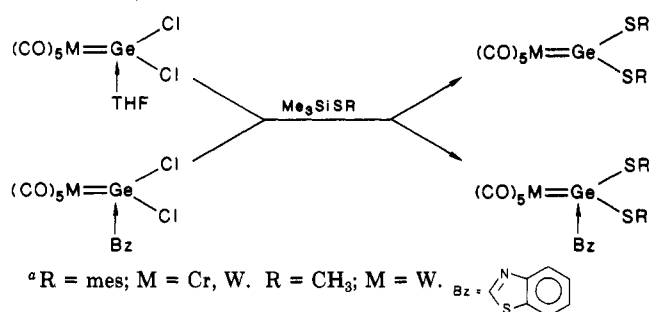
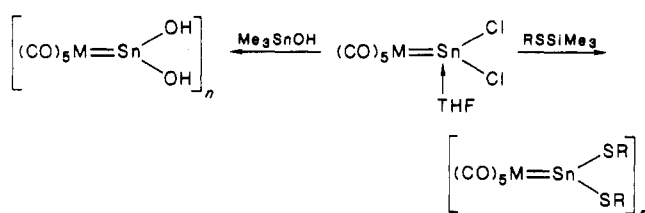
Like the transition-metal carbenes the homologous germylene and germylene ylide complexes show extensive replacement reactions of the ligands X and Y by various nucleophiles with retention of the L_mM=Ge fragment. Several systems have been studied by Jutzi and his group since 1976, resulting in new mono- and disubstituted compounds mainly starting from the readily available ylide complexes (CO)₅M=GeCl₂←THF. As outlined in Scheme 9, the action of the nucleophilic agents Me₃SiSR, Me₃SnNPh₂, and RMgBr involves replacement of both halogen atoms under very mild reaction conditions to give type I species. Because the resulting products are less acidic than the starting material, the additional coordinated base THF is lost during the reaction.⁵⁶

A further replacement reaction proceeds by the action of boron halides on (CO)₅Cr=Ge(Smes)₂ (mes = mesityl) with formation of the base-free starting complex. In a typical procedure the germylene complex is added at -30 °C to a solution of the boron halide in petroleum ether to give orange crystals. The stability of the product decreases in going from Cl to I with the effect that BI₃ reacts even at -78 °C to give a red solution that immediately darkens, thus indicating rapid decomposition of the initially formed germylene complex.⁵⁷

Boron halides are well-known in the chemistry of carbene complexes to be a key to the new class of carbyne complexes, which have become accessible by the excellent studies of E. O. Fischer and his group since 1973.⁵⁸

The substitution of the halogen atoms via Grignard reagents was only successful with mesityl bromide. The resulting complex (CO)₅Cr=Ge(C₆H₂Me₃)₂ is surprisingly stable in air and does not decompose below 80 °C.⁵⁹

An interesting mutual exchange of the mesitylthio vs. the diphenylamino group was also observed from the different bond strengths of the covalent 14-15 and 14-16 element bonds. The exchange reaction between (CO)₅W=Ge(NPh₂)₂ and (CO)₅W=Ge(Smes)₂ (Scheme 9) proceeds with 30-50% yield. The OR-substituted germylene complexes are too unstable to be isolated. However, when the starting ylide complex is treated with Me₃SnOR, separation of Me₃SnCl/THF is ob-

SCHEME 10^aSCHEME 11^a

served, thus indicating, in principle, an analogous reaction pathway.⁵⁶

As shown in Scheme 10 the Cl/SR exchange is accompanied by simultaneous loss of the coordinated THF molecule. Stronger bases such as benzothiazole, however, remain unaffected, and the corresponding type II complexes are obtained.¹⁴

The replacement of both halogen atoms of (CO)₅M=M'Cl₂←THF is mainly restricted to germanium ylide complexes, and a similar treatment of the tin derivatives with Me₃SiSR results in the formation of insoluble products. This property indicates a high degree of association.^{48,60}

Polymeric compounds with the Sn(OH)₂ ligand were obtained by a synthetic method based on the Cl/OH exchange reaction via trialkyltin hydroxide;⁶¹ this method was first described by Zuckerman in preparing the free ligand [Sn(OH)₂]_n⁶² (Scheme 11).

As already shown in Scheme 9 the replacement reaction with Me₃SnC₅Me₅ leads only to the exchange of

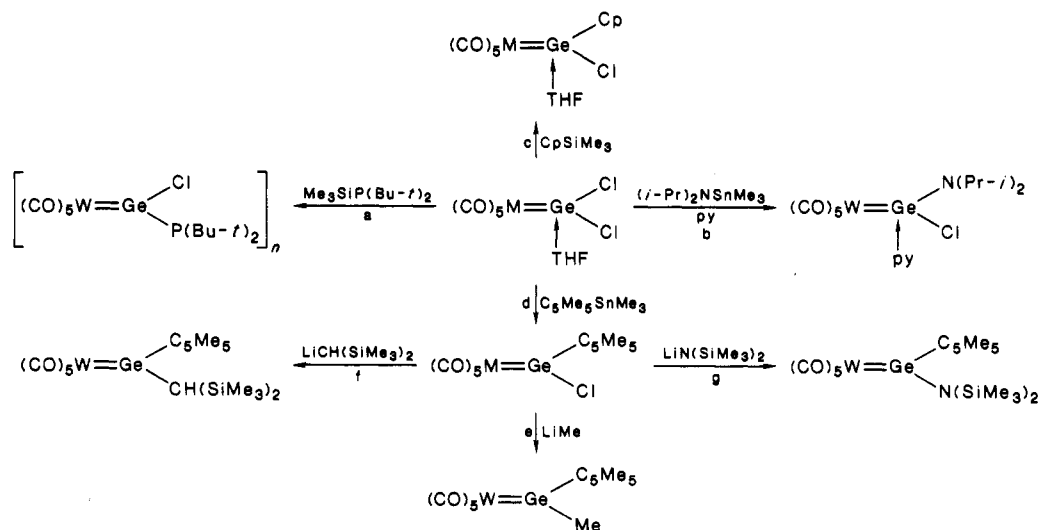
SCHEME 12^a

TABLE 4. Type I Compounds and Bases B That Give Stable Adducts

type I complex	B	ref
(CO) ₅ Cr=GeCl ₂	THF, NMe ₃ , C ₅ H ₅ N, Bz, ^a PPh ₃	56
(CO) ₅ Cr=GeBr ₂	THF, NMe ₃ , C ₅ H ₅ N, Bz, ^a PPh ₃	56
(CO) ₅ Cr=Ge(SC ₆ H ₁₁) ₂ ^b	NMe ₃ , C ₅ H ₅ N, PPh ₃ , Bz ^a	14, 21
(CO) ₅ Cr=Ge(NPh ₂) ₂	C ₅ H ₅ N, HNMe ₂	56
(CO) ₅ Cr=Ge(C ₆ H ₁₁) ₂ ^b	C ₅ H ₅ N	59
(CO) ₅ Cr=Ge[CH(SiMe ₃) ₂] ₂		11
(CO) ₅ W=SnW ₂ (CO) ₁₀	THF	26

^a Bz = benzothiazole. ^b C₆H₁₁ = mesityl.

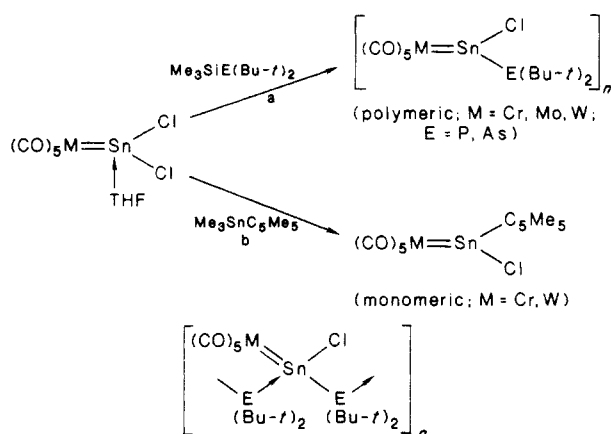
one halogen atom to give high yields of (CO)₅M=GeCl(η²-C₅Me₅). According to Scheme 12 these compounds are starting points for selective halogen replacement reactions with retention of the C₅Me₅ ligand.^{19,20}

The replacement of only one halogen atom of a type II complex is also known in the corresponding tin series, but only one type I species is obtained by this procedure, as shown in Scheme 13.²⁰ The reaction with silylphosphines or -arsines generates polymeric compounds in both series. These polymers, which can be considered to be intermolecularly stabilized stannylenylidene complexes, are insoluble in organic solvents and probably contain an infinite -E-Sn-E-Sn- chain. From spectroscopic studies it is suggested that the polymeric ligand behaves like a phosphite ligand.^{48,52-54}

E. Addition of Base Molecules to Type I Species

As mentioned earlier, the removal of the neutral base molecule from a type II complex to generate the basic type I species has never been reported, thus indicating the strong bonds between the bases and the divalent group 14 element. Attempts in this direction have always failed due to product decomposition.

The reverse reaction, the addition of a neutral donor to a type I complex, is possible but described for only a few compounds. This results not only from the small number of available ylene complexes but also from steric or electronic difficulties.

SCHEME 13^a

^a Reference key: (a) 52–54; (b) 20.

What base molecule can be added depends on the base strength, the Lewis acidity of the type I complex, and the steric requirements of both the ligands X, Y and the base molecule.

As shown in Table 4, only the samples with the GeCl₂ and GeBr₂ ligands possess enough Lewis acidity to give stable ylide complexes with weak bases such as THF. The environment at the Ge atom also allows coordination of bulkier donors such as PPh₃ or benzothiazole (Bz). The ligands SR and NR₂ diminish the Lewis acidity, and adducts with weaker donors become less stable.

The mesityl group causes a slightly weaker acidity relative to the halogens, but its bulkiness apparently allows only the addition of strong but small donors.⁵⁹ For comparison, the steric requirements of the CH-(SiMe₃)₂ group do not allow extension to coordination number 4.

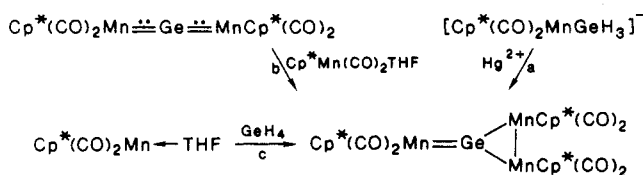
In contrast to (CO)₅W=Sn[W₂(CO)₁₀], which is able to add a THF molecule, the corresponding germylene complex shows no affinity to the base THF. The different behavior is explained by a reversed polarization of the M=M' bond.²⁶

F. Miscellaneous Syntheses

Less common pathways that have been used for the preparation of complexes with low-valent tin or germanium compounds are limited to a few examples and are summarized in this chapter.

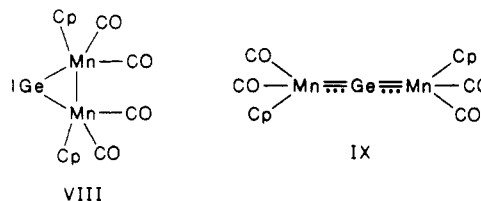
The first complex having a "naked" germanium atom attached to three transition-metal atoms was discovered in the research group of Weiss as a side product in 1% yield by the action of Hg²⁺ on K[C₅H₄Me-(CO)₂MnGeH₃], giving mainly [C₅H₄Me(CO)₂MnHg]₄, as shown in pathway a from Scheme 14. It was supposed that the mercury ion acts as a weak oxidizing agent.¹⁵ Other synthetic approaches, however, give more satisfying yields of 22% (pathway b) and 40–60% (pathway c).⁶³ From electron-counting and structural features these new compounds are typical type I complexes in which two σ-bonded manganese atoms represent the substituents X and Y.

The complexes can formally be understood as derived from the coordination of the hypothetical neutral germylene ligand VIII to the electronically unsaturated Cp(CO)₂Mn moiety. VIII is an isomer of the known

SCHEME 14^a

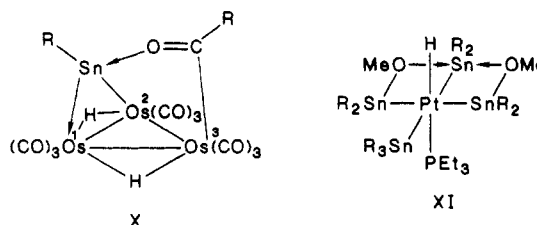
^a Cp* = C₅H₅, C₅H₄Me. Reference key: (a) 15; (b) 22; (c) 63.

complex IX, which contains the linear Mn–Ge–Mn unit with partial Mn–Ge triple bond.⁶⁴



According to pathway b in Scheme XIV it is assumed that electrophilic attack of the 16-electron fragment Cp(CO)₂Mn occurs at the central Ge atom of IX, causing a rearrangement from the linear array to the GeMn₂ triangle. Nothing is reported about the possibility of transferring this interesting reaction to other transition-metal Lewis acids such as M(CO)₅·THF (M = Cr, Mo, W) or (CO)₄Fe·THF to obtain compounds of the general formula (CO)₅MGe[Mn(CO)₂Cp]₂ or (CO)₄FeGe[Mn(CO)₂Cp]₂.

Intramolecular redox processes are responsible for the formation of two unusual complexes containing formally subvalent tin atoms coordinated to Os or Pt. Thus, the trinuclear cluster [Os₃Sn(μ-H)₂(CO)₁₀R₂] (R = CH-(SiMe₃)₂) forms the type II complex X essentially



quantitatively upon heating in heptane. The structure of this complex is depicted in Figure 3 (compound P) and shows that one of the bulky alkyl groups has migrated from the tin atom to the carbon of a coordinated carbon monoxide on Os(3), forming an η²-acyl group. The oxygen atom of this group is coordinated by electron donation into the vacant p orbital of the formally divalent tin atom.²⁵

High yields of the type II' complex XI are obtained if the complex Pt(CO₃)(SEt₂)(PEt₃) is treated with SnR₃H (R = C₆H₄Me-*p*) in methanol. During the procedure the Pt(II) of the starting material is oxidized to Pt(IV) upon reduction of a SnR₃H molecule to a neutral SnR₂ ligand, which is stabilized by OMe groups in a pentacoordinated environment. The molecular structure of XI is shown in Figure 4 (compound T).³³

IV. Listing of Compounds

This collection contains all known M'XY and M'XY←B ligands attached to various transition-metal fragments. The resulting complexes generally obey the 18-electron rule.

Some Cp_2M' compounds have been studied, too, with respect to their ability for complex formation. In contrast to earlier reports,⁶⁵ Cp_2Sn and Cp_2Ge are monomeric and fairly stable at room temperature. X-ray studies establish an angular sandwich structure with η^5 -bonded Cp rings.^{27,66} This arrangement with 40–50° angles between the ring planes indicates approximate sp^2 hybridization at the formally divalent M' metal atom with a lone pair of electrons probably capable of σ -donor bond formation. In contrast, the more bulky $C_5(C_6H_5)_5$ ligand induces parallel rings.⁶⁶

In the literature one paper is found that deals with the preparation and spectroscopic properties of complexes containing the Cp_2Sn and $(CH_3C_5H_4)_2Sn$ molecules as ligands at various $M(CO)_5$ fragments ($M = Cr, Mo, W$). From spectroscopic studies a structure with three-coordinate Sn atoms similar to the type I complexes was derived, and it was supposed that no $\eta^5 \rightarrow \eta^1$ rearrangement occurs on complex formation.⁶⁷ Unfortunately, no X-ray study of these compounds has been performed to establish the proposed structure.

In contrast to these results, Jutzi and his group recently reported that they were unsuccessful in transforming Cp_2Sn or Cp_2Ge into the corresponding $Cp_2M' = M(CO)_5$ complexes by the THF replacement method (method B in Tables 5 and 6) and that the identity of the complexes described earlier may be questioned.²⁰ This should be a challenge for X-ray crystallographers to answer these questions as to the nature of the adducts. Due to these well-founded doubts, this series of compounds will be excluded from discussions in this review.⁶⁸

However, Jutzi's group was successful in introducing one C_5Me_5 ligand at a type II germanium ylide complex by a nucleophilic substitution reaction, resulting in compounds for which are η^2 bonding of the ligand has been established. The C_5Me_5 ligand occupies one coordination site at the divalent germanium, and we class them as type I complexes.^{19,20}

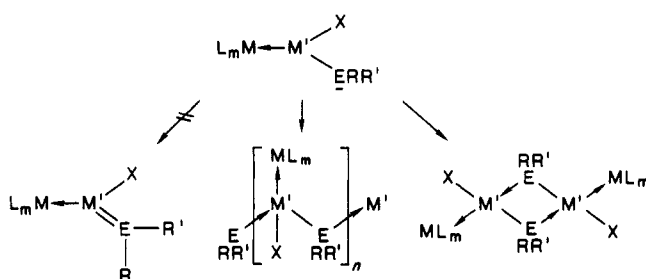
A. Monomeric Type I and Type II Compounds

Tables 5 and 6 contain complexes with three- or four-coordinate divalent group 14 atoms M' . Only a few of the basic ligands $M'XY$ or the corresponding ylides $M'XY \leftarrow B$ equipped with a stereochemical active pair of electrons are known in the free state; the majority of them are only stable when bonded to a 16-electron transition-metal moiety.⁶⁹

In addition to all known compounds, the corresponding type I species are presented too, but those that have not yet been isolated are marked as being not reported. A small number of compounds exist exclusively in the type I form, but with the majority of $M'XY$ ligands no one has been able to isolate the base-free complexes.

In the complex $(CO)_5CrSn(SCH_2CH_2)_2NC_4H_9-t$ (151, Table 6) the donor molecule B is already part of the stannylene ligand, forming the "tail" of the molecule, and the separation of the tin and the nitrogen atoms by two SCH_2CH_2 chains meets the stereochemical requirement for a ring strain-free transannular $Sn \leftarrow N$ donor bond.^{24,70} A similar $Sn \leftarrow O$ coordination has been found in the complex $Os_3Sn(\mu-H)_2(CO)_{10}[CH(SiMe_3)_2]_2$ (182, Table 6);²⁵ for both complexes no basic type I species can therefore be formulated.

SCHEME 15



B. Dimeric and Polymeric Type II Compounds

Table 7 contains dimeric and polymeric type II complexes of divalent germanium and tin compounds. This structural feature results from the replacement of X or Y in $M'XY$ by a group 15 or 16 element E equipped with a stereochemically active pair of electrons capable for a donor bond, too. Typically, for main-group element homologues, no π back-donation similar to that operative in carbene complexes occurs and electronic saturation of M' is achieved by forming four-membered rings or infinite chains as depicted in Scheme 15.

The formation of dimers predominates if $E = N, O,$ or S (R' thus represents an unshared pair of electrons in the case of O and S), whereas if $E = P$ or As , electronic saturation through formation of polymeric chains is clearly favored. It was suggested that the arrangement of the free ligands $(M'XERR')_2$ or $(M'XERR')_n$ does not differ markedly from those of the corresponding type II complexes. With the aid of spectroscopic arguments a possible E to transition-metal coordination of the type $M \leftarrow E(RR')M'X$ could always be excluded.

C. Complexes with Pentacoordinate Germanium and Tin

The chelating nature of β -keto enolates or porphyrins as substituents X and Y at the divalent main group 14 element gives rise to the coordination number 4 in the free ligand $M'XY(B)_2$ and 5 in the corresponding transition-metal complex $M = M'XY(B)_2$ by the additional donor functions of the neighboring oxygen or nitrogen atoms. An X-ray structure determination of $Sn(PhCOCHCOCH_3)_2$ shows indeed that the central tin atom has a distorted trigonal-bipyramidal geometry, with the stereochemical active pair of electrons occupying an equatorial site.⁷⁴ This conformation makes molecules of this type also capable of complex formation with unsaturated transition-metal fragments.

As mentioned earlier we will designate transition-metal complexes containing these ligands type II' complexes with the general assumption that the divalent oxidation state at the main-group element M' has been retained.

No similar compounds are known in the chemistry of carbene complexes, which demonstrates the inability of the carbon atom to extend its coordination number to 5 (if only "normal" σ bonds are involved) (Table 8).

V. The Chemistry of Silylenes

In contrast to the well-established chemistry of germylene and stannylene complexes and the corresponding ylide complexes, little is known about silylenes, SiR_2 ,

TABLE 5. Monomeric Type I and Type II Germylene Complexes

no.	compound ^b	prep method (% yield)	remarks ^{a,d}	ref
GeMe₂				
1 ^c	(CO) ₅ CrGeMe ₂			
2	(CO) ₅ CrGeMe ₂ ·THF	A	yellow; IR 1922 s, 1942 ms, 2043 w; ¹ H NMR 1.00 (CH ₃)	6
3 ^c	(CO) ₄ FeGeMe ₂		dimer	9
4	(CO) ₄ FeGeMe ₂ ·THF	A	dark orange; IR 1990 vs, 1920 sh, 2010 m	9
5	(CO) ₄ FeGeMe ₂ ·py	A (92)	dark orange; IR 2010 m, 1920 sh, 1990 vs	9
GePh₂				
6 ^c	(CO) ₄ FeGePh ₂		dimer	9
7	(CO) ₄ FeGePh ₂ ·THF	A	in THF solution; IR 1914 vs, 1948 m, 2029 s	9
8	(CO) ₄ FeGePh ₂ ·py	A	in pyridine solution; IR 1912 vs, 1947 m, 2030 m	9
Ge(C₆H₂Me₃)₂				
9	(CO) ₅ CrGe(C ₆ H ₂ Me ₃) ₂	D (50)	red; mp 80 dec; IR (CH ₂ Cl ₂) 1945 s, 1995 s, 2075 m ¹ H NMR (CH ₂ Cl ₂) 2.3 (CH ₃), 6.8 (CH)	59
10	(CO) ₅ CrGe(C ₉ H ₂ Me ₃) ₂ ·py	E(91)	yellow; mp 114; IR 1925 s, 2065 m; ¹ H NMR (CH ₂ Cl ₂) 2.3 (CH ₃), 6.85 (CH), 7.2–7.9 (CH, py)	59
Ge[CH(SiMe₃)₂]₂=GeR₂				
11	(CO) ₅ CrGeR ₂	B	yellow; mp 140; X-ray	12
12	<i>trans</i> -(CO) ₄ W(GeR ₂) ₂	B	yellow; mp 240	12
Ge(C₅Me₅)Me				
13	(CO) ₅ WGe(C ₅ Me ₅)Me	D (48)	orange needles; mp 89–90 dec; IR 2061 m, 1978 s, 1930 vs; ¹ H NMR 1.01 (GeCH ₃), 2.02 (CH ₃); ¹³ C NMR 196.90 (CO), 126.90 (C ₅), 11.62 (CCH ₃), 11.16 (GeCH ₃)	19
Ge(C₅Me₅)CH(SiMe₃)₂=Ge(C₅Me₅)R				
14	(CO) ₅ WGe(C ₅ Me ₅)R	D (63)	yellow orange prisms; mp 113–115 dec; IR 2060 s 1979 s, 1935 vs; ¹ H NMR 0.15 (SiMe), 1.98 (CH ₃); ¹³ C NMR 197.83 (CO), 127.43 (C ₅), 12.85 (CCH ₃), 3.11 (SiMe); ²⁹ Si NMR -40.60	19
Ge(C₅Me₅)N(SiMe₃)₂=Ge(C₅Me₅)R'				
15	(CO) ₅ WGe(C ₅ Me ₅)R'	D (67)	orange crystals; mp 122–124; IR 2061 m, 1980 s, 1940 vs; ¹ H NMR 1.90 (CCH ₃) 0.41 (SiMe); ¹³ C NMR 197.55 (CO) 127.66 (C ₅), 12.29 (CCH ₃), 4.98 (SiMe)	19
Ge(C₅Me₅)Cl				
16	(CO) ₅ CrGe(C ₅ Me ₅)Cl	D (28)	yellow green; decept 45; IR = 2075 m, 1980 m, 1950 vs, ¹ H NMR 2.18 (CH ₃); ¹³ C NMR 204.1 (CO), 121.00 (C ₅) 9.99 (CH ₃)	19, 20
17	(CO) ₅ WGe(C ₅ Me ₅)Cl	D (67)	yellow; decept 45; IR 2075 m, 1980 m, 1945 vs; ¹ H NMR 2.10 (CH ₃); ¹³ C NMR 195.11 (CO), 127.05 (C ₅), 11.28 (CH ₃)	19, 20
GeCpCl				
18 ^c	(CO) ₅ CrGeCpCl			
19	(CO) ₅ CrGeCpCl·THF	D (40)	ocher needles; mp 90 dec; IR 2068 m, 1929 s; ¹ H NMR 6.38 (Cp)	20
20 ^c	(CO) ₅ WGeCpCl			
21	(CO) ₅ WGeCpCl·THF	D (53)	ocher needles; mp 95 dec; IR 2067 m, 1987 m, 1925 s; ¹ H NMR 6.45 (Cp)	20
Ge(NPh₂)₂				
22	(CO) ₅ CrGe(NPh ₂) ₂	D (50)	orange; mp 80 dec; IR 1955 s, 1960 sh, 2074 m; ¹ H NMR 6.27–7.52 (C ₆ H ₅)	56
23	(CO) ₅ WGe(NPh ₂) ₂	D (50)	orange; mp 138 dec; IR 1948 s, 1960 sh, 2074 m; ¹ H NMR 6.37–7.30 (C ₆ H ₅)	56
24	(CO) ₅ WGe(NPh ₂) ₂ ·py	E (49)	mp 122 dec; IR 1938 s, 2061 m; ¹ H NMR 6.73–7.53 (C ₆ H ₅)	56
25	(CO) ₅ WGe(NPh ₂) ₂ ·HNPh ₂	E (49)	mp 80 dec; IR 1955 s, 1982 sh, 2075 w; ¹ H NMR 6.66–7.53 (C ₆ H ₅)	56
Ge[N(SiMe₃)₂]₂=GeR'₂				
26	(CO) ₅ CrGeR' ₂	B (40)	yellow; mp 90 dec; IR 2064, 1925	41
27	(CO) ₅ MoGeR' ₂	B (25)	yellow; pasty; IR 2077, 1936; ¹ H NMR 0.42 (CH ₃)	41
28	<i>trans</i> -(CO) ₄ Mo[GeR' ₂] ₂	B (60)	yellow; mp 145–148; IR 1938; ¹ H NMR 0.52 (CH ₃)	41
29	(CO) ₅ WGeR' ₂	B (30)	mp 96–98; IR 2069, 1932; ¹ H NMR 0.53 (CH ₃)	12, 41
30	<i>trans</i> -(CO) ₄ W[GeR' ₂] ₂	B (55)	yellow; mp 90–92 dec; IR 1933; ¹ H NMR 0.53 (CH ₃)	41
31	Pd[GeR' ₂] ₃	B (75)	red; mp 210–212 dec	17
32	Pt[GeR' ₂] ₃	B (95)	bright yellow; mp 140–142 dec	17
Ge(NPr₂)Cl				
33 ^c	(CO) ₅ WGe(NPr ₂)Cl			
34	(CO) ₅ WGe(NPr ₂)Cl·py	D	yellow; mp 90 dec; IR 1938 s, 2067 m; ¹ H NMR 1.34 [d, CH ₃ , J(C,H) = 9 Hz], 3.38–4.00 (m, CH), 7.60–9.20 (CH, py)	56
Ge(SMe)₂				
35	(CO) ₅ CrGe(SMe) ₂	D (19)	yellow green; mp 112 dec; IR 1945 s, 1990 m, 2050 ss, 390 ν(GeS); ¹ H NMR 2.75 (CH ₃)	14, 57
36	(CO) ₅ CrGe(SMe) ₂ ·Bz	D (50)	yellow green; mp 145; IR 1930 vs, 1975 m, 2050 m, 380 ν(GeS); ¹ H NMR 2.45 (CH ₃)	14
Ge(SET)₂				
37 ^c	(CO) ₅ CrGe(SET) ₂			
38	(CO) ₅ CrGe(SET) ₂ ·Bz	D (51)	yellow green; mp 82; IR 1935 vs, 1975 m, 2050 m; 425 ν(GeS); ¹ H NMR 1.45 (t, CH ₃), 3.05 [q, CH ₂ J(C,H) = 7 Hz]	14

TABLE 5 (Continued)

no.	compound ^b	prep method (% yield)	remarks ^{a,d}	ref
Ge(SPh) ₂				
39 ^c	(CO) ₅ CrGe(SPh) ₂			
40	(CO) ₅ CrGe(SPh) ₂ ·Bz	D (29)	yellow green; mp 121; IR 1940 vs, 1970 m, 380 and 425 ν(GeS); ¹ H NMR 6.8–7.2 (C ₆ H ₅)	14
Ge(SCH ₂ Ph) ₂				
41 ^c	(CO) ₅ CrGe(SCH ₂ Ph) ₂			
42	(CO) ₅ CrGe(SCH ₂ Ph) ₂ ·Bz	D	yellow green; mp 110; IR 1935 vs, 1970 m, 2050 m, 400 and 425 ν(GeS); ¹ H NMR 4.72 (CH ₂), 7.15–7.45 (C ₆ H ₅)	14
Ge(Smes) ₂ (mes = Mesityl)				
43	(CO) ₅ CrGe(Smes) ₂	D (79)	yellow orange; mp 141; IR 1955 vs, 1990 sh, 2060 m, 385 w and 420 m ν(GeS); ¹ H NMR 2.25 (CH _{3-p}), 2.30 (CH _{3-o}), 6.75 (CH)	14, 56, 57
44	(CO) ₅ CrGe(Smes) ₂ ·NMe ₃	E	yellow green; mp 98	14
45	(CO) ₅ CrGe(Smes) ₂ ·py	E	yellow green; mp 151	14
46	(CO) ₅ CrGe(Smes) ₂ ·PPh ₃	E	yellow green; mp 136	14
47	(CO) ₅ CrGe(Smes) ₂ ·Bz	E	yellow green; mp 106	14
48	(CO) ₅ WGe(Smes) ₂	D (72)	bright yellow; mp 142; IR 1960 vs, 1990 sh, 2065 m; ¹ H NMR 2.25 (CH _{3-p}), 2.30 (CH _{3-o}), 6.80 (CH)	14, 56
GeCl ₂				
49	(CO) ₅ CrGeCl ₂	D (37)	orange red; mp 105 dec; IR 1960 s, 1985 m, 2075 s	57
50	(CO) ₅ CrGeCl ₂ ·THF	A	yellow; mp 70–72; IR 1960 s, 1985 m, 2075 s	35, 43
51	(CO) ₅ CrGeCl ₂ ·NMe ₃	E (94)	mp 57; IR 1940 vs, 1970 m; ¹ H NMR 2.90	56
52	(CO) ₅ CrGeCl ₂ ·py	E (93)	mp 97; IR 1940 s, 1980 m, 2065 m; ¹ H NMR 7.7–9.1	56
53	(CO) ₅ CrGeCl ₂ ·Bz	E (92)	mp 145; IR 1940 vs, 1980 m, 2065 s	56
54	(CO) ₅ CrGeCl ₂ ·PPh ₃	E (87)	mp 153; IR 1940 s, 1975 m, 2965 m; ¹ H NMR 7.4–7.9	48, 56
55	(CO) ₅ CrGeCl ₂ ·P(Bu- <i>t</i>) ₃		no data available	48
56 ^c	(C ₆ H ₆)(CO) ₂ CrGeCl ₂			
57	(C ₆ H ₆)(CO) ₂ CrGeCl ₂ ·Bz	B (59)	orange red; mp 94–95 dec; IR 1800 m, 1825 s, 1860 m, 1905 s; 350, 375, 385 ν(GeCl)	43
58 ^c	(C ₆ H ₃ Me ₃)(CO) ₂ CrGeCl ₂			
59	(C ₆ H ₃ Me ₃)(CO) ₂ CrGeCl ₂ ·Bz	B (38)	red; mp 110–112 dec; IR 1815 m, 1855 s, 1990 s, 1930 s; 315, 345, 375 ν(GeCl)	43
60 ^c	(C ₆ Me ₆)(CO) ₂ CrGeCl ₂			
61	(C ₆ Me ₆)(CO) ₂ CrGeCl ₂ ·THF	B (29)	dark red; mp 95 dec; IR 1860 s, 1920 w, 1945 w, 330 and 365 ν(GeCl)	43
62	(C ₆ Me ₆)(CO) ₂ CrGeCl ₂ ·Bz	B (39)	dark red; mp 122–124; IR 1800 sh, 1830 m, 1870 s, 1915 w, 1945 m; 320, 345, 380 ν(GeCl)	43
63 ^c	(CO) ₅ WGeCl ₂			
64	(CO) ₅ WGeCl ₂ ·THF	A (70)	yellow; mp 104–108; IR 1905 s, 1930 m, 2075 m, 380 and 350 ν(GeCl)	43, 56
65 ^c	(CO) ₅ MoGeCl ₂			
66	(CO) ₅ MoGeCl ₂ ·THF	A (61)	IR 1965 vs, 1985 sh, 2000 sh, 2983 s	35, 56
67 ^c	MeC ₅ H ₄ (CO) ₂ MnGeCl ₂			
68	MeC ₅ H ₄ (CO) ₂ MnGeCl ₂ ·THF	B (56)	yellow; mp 125 dec; IR 1875 s, 1930 s, 355 ν(GeCl)	43
69	MeC ₅ H ₄ (CO) ₂ MnGeCl ₂ ·Bz	B (52)	yellow orange; mp 120–121 dec; IR 1875 s, 1945 s, 325 and 355 ν(GeCl)	43
70 ^c	(CO) ₄ FeGeCl ₂			
71	(CO) ₄ FeGeCl ₂ ·THF	B (43)	orange red; mp 66–68; IR 1985 s, 2030 s, 2080 m, 380 ν(GeCl)	43
72	(CO) ₄ FeGeCl ₂ ·Bz	B (46)	orange red; mp 95–98; IR 1985 m, 2040 s, 2080 m, 360 and 375 ν(GeCl)	43
GeBr ₂				
73	(CO) ₅ CrGeBr ₂	D	bright red; stable below 0 °C	56
74	(CO) ₅ CrGeBr ₂ ·THF	A (72)	green yellow; mp 98; IR 1930 s, 1965 m, 2065 m	35, 56
75	(CO) ₅ CrGeBr ₂ ·NMe ₃	E (92)	green yellow, mp 78 dec; IR 1935 vs, 1980 m, 2060 m	56
76	(CO) ₅ CrGeBr ₂ ·py	E (85)	green yellow, mp 106; IR 1935 s, 1975 m, 2060 s	56
77	(CO) ₅ CrGeBr ₂ ·Bz	E (87)	green yellow; mp 105 dec; IR 1930 vs, 1975 m, 2060 s	56
78	(CO) ₅ CrGeBr ₂ ·PPh ₃	E (82)	green yellow, mp 134 dec; IR 1935 vs, 1970 m, 2055 s	56
79 ^c	(CO) ₅ MoGeBr ₂			
80	(CO) ₅ MoGeBr ₂ ·THF	A (65)	IR 1960 s, 1983 sh, 2080 vs	35
81 ^c	(CO) ₅ WGeBr ₂			
82	(CO) ₅ WGeBr ₂ ·THF	A (74)	IR 1955 vs, 1985 sh, 2080 w	35
GeI ₂				
83	(CO) ₅ CrGeI ₂	D	probably obtained at low temperature	56
84	(CO) ₅ CrGeI ₂ ·THF	A (54)	IR 1922 vs, 1942 sh, 1985 w, 2062 w	35
85 ^c	(CO) ₅ MoGeI ₂			
86	(CO) ₅ MoGeI ₂ ·THF	A (61)	IR 1920 s, 1942 vs, 1985 vs, 2011 sh, 2080 w	35
87 ^c	(CO) ₅ WGeI ₂			
88	(CO) ₅ WGeI ₂ ·THF	A (65)	IR 1930 vs, 1950 sh, 1990 w, 2026 w	35
GeMn ₂ =Ge[Mn(CO) ₂ MeC ₅ H ₄] ₂				
89	MeC ₅ H ₄ (CO) ₂ MnGeMn ₂	F (22)	dark red; mp 100 dec	15
GeMn' ₂ =Ge[Mn(CO) ₂ Cp] ₂				
90	Cp(CO) ₂ MnGeMn' ₂	F (60)	red crystals; mp 163 dec; IR 1970, 1930 vs, 1920 vs, 1893 s, 1870 vs; ¹ H NMR 4.39, 4.22 (s, Cp)	22, 63
Ge[W(CO) ₅] ₂				
91	(CO) ₅ WGe[W(CO) ₅] ₂	A (8)	orange; mp 110 dec; IR 2107 w, 2082 w, 2065 s, 2059 s, 2013 w, 1990 s, 1973 sh, 1937 w	16

^aThe nonassigned IR data belong to CO vibrations. ^bBz = benzothiazole. ^cBasic Type I complex not reported. ^dUnits: IR, cm⁻¹; NMR, δ; mp, °C; dec pt, °C.

TABLE 6. Monomeric Type I and Type II Stannylene and Plumbylene Complexes

no.	compound	prep method (% yield)	remarks ^{a,c}	ref
SnMe ₂				
92 ^b	(CO) ₅ CrSnMe ₂			
93	(CO) ₅ CrSnMe ₂ ·THF	A	yellow; IR 1920 s, 1941 m, 2038 w; ¹ H NMR 0.80	6
94	(CO) ₄ FeSnMe ₂		dimer	9
95	(CO) ₄ FeSnMe ₂ ·THF	A	stable in THF solution; IR 1908 vs, 1939 s	9
96	(CO) ₄ FeSnMe ₂ ·py	A	stable in pyridine solution; IR 1895 sh, 1903 vs, 1928 m, 2010 s; ¹ H NMR 1.00 [CH ₃ , ² J(Sn,H) = 41.2 Hz]	9
97	P(Bu- <i>t</i>) ₃ (CO) ₃ FeSnMe ₂ ·py	A	stable in pyridine solution; IR 1839	9
Sn(Bu- <i>t</i>) ₂				
98 ^b	(CO) ₅ CrSn(Bu- <i>t</i>) ₂			
99	(CO) ₅ CrSn(Bu- <i>t</i>) ₂ ·THF	A	pale yellow crystals; mp 120–122 dec; IR 1918 s, 1938 m, 2031 s; ¹ H NMR 1.40 [³ J(Sn,H) = 56.0 Hz]	6, 71
100	(CO) ₅ CrSn(Bu- <i>t</i>) ₂ ·py	A	yellow; ³ J(Sn,H) = 59.5 Hz; X-ray, Mössbauer	23, 71
101	(CO) ₅ CrSn(Bu- <i>t</i>) ₂ Me ₂ SO	A	³ J(Sn,H) = 58.0 Hz; Mössbauer	71
102	(CO) ₄ FeSn(Bu- <i>t</i>) ₂		dimer	9
103	(CO) ₄ FeSn(Bu- <i>t</i>) ₂ ·py	A (88)	orange brown; IR 1885 vs, 1930 m, 2010 m; ³ J(Sn,H) = 67.2 Hz	9
104	(CO) ₄ FeSn(Bu- <i>t</i>) ₂ ·THF	A	stable in THF solution; IR 1900 vs, 1940 m, 2018	9
Sn(Cp) ₂				
105	(CO) ₄ FeSn(η ¹ -Cp) ₂		dimer	67
106	(CO) ₄ FeSn(η ¹ -Cp) ₂ ·py		stable in pyridine solution; IR 1929 vvs, 2028 ms	67
107	(CO) ₄ FeSn(η ¹ -Cp) ₂ ·THF		stable in THF solution; dimer also present in THF solution	67
Sn(C ₅ H ₄ Me) ₂				
108	(CO) ₄ FeSn(η ¹ -C ₅ H ₄ Me) ₂		dimer	67
109	(CO) ₄ FeSn(η ¹ -C ₅ H ₄ Me) ₂ ·py		stable in pyridine solution; IR 1934 vvs, 2031 vs	67
110	(CO) ₄ FeSn(η ¹ -C ₅ H ₄ Me) ₂ ·THF		monomeric and dimeric species present in solution	67
SnPh ₂				
111 ^b	(CO) ₄ FeSnPh ₂			
112	(CO) ₄ FeSnPh ₂ ·py	A	stable in pyridine solution; IR 1907 vs, 1034 sh, 2021 s	9
113	(CO) ₄ FeSnPh ₂ ·THF	A	stable in THF solution; IR 1915 s, 1945 w, 2028 m	9
Sn[CH(SiMe ₃) ₂] ₂ =SnR ₂				
114	(CO) ₅ CrSnR ₂	B (43)	orange needles; mp 120; IR 1938 sh, 1942 vs, 1984 vs, 1962 s, 2053 s; ¹ H NMR 0.31 (CH ₃), 2.29 [CH, ² J(Sn,H) = 53 Hz]; X-ray	11, 40
115	<i>trans</i> -(CO) ₄ Cr(SnR ₂) ₂	B (41)	orange; mp 215–216; IR 1901 vs; ¹ H NMR 0.45 (CH ₃), 1.94 [CH, ² J(Sn,H) = 52 Hz]	11
116	(CO) ₅ MoSnR ₂	B (64)	pale yellow; mp 109–110; IR 1950 vs, 1958 vs, 2068 s; ¹ H NMR 0.30 (CH ₃), 2.17 [CH, ² J(Sn,H) = 47]	11, 40
117	<i>trans</i> -(CO) ₄ Mo(SnR ₂) ₂	B (73)	orange; mp 204–205; IR 1919 vs; ¹ H NMR 0.42 (CH ₃), 2.15 [CH, ² J(Sn,H) = 48 Hz]	11, 39
118	Cp ₂ (CO) ₃ Fe ₂ SnR ₂	B (41)	brown; mp 167–170; IR 1770 s, 1939 vs	11, 39
119	<i>cis</i> -Cl(PEt ₃)PtSnR ₂ (SnR ₂ Cl)	B (80)	pale yellow; mp 154–156; IR 285 sh, 275 m (SnCl, PtCl); ³¹ P NMR -125 [J(Pt,P) = 4497 Hz]	11, 39
120	<i>trans</i> -Cl(PEt ₃)PtSnR ₂ (SnR ₂ Cl)		³¹ P NMR -127.6 [J(Pt,P) = 2490 Hz]	39
121	Cl(PPh ₃) ₂ Rh(SnR ₂) ₂	B (10)	purple; mp 184–187	11, 39
Sn(C ₅ Me ₅)Cl				
122	(CO) ₅ CrSn(C ₅ Me ₅)Cl	D (22)	yellow green; dec pt 45; IR 2075 m, 1980 m, 1950 vs; ¹ H NMR 2.17; ¹³ C NMR 198.5 (CO), 120.59 (C ₅), 9.71 (CH ₃)	19
123	(CO) ₅ WSn(C ₅ Me ₅)Cl	D (16)	yellow orange; dec pt 40; IR 2075 m, 1980 m, 1950 vs; ¹ H NMR 2.13; ¹³ C NMR 197.30 (CO), 121.95 (C ₅), 11.21 (CH ₃)	19
Sn(NMe ₂) ₂				
124	(CO) ₅ CrSn(NMe ₂) ₂		dimer	28
125	(CO) ₅ CrSn(NMe ₂) ₂ ·THF	C	in THF solution	28
126	(CO) ₅ MoSn(NMe ₂) ₂		dimer	28
127	(CO) ₅ MoSn(NMe ₂) ₂ ·THF	C	in THF solution	28
128	(CO) ₅ WSn(NMe ₂) ₂		dimer	28
129	(CO) ₅ WSn(NMe ₂) ₂ ·THF	C	in THF solution	28
Sn(NBu- <i>t</i>) ₂ SiMe ₂				
130	(CO) ₅ CrSn(NBu- <i>t</i>) ₂ SiMe ₂	A (50)	colorless; mp 90; IR 1920 s, 1965 sh, 2050 s; ¹ H NMR 0.32 (SiMe), 1.27 (CH ₃)	44
131	(CO) ₅ MoSn(NBu- <i>t</i>) ₂ SiMe ₂	A (32)	colorless; mp 91; IR 1938 s, 1970 sh, 2070 s; ¹ H NMR 0.31 (SiMe), 1.19 (CH ₃)	44
132	(CO) ₄ Mo[Sn(NBu- <i>t</i>) ₂ SiMe ₂] ₂	A (11)	yellow; mp 175; IR 1918 s, 2010 s; ¹ H NMR 0.32 (SiMe), 1.23 (CH ₃)	44
Sn[N(SiMe ₃) ₂] ₂ =SnR' ₂				
133	(CO) ₅ CrSnR' ₂	B (50)	orange yellow; mp 58–60; IR 2063, 1929; ¹ H NMR 0.38	41
134	(CO) ₅ MoSnR' ₂	B (25)	yellow; pasty; IR 2076, 1928; ¹ H NMR 0.37	41, 42
135	<i>trans</i> -(CO) ₄ Mo(SnR' ₂) ₂	B (65)	orange; mp 78–80; IR 1938; ¹ H NMR 0.34	41, 42
136	(CO) ₅ WSnR' ₂	B (35)	yellow; mp 87–89; IR 1931, 1958, 1969, 2037; ¹ H NMR 0.38	41, 42, 72
137	<i>trans</i> -(CO) ₄ W(SnR' ₂) ₂	B (60)	orange; mp 162–164 dec; IR 1931; ¹ H NMR 0.47	41
138	Cp ₂ MeScSnR' ₂	B	pale yellow oil; ¹ H NMR 0.11 (ScMe), 0.32 (SiMe), 5.27 (Cp)	41
139	η ³ -C ₃ H ₅ CIPdSnR' ₂	B	yellow; dec pt 20; ¹ H NMR 0.28 (SiMe), 3.12 (dd, CH ₃), 5.04 (m, CH)	41

TABLE 6 (Continued)

no.	compound	prep method (% yield)	remarks ^{a,c}	ref
140	Pd(SnR' ₂) ₃	B (80)	orange; mp 190–195 dec; X-ray	17
141	Pt(SnR' ₂) ₃	B (85)	yellow; mp 202–204 dec; X-ray SnClN(SiMe ₃) ₂ =SnClR'	17
142 ^b	(CO) ₅ WSnClR'			
143	(CO) ₅ WSnClR' ₂ ·THF	B (33)	pale yellow; mp > 90 dec Sn(OH) ₂	41
144	(CO) ₅ CrSn(OH) ₂		polymer	61
145	(CO) ₅ CrSn(OH) ₂ ·THF	D	stable in THF solution; IR 1950 vs, 2000 sh, 2072 s, 3505 (OH); ¹¹⁹ Sn NMR 9.5	61
146	(CO) ₅ WSn(OH) ₂		polymer	61
147	(CO) ₅ WSn(OH) ₂ ·THF	D	in THF solution; IR 1940 vs, 2000 sh, 2088 s, 3530 (OH); ¹¹⁹ Sn NMR –198	61
148	(CO) ₅ CrSnR'' ₂	B (80)	Sn[OC(NMe ₂) ₂ Fe(CO) ₃ =SnR'' ₂ yellow; IR 1920 vs br, 1950 sh, 1996 s, 2035 s, 2070 s; ¹ H NMR 2.51 (Me cis), 2.77 (Me trans); ¹³ C NMR 224.8 (CO trans), 218.0 (CO cis)	28
149	(CO) ₅ MoSnR'' ₂	B (80)	yellow; IR 1930 vs, 1995 s, 2040 s, 2080 vs; ¹ H NMR 2.41 (CH ₃ cis), 2.66 (CH ₃ trans)	28
150	(CO) ₅ WSnR'' ₂	B (80)	yellow; IR 1925 vs, 1970 sh, 1998 s, 2040 s, 2080 s; ¹ H NMR 2.38 (CH ₃ cis), 2.64 (CH ₃ trans)	28
151	(CO) ₅ CrSn(SCH ₂ CH ₂) ₂ NC ₄ H ₉ -t	B (64)	Sn(SCH ₂ CH ₂) ₂ NC ₄ H ₉ -t yellow; mp 190 dec; IR 1910, 1948, 1972; ¹ H NMR 3.05, 3.17, 3.35 (CH ₂); ¹³ C NMR 217.5 (CO)	24
152	(CO) ₅ CrSn(SAr) ₂	B (39)	Sn(SAr) ₂ (Ar = 2,4,6-t-Bu ₃ C ₆ H ₂) yellow; mp 204–206 SnCl ₂	73
153 ^b	(CO) ₅ CrSnCl ₂			
154	(CO) ₅ CrSnCl ₂ ·THF	A (60)	IR 1910 sh, 1950 s, 1984 vs, 2070 w; ¹¹⁹ Sn NMR 193	35, 50
155	(CO) ₅ CrSnCl ₂ ·PEt ₃	C	¹¹⁹ Sn NMR 228.5	50
156	(CO) ₅ CrSnCl ₂ ·P(Bu-n) ₃	C	¹¹⁹ Sn NMR 269	50
157	(CO) ₅ CrSnCl ₂ ·PPh ₃	C	¹¹⁹ Sn NMR 238	50
158 ^b	(CO) ₅ MoSnCl ₂			
159	(CO) ₅ MoSnCl ₂ ·THF	A (54)	IR 1960 sh, 1985 vs, 2060 w	35
160 ^b	(CO) ₅ WSnCl ₂			
161	(CO) ₅ WSnCl ₂ ·THF	A (73)	IR 1915 sh, 1950 vs, 1987 sh, 2090 w	35
162	(CO) ₅ WSnCl ₂ ·P(Bu-t) ₃	C (84)	yellow; mp 96–100; IR 1919, 1940, 1984, 2075, 324, 309 (SnCl); ¹¹⁹ Sn NMR 2.6 [J(Sn,W) = 1470 Hz]; ³¹ P NMR 40.8 [J(Sn,P) = 1560 Hz]	49, 50
163	(CO) ₅ WSnCl ₂ ·PEt ₃	C	¹¹⁹ Sn NMR –5.8 [J(Sn,W) = 1350 Hz]	49
164	(CO) ₅ WSnCl ₂ ·P(Bu-n) ₃	C	¹¹⁹ Sn NMR 9.5 [J(Sn,W) = 1490 Hz]	49
165	(CO) ₅ WSnCl ₂ ·PPh ₃	C	¹¹⁹ Sn NMR –15.1	49
166	MeC ₅ H ₄ (CO) ₂ MnSnCl ₂	B (80)	red brown; mp >140 dec; IR 1870 m br, 1940 s br, 1970 m sh SnBr ₂	45
167 ^b	(CO) ₅ CrSnBr ₂			
168	(CO) ₅ CrSnBr ₂ ·THF	A (64)	IR 1950 vs, 1984 w, 2070 w	35
169 ^b	(CO) ₅ MoSnBr ₂			
170	(CO) ₅ MoSnBr ₂ ·THF	A (58)	IR 1955 sh, 1985 vs, 2080 w	35
171 ^b	(CO) ₅ WSnBr ₂			
172	(CO) ₅ WSnBr ₂ ·THF	A (70)	IR 1953 sh, 1978 vs, 2015 sh, 2080 w; ¹¹⁹ Sn NMR –2.6 [J(Sn,W) = 1440 Hz]	35, 50
173	MeC ₅ H ₄ (CO) ₂ MnSnBr ₂	B (50)	red brown; mp >150 dec; IR 1870 m br, 1930 s, 1970 m sh SnI ₂	45
174 ^b	(CO) ₅ CrSnI ₂			
175	(CO) ₅ CrSnI ₂ ·THF	A (69)	IR 1915 sh, 1974 s, 1984 w, 2070 w	35
176 ^b	(CO) ₅ MoSnI ₂			
177	(CO) ₅ MoSnI ₂ ·THF	A (64)	IR 1985 vs, 2060 m	35
178 ^b	(CO) ₅ WSnI ₂			
179	(CO) ₅ WSnI ₂ ·THF	A (63)	IR 1945 sh, 1985 vs, 1915 sh, 2075 w	35
180	(CO) ₅ WSn[W(CO) ₅] ₂	A (37)	Sn[W(CO) ₅] ₂ orange; mp 176 dec; IR 1949 vs, 1976 vs, 2008 sh, 2049 s, 2056 s, 2093 w	16
181	(CO) ₅ WSn[W(CO) ₅] ₂ ·THF	A, E	orange; IR 1951 vs, 1977 vs, 2008 sh, 2049 s, 2075 s, 2094 w	26
182	Os ₃ Sn(μ-H) ₂ (CO) ₁₀ [CH(SiMe ₃) ₂] ₂	F (100)	Os ₃ Cluster ¹ H NMR –16.138, –19.596 [ds, 2 H, J(H,H) = 1.21 Hz]; IR 1394 ν(>CO)	25
183	(CO) ₅ MoPbR ₂	B	Pb[CH(SiMe ₃) ₂] ₂ =PbR ₂ yellow; mp 93–94; IR 1957 vs, 1960 vs, 2072 m	11
184	η ³ -C ₃ H ₅ ClPbR' ₂	B	Pb[N(SiMe ₃) ₂] ₂ =PbR' ₂ dark yellow; mp 80–82 dec; ¹ H NMR 0.57 (SiCH ₃), 2.92 (dd, CH ₂), 5.05 (m, CH)	41

^a The nonassigned IR data belong to CO vibrations. ^b Basic type I complex not reported. ^c Units: IR, cm⁻¹; NMR, δ; mp, °C; dec pt, °C.

TABLE 7. Dimeric and Polymeric Ge and Sn Ylide Complexes

no.	compound	prep method (% yield)	remarks ^d	ref
185	$[(CO)_5NiGe(OC_4H_9-t)_2]_2^a$	B (<95)	colorless; mp 136 dec; IR 2000, 2070 [Ge(OC ₄ H ₉ -t) ₂] ₂	27
186	$[(CO)_6CrSn(OSiMe_3)_2]_2$	B	yellow; mp 40 dec; IR 1940 br, 2050 [Sn(OSiMe ₃) ₂] ₂	46
187	$(CO)_3Ni[Sn(OSiMe_3)_2]_2$	B	colorless; mp 112 dec; IR 2000, 2075; ¹³ C NMR 3.5 (CH ₃), 195.2 (CO); ¹¹⁹ Sn NMR ^b	46
188	$[(CO)_5Wsn(OSiPh_3)_2]_2$	B	pale yellow; mp 58; IR 1930, 1972, 2065; ¹³ C NMR 196, 197.5 (CO); ¹¹⁹ Sn NMR ^b	46
189	$[(CO)_3NiSn(OC_4H_9-t)_2]_2$	B	colorless; mp 120 dec; IR 2000, 2060; ¹³ C NMR 195.7 (CO), 73.0, 79.5 (C), 34.0, 35.2 (CH ₃); ¹¹⁹ Sn NMR ^b	46
190	$[(CO)_6CrSn(NMe_2)_2]_2$	B (70)	yellow; IR 1920 vs, 1945 sh, 2058 s [Sn(NMe ₂) ₂] ₂	28
191	$[(CO)_6MoSn(NMe_2)_2]_2$	B (70)	yellow; IR 1930 vs, 2075 s	28
192	$[(CO)_5Wsn(NMe_2)_2]_2$	B (70)	yellow; IR 1930 vs, 1970 sh, 2070 s	28
193	$[(CO)_5CrSnCl(SC_4H_9)_2]_2$	D	[SnCl(SC ₄ H ₉ -t) ₂]	60, 48
194	$[(CO)_5WsnCl(SC_4H_9)_2]_2$	D		60, 48
195	$[(CO)_6CrGeClP(C_4H_9)_2]_n$		[GeClP(C ₄ H ₉) ₂] _n	48
196	$[(CO)_6WGeClP(C_4H_9)_2]_n$			48
197	$[(CO)_5CrSnClP(C_4H_9)_2]_n$	D	yellow; mp 140 dec; IR 1908, 1945, 1995, 2061; Raman ν (SnCl) 309, ν (PC ₂) 610, 550 [SnClP(C ₄ H ₉ -t) ₂] _n	54
198	$[(CO)_6MoSnClP(C_4H_9)_2]_n$	D	yellow; mp 140 dec; IR 1914, 1947, 2001, 2079; Raman ν (SnCl) 310, ν (PC ₂) 610	54
199	$[(CO)_5WsnClP(C_4H_9)_2]_n$	D	yellow; dec pt 175–178; IR 1905, 1940, 1991, 2075; Raman ν (SnCl) 310, 315, ν (PC ₂) 595, 570	53
200	$[(CO)_6CrSnClAs(C_4H_9)_2]_n$	D	yellow; mp 140 dec; IR 1943, 1998, 2068; Raman ν (SnCl) 309 [SnClAs(C ₄ H ₉ -t) ₂] _n	52
201	$[(CO)_6MoSnClAs(C_4H_9)_2]_n$	D	yellow; dec pt 162–164; IR 1919, 1948, 2000, 2080; Raman ν (SnCl) 308	52
202	$[(CO)_5WsnClAs(C_4H_9)_2]_n$	D	yellow; dec pt 162–164; IR 1905, 1992, 2078; Raman ν (SnCl) 310; Mössbauer ^c	52, 53
203	$[(CO)_5CrSn(OH)_2]_n$	D	yellow; mp >150 dec; IR 1950, 2000, 2088, ν (OH) 3505 [Sn(OH) ₂] _n	61
204	$[(CO)_5Wsn(OH)_2]_n$	D	colorless; IR 1940, 2000, 2088, ν (OH) 3530	61

^a See Table 2. ^b See Table 13. ^c See Table 10. ^d Units: IR, cm⁻¹; NMR, δ ; mp, °C; dec pt, °C.

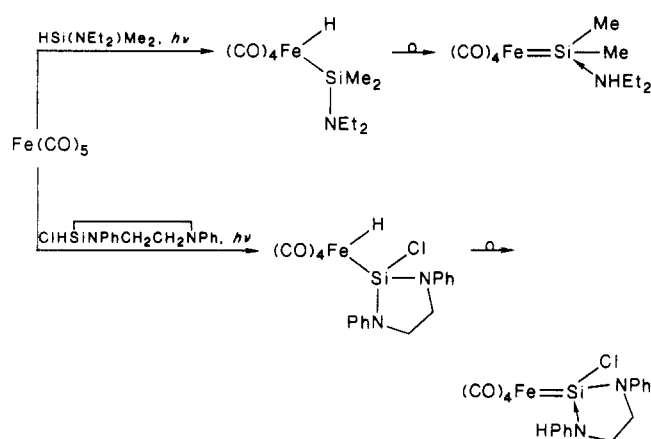
coordinated at transition-metal compounds. On the other hand, silylenes are well-known in organic chemistry as short-lived intermediates that can be detected by various trapping reactions.⁷⁸

The existence of the stable disilene, (mes)₂Si=Si-(mes)₂, with a silicon-silicon double bond⁷⁹ gives rise to the assumption that transition-metal complexes in which half of this formal "silylene dimer" is replaced by a 16-electron transition-metal moiety should not be out of the question. A clean preparative route to this type of complex may be considered as a challenge for silicon and organometallic chemists.

In 1978, Sakurai et al. described the first and, until now, only type I silylene complex, Me₂Si=FeH-(CO)₃SiMe₂R (R = H, CH₃), prepared by extrusion of SiMe₂ from the disilanes HMe₂SiSiMe₂R via Fe₂(CO)₉. The presence of an iron-silicon double bond in these air-sensitive and volatile compounds has been deduced from IR, ¹H NMR, and mass spectroscopic data. A signal at δ 0.71 in the ¹H NMR spectrum of the complexes was assigned to the iron-bonded SiMe₂ group. Nothing was reported about the stereochemistry at the hexacoordinate iron atom. Reactions with PPh₃ or 1,4-diphenyl-1,3-butadiene gave the corresponding Fe-(CO)₃ complexes whereas the action of toluene resulted in the formation of various silylated olefins.⁸⁰

A short time before, Schmid et al. reported an unusual rearrangement reaction, which involved conversion

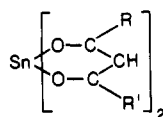
SCHEME 16



of a silylated hydride complex into a type II species as depicted in Scheme 16.

The intermediate hydride complex could not be isolated. The formation of the silicon ylide complexes was deduced from the appearance of N-H vibrations in the IR spectrum of the products at 3220 and 3185 cm⁻¹. The complexes were found to be stable only below -20 °C. Attempts to produce a carbene congener of type I by removal of HCl from the ylide complexes via a base failed.⁸¹

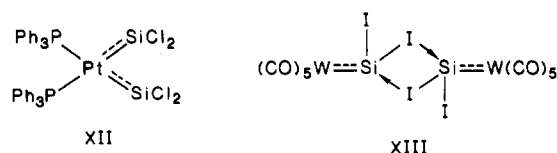
TABLE 8. Compounds with the Type II' Ligands, Porphyrinato, or



no.	compound ^a	remarks ^b	ref
205	(CO) ₅ CrSn(pd) ₂	yellow cream; mp 87–88; IR ν(CO) 1910 sh, 1935 vs, 1980 s, 2060 ms; ¹ H NMR δ(CH) 5.48, δ(CH ₃) 2.01	75
206	(CO) ₅ MoSn(pd) ₂	brown; mp >90 dec; IR ν(CO) 1930 ms br, 1985 s, 2070 w; ¹ H NMR δ(CH) 5.51, δ(CH ₃) 1.94	75
207	(CO) ₅ WSn(pd) ₂	pale cream; mp 96–97; IR ν(CO) 1925 vs br, 1980 s, 2080 ms; ¹ H NMR δ(CH) 5.88, δ(CH ₃) 2.00	75
208	(CO) ₅ CrSn(pbd) ₂	lime green; mp 95–97; IR ν(CO) 1920 s br, 1940, 1980 m, 2065 m; ¹ H NMR δ(CH) 6.61, δ(CH ₃) 2.17	75
209	(CO) ₅ MoSn(pbd) ₂	purple brown; mp 105; IR ν(CO) 1925 s, 1950 vs br, 1990 w sh, 2090 ms; ¹ H NMR δ(CH) 6.13, δ(CH ₃) 2.17	75
210	(CO) ₅ WSn(pbd) ₂	cream; mp 130; IR ν(CO) 1930 vs br, 1950, 1980, 2080 ms; ¹ H NMR δ(CH) 6.14, δ(CH ₃) 2.08	75
211	(CO) ₅ CrSn(tbd) ₂	pale green; dec pt >120; IR ν(CO) 1940 s br, 1985 m sh, 2070 m; ¹ H NMR δ(CH) 5.88, δ(CH ₃) 2.23; ¹⁹ F NMR δ(CF ₃) 77.27	75
212	(CO) ₅ MoSn(tbd) ₂	dark red brown oil; IR ν(CO) 1925 vs br, 1985 sh, 2080 m; ¹ H NMR δ(CH) 5.90, δ(CH ₃) 2.26; ¹⁹ F NMR δ(CF ₃) 77.33	77
213	(CO) ₅ WSn(tbd) ₂	orange yellow oil; IR ν(CO) 1930 vs br, 1990 w sh, 2085 m; ¹ H NMR δ(CH) 5.94, δ(CH ₃) 2.27; ¹⁹ F NMR δ(CF ₃) 77.19	77
214	(CO) ₅ CrSn(bpd) ₂	pale green; dec pt >120; IR ν(CO) 1935 vs br, 1985 s, 2075 ms; ¹ H NMR δ(CH) 6.25; ¹⁹ F NMR δ(CF ₃) 76.60	77
215	(CO) ₅ MoSn(bpd) ₂	dark brown; dec pt >130; IR ν(CO) 1940 s br, 1980 s, 2080 m; ¹ H NMR δ(CH) 6.26; ¹⁹ F NMR δ(CF ₃) 76.46	77
216	(CO) ₅ WSn(bpd) ₂	red purple oil; IR ν(CO) 1940 vs br, 1990 m sh, 2085 m; ¹ H NMR δ(CH) 6.24; ¹⁹ F NMR δ(CF ₃) 76.51	77
217	MeC ₅ H ₄ (CO) ₂ MnSn(bppd) ₂	orange yellow; mp 135; IR ν(CO) 1930 m br, 1865 m br	45
218	MeC ₅ H ₄ (CO) ₂ MnSn(pbd) ₂	yellow; mp >120 dec; IR ν(CO) 1940 s, 1920 m sh, 1850 m	45
219	MeC ₅ H ₄ (CO) ₂ MnSn(tbd) ₂	cream yellow; mp 88–89; IR ν(CO) 1970 sh, 1940 m br, 1870 m br	45
220	MeC ₅ H ₄ (CO) ₂ MnSn(bpd) ₂	yellow brown; mp 99–101; IR ν(CO) 1965 w sh, 1940 m br, 1865 s br	45
221	MeC ₅ H ₄ (CO) ₂ MnSn(pd) ₂	orange red oil; IR ν(CO) 1930 s br, 1865 s br	45
222	MeC ₅ H ₄ (CO) ₂ MnSn(chtd) ₂	orange; mp >140 dec; IR ν(CO) 1920 s br, 1855 s	45
223	(CO) ₃ Fe ₂ Sn(pbd) ₂	IR ν(CO) 2030, 1995, 1925, ν(>CO) 1800	76
224	(CO) ₄ FeSn(pbd) ₂ py		77
225	(CO) ₄ FeSn(tbd) ₂ py		77
226	(CO) ₄ FeSn(bpd) ₂ py		74
227	(PPh ₃) ₂ Pt[Sn(pd) ₂] ₂	pale yellow; mp 183–185 dec; ³¹ P NMR 110.1 [J(Pt,P) = 5252 Hz, J(Sn,P) = 445 Hz]; ¹¹⁹ Sn NMR -601 [J(Pt,Sn) = 12891 Hz, J(¹¹⁷ Sn, ¹¹⁹ Sn) = 4517 Hz]	32
228	(CO) ₅ MnHg(CO) ₄ MnSn(tpp)-0.5CH ₂ Cl ₂	dark purple green; IR 2070 s, 2030 w br, 2004 s, 1975 vs, 1925 s	31
229	(CO) ₄ CoHg(CO) ₃ CoSn(tpp)-0.5CH ₂ Cl ₂	dark purple green; IR 2065 s, 2000 m, 1975 vs, 1933 m	31
230	(CO) ₄ CoCd(CO) ₃ CoSn(tpp)	dark purple green; IR 2065 s, 2000 m, 1973 vs, 1930 m	31
231	(CO) ₄ CoZn(CO) ₃ CoSn(tpp)	dark purple green; IR 2060 s, 2000 m, 1973 vs, 1935 m	31
232	(CO) ₄ FeSn(oep)	orange red; IR 2019, 1938, 1905	29
233	(CO) ₄ FeSn(tptp)	IR 2023, 1943, 1917–1905	29
234	(CO) ₄ FeGe(oep)	IR 2023, 1940, 1912–1903	29
235	(CO) ₄ FeGe(tptp)	IR 2026, 1945, 1919–1905	29
236	PEt ₃ HPtSnR ₃ (SnR ₂ OMe) ₂ SnR ₂ (R = C ₆ H ₄ Me- <i>p</i>)	pale yellow; mp 180 dec; IR 2060 (PtH); ¹ H NMR -10.70 [d, PtH, J(P,H) = 157.6 Hz, J(Pt,H) 501 Hz]; ³¹ P NMR -169.1 [s, J(Pt,P) = 1960 Hz]; ¹¹⁹ Sn NMR 132.5 [R ₂ SnO, J(Pt,Sn) = 7034 Hz, J(P,Sn) = 121 Hz], -17.5 [J(Pt,Sn) = 5568, J(P,Sn) = 116 Hz], -113.8 [J(Pt,Sn) = 5952, J(P,Sn) = 101 Hz]	33
237	PEt ₃ HPtSnR ₃ (SnR ₂ OH) ₂ SnR ₂ (R = C ₆ H ₄ Me- <i>p</i>)	¹ H NMR -10.56 [PtH, J(Pt,H) = 503, J(P,H) = 158.8 Hz]; ³¹ P NMR -167.9 [J(Pt,P) = 1957, J(Sn,P) = 118.4 Hz]	33

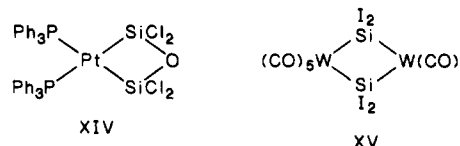
^aR = R' = CH₃ (pd); R = CH₃, R' = C₆H₅ (pbd); R = CF₃, R' = CH₃ (tbd); R = R' = CF₃ (bpd); R = R' = C₆H₅ (bppd); 2-hydroxycyclohepta-2,4,6-trienonate (chtd); tetraphenylporphyrinato (tpp); octaethylporphyrinato (oep); *meso*-tetra-*p*-tolylporphyrinato (tptp).
^bUnits: IR, cm⁻¹; NMR, δ, mp, °C; dec pt, °C.

The same authors also reported the formation of the bis-silylene complex XII by dehalogenation of



(PPh₃)₂Pt(SiCl₂)₂ with triphenylphosphine.⁸² They also suggested that the reaction of W(CO)₆ with Si₂I₆ upon irradiation leads to the halogen-bridged silylene complex XIII.⁸³ A trimeric complex of the composition [Fe(CO)₄SiCl₂]₃ was also formulated with silylene ligands.⁸⁴

Others, however, reported that XII is probably a product of hydrolysis and should be reformulated as a cyclic platinadisiloxane XIV with silicon-oxygen bonds.⁸⁵ It was also stated from another research group that XIII may also be formulated with bridging SiI₂ groups between the W(CO)₅ units as in XV, resembling the similarly arranged complex [(CO)₄FeSiCl₂]₂.⁷⁸



The small number of papers on this field of chemis-

TABLE 9. ^{119}Sn Mössbauer Parameter of Monomeric Type I Stannylene Complexes (mm/s, Relative to SnO_2)

complex	δ	$\Delta(\delta)^a$	ΔE^Q	$\Delta(\Delta E^Q)$	ref
$(\text{CO})_5\text{Cr}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$	2.21	0.05	4.43	2.12	89
<i>trans</i> - $(\text{CO})_4\text{Cr}\{\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2\}_2$	2.21	0.05	4.04	1.73	89
$(\text{CO})_5\text{Mo}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$	2.15	-0.01	4.57	2.26	89
<i>trans</i> - $(\text{CO})_4\text{Mo}\{\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2\}_2$	2.13	-0.03	4.24	1.87	89
$\text{ClPtEt}_3\text{Pt}\{\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2\}_2\text{SnCl}[\text{CH}(\text{SiMe}_3)_2]_2^b$	2.05	-0.11	4.23	1.92	89
$(\text{CO})_5\text{W}=\text{SnW}_2(\text{CO})_{10}$	2.56		4.60		26
$(\text{CO})_5\text{Cr}=\text{Sn}[\text{OC}(\text{NMe}_2)]_2\text{Fe}(\text{CO})_3$	2.17	-0.85	2.84	0.51	92
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{SnCl}_2$	1.77		1.81		45
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{SnBr}_2$	2.03		1.65		45

^a $\Delta(\delta) = \delta(\text{complex}) - \delta(\text{ligand})$; $\Delta(\Delta E^Q) = \Delta E^Q(\text{complex}) - \Delta E^Q(\text{ligand})$. ^b $\text{SnCl}[\text{CH}(\text{SiMe}_3)_2]_2$: δ 1.73, ΔE^Q 2.66.

try, and the controversial discussion concerning some compounds, gives rise to the assumption that the question of silylene and silicon ylide transition-metal complexes is still open and a reinvestigation would be timely. Unfortunately nothing has been done in the last 8 years to confirm the existence of a transition-metal to silicon double or partial double bond (required for such compounds) by an X-ray structural determination although this method now has become available for the majority of chemists.

VI. Spectroscopic Properties

A. Introduction

The main spectroscopic interest for these compounds has focused on methods that detect the electronic arrangement around the element in the formal divalent oxidation state. For this purpose, Mössbauer and NMR spectroscopy are useful; unfortunately, both methods are restricted to the element tin and no similarly effective probe is available for germanium. While ^{119}Sn Mössbauer spectroscopy has been used since the beginning of this chemistry, ^{119}Sn NMR spectroscopy has been employed just recently, and the data of tin(II) derivatives are limited to a few examples. Modern techniques probably will make this important diagnostic method more accessible in the future.

Many structural assignments are based on infrared spectroscopy. The majority of type I and type II compounds contain a transition metal-carbonyl fragment, which allows us to study the influence of new ligands on the $\nu(\text{CO})$ frequencies of adjacent carbonyl groups and to classify the ylene or ylide ligands in terms of their σ -donor and π -acceptor abilities. Such considerations are widely used and have been found very helpful in the characterization of a variety of soft donors⁸⁶ including carbene ligands.¹⁰ Other infrared data such as $\text{M}-\text{M}'$ or $\text{M}'-\text{X}$ frequencies ($\text{X} = \text{halogen}$) have also been mentioned in some papers but will not be discussed further.

B. Mössbauer Spectroscopy

^{119}Sn Mössbauer spectroscopy has found a widespread application in the structural analysis of tin compounds and the interpretation of the electronic arrangement around the tin atom.^{87,88}

The isomer shift (I.S.) is customarily presented as an important parameter in distinguishing between the two oxidation states of the element. Compounds with a stereochemically active lone pair of electrons are commonly considered to contain Sn(II) and generally exhibit I.S. values in the range well above 2.56 mm/s (the

I.S. of β -tin relative to that of BaSnO_3), which is the empirical dividing line between the two states.^{71,87} Others prefer the I.S. value of α -tin at 2.05 mm/s as the borderline.⁸⁹ The I.S. values δ of Sn(IV) compounds range below these lines.

Upon complex formation of such tin(II) compounds with transition-metal Lewis acids, the generally observed trend is that the I.S. values are always lowered and fall into a narrow range with an average value of about 2.1 ± 0.2 mm/s.⁹⁰ This lowering is conventionally explained with a synergistic σ plus π interaction with the transition metal causing a shielding of electron density from the tin nucleus by populating non s atomic orbitals.^{67,91} Electron withdrawal initiated by the σ -donor bond to the metal also has an effect on the real shielding of the tin nucleus.^{90,91} The I.S. decrease by formation of a donor bond to a low-valent transition-metal system is relatively independent of the coordination number at the tin atom. The small change in I.S. of the ligand $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ upon complex formation is due to the fact that this stannylyene forms a dimer in the solid state with a bent Sn-Sn bond, which is weak and can be cleaved even by solvent molecules.⁸⁹

This I.S. lowering is observed both with monomeric stannylyenes and with ylides upon complex formation, thus indicating a formal oxidation of the tin atoms therein. It should be noticed in this context that the participation of the tin lone pair of electrons at the coordination sphere of the transition metal can be regarded as a kind of oxidation that causes the I.S. value to fall into the range of tin(IV); i.e., the donation of a lone pair of electrons to a Lewis acid can be defined as an oxidation. The I.S. values of the title compounds are relatively insensitive to the coordination number at the tin atom and even to the nature of the transition metal.^{71,89} A decrease of the I.S. outside of the typical tin(II) range has been used as an important argument to demonstrate the presence of a tin-transition metal interaction. This is especially true for compounds such as the polymeric $[\text{SnClE}(\text{Bu}-n)_2]_n$ ($\text{E} = \text{P, As}$) where coordination with the group 15 element can also be discussed.⁵⁰

The donor bond to the transition metal is usually accompanied by a dramatic increase in quadrupole splitting ($\text{QS} = \Delta E^Q$). This parameter is a measure of the deviation of the electronic environment at the tin nucleus from cubic symmetry.⁷¹

Extremely large QS values of more than 4.0 mm/s have been measured for some type I complexes containing the three-coordinated tin atom as depicted in Table 9. The vacant $5p_z$ orbital on Sn and the lack of interaction between tin and any atom in the z direction produce a large p imbalance between the z and the x

TABLE 10. ^{119}Sn Mössbauer Parameter of Type II Tin Ylide Complexes (mm/s, Relative to SnO_2)

complex	δ	$\Delta(\delta)^a$	ΔE^Q	$\Delta(\Delta E^Q)^a$	ref
Monomeric Compounds					
$(\text{CO})_4\text{Fe}=\text{Sn}(\text{Bu}-t)_2\text{Me}_2\text{SO}$	1.87		3.45		71
$(\text{CO})_4\text{Fe}=\text{Sn}(\text{Bu}-t)_2\text{py}$	1.82		3.06		71
$(\text{CO})_5\text{Cr}=\text{Sn}(\text{Bu}-t)_2\text{THF}$	2.11		4.14		71
$(\text{CO})_5\text{Cr}=\text{Sn}(\text{Bu}-t)_2\text{Me}_2\text{SO}$	1.98		3.60		71
$(\text{CO})_5\text{Cr}=\text{Sn}(\text{Bu}-t)_2\text{py}$	2.01		3.44		71
$(\text{CO})_4\text{Fe}=\text{SnCl}_2\text{py}$	1.53	-1.71	1.98	1.00	76
$(\text{CO})_5\text{Cr}=\text{SnCl}_2\text{THF}$	2.19	-1.15	2.69	1.01	54
$(\text{CO})_5\text{W}=\text{SnCl}_2\text{THF}$	2.16	-1.18	2.85	1.17	54
$(\text{CO})_5\text{W}=\text{SnCl}_2\text{P}(\text{Bu}-t)_3$	2.05	-1.15	2.07	0.64	54
$(\text{CO})_4\text{Fe}=\text{SnBr}_2\text{py}$	1.40		2.25		76
$(\text{CO})_4\text{Fe}=\text{Sn}(\eta^1\text{-C}_5\text{H}_4\text{Me})_2\text{py}$	1.45		1.89		67
Dimeric Compounds					
$[(\text{CO})_5\text{Cr}=\text{Sn}(\text{NMe}_2)_2]_2$	1.89	-0.83	2.22	0.15	92
Polymeric Compounds					
$[(\text{CO})_5\text{Cr}=\text{SnClAs}(\text{Bu}-t)_2]_n$	2.26	-0.77	2.06	0.37	52, 90
$[(\text{CO})_5\text{Mo}=\text{SnClAs}(\text{Bu}-t)_2]_n$	2.10	-0.93	2.20	0.51	52, 90
$[(\text{CO})_5\text{W}=\text{SnClAs}(\text{Bu}-t)_2]_n$	2.11	-0.92	2.37	0.68	52, 90
$[(\text{CO})_5\text{Cr}=\text{SnClP}(\text{Bu}-t)_2]_n$	2.32	-0.64	2.12	0.43	90
$[(\text{CO})_5\text{Mo}=\text{SnClP}(\text{Bu}-t)_2]_n$	2.28	-0.68	2.17	0.48	90
$[(\text{CO})_5\text{W}=\text{SnClP}(\text{Bu}-t)_2]_n$	2.16	-0.90	2.17	0.48	90
$[(\text{CO})_5\text{Cr}=\text{Sn}(\text{OH})_2]_n$	1.95	-0.88	2.72	0.52	61, 90
$[(\text{CO})_5\text{W}=\text{Sn}(\text{OH})_2]_n$	1.98	-0.85	2.76	0.56	61, 90

^a $\Delta(\delta) = \delta(\text{complex}) - \delta(\text{ligand})$; $\Delta(\Delta E^Q) = \Delta E^A(\text{complex}) - \Delta E^Q(\text{ligand})$. ^b In pyridine solution.

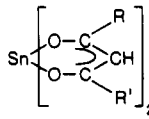
and γ directions. This leads to QS values that are among the largest recorded for an organotin system.⁸⁹ Within this series a surprisingly low value of about 2.9 mm/s was measured for the complex containing the unusual ligand $\text{Sn}[\text{OC}(\text{NMe}_2)]_2\text{Fe}(\text{CO})_3$. It was suggested that this lowering of QS arises from an additional tin-iron interaction in the six-membered ring system.⁹² From Mössbauer considerations the monomeric character of the compounds $\text{MeC}_5\text{H}_4(\text{CO})_2\text{MnSnX}_2$ ($X = \text{Cl}, \text{Br}$) should be questioned⁴⁵ (Table 10).

The QS value is very sensitive toward variation of the substituents at the tin atom, and for a given transition-metal stannylenic unit of type II ($M=\text{SnX}_2\leftarrow\text{B}$) the QS is a measure for the interaction between the metal-bonded Sn(II) moiety and the base B. It depends on the relative donor ability and decreases with an increase of the base strength. Thus, the QS value decreases in the range $\text{THF} > \text{Me}_2\text{SO} > \text{C}_5\text{H}_5\text{N}$.^{71,89,90}

A similar trend concerning the Mössbauer parameter is found for tin(II) bis(keto-enolates) when coordinated to transition-metal moieties. The isomer shift is lowered to the range 1.80–2.11 mm/s, thus illustrating the participation of the stereochemically active lone pair of electrons of the free ligand in the bond to the transition metal. As expected, the magnitude of the quadrupole splitting increases about 0.09–0.94 mm/s.^{45,75} Unusually low I.S. values of about 1.30 mm/s are recorded for ligands when coordinated to the $\text{Fe}(\text{CO})_4$ fragment; this is accompanied by only a small increase (0.03–0.28 mm/s) of the quadrupole splittings. This indicates a high degree of oxidation of the coordinated tin atom⁷⁶ (Table 11).

In a few cases where the transition metal bonded to the divalent group 14 ligand is an iron atom, the more common ^{57}Fe Mössbauer spectroscopy is used. The Mössbauer parameters of those compounds are collected separately in Table 12. Similar to the ^{119}Sn Mössbauer parameters, but even more dramatic, the position of the monomer-dimer equilibrium of the

TABLE 11. ^{119}Sn Mössbauer Parameter of Type II Complexes Containing the Ligand (mm/s, Relative to SnO_2)

complex ^c	δ	$\Delta(\delta)^a$	ΔE^Q	$\Delta(\Delta E^Q)^a$	ref
					
Sn(pd) ₂ (R = R' = CH ₃)					
$(\text{CO})_5\text{Cr}=\text{Sn}(\text{pd})_2$	1.81	-1.31	2.28	0.39	75
$(\text{CO})_5\text{Mo}=\text{Sn}(\text{pd})_2$	1.81	-1.31	2.30	0.41	75
$(\text{CO})_5\text{W}=\text{Sn}(\text{pd})_2$	1.80	-1.32	2.35	0.46	75
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{Sn}(\text{pd})_2$	1.93	-1.19	2.48	0.59	45
$(\text{CO})_4\text{Fe}=\text{Sn}(\text{pd})_2^b$	1.42	-1.70	2.02	0.13	76
Sn(pbd) ₂ (R = Ph, R' = CH ₃)					
$(\text{CO})_5\text{Cr}=\text{Sn}(\text{pbd})_2$	2.02	-1.05	2.07	0.09	75
$(\text{CO})_5\text{Mo}=\text{Sn}(\text{pbd})_2$	1.93	-1.14	2.51	0.53	75
$(\text{CO})_5\text{W}=\text{Sn}(\text{pbd})_2$	1.90	-1.17	2.39	0.41	75
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{Sn}(\text{pbd})_2$	1.99	-1.08	2.40	0.42	45
$(\text{CO})_4\text{Fe}=\text{Sn}(\text{pbd})_2$	1.27	-1.80	2.01	0.03	76
Sn(tbd) ₂ (R = CF ₃ , R' = CH ₃)					
$(\text{CO})_5\text{Cr}=\text{Sn}(\text{tbd})_2$	1.95	-1.45	2.29	0.42	75
$(\text{CO})_5\text{Mo}=\text{Sn}(\text{tbd})_2$	1.93	-1.47	2.42	0.55	75
$(\text{CO})_5\text{W}=\text{Sn}(\text{tbd})_2$	2.00	-1.40	2.31	0.44	75
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{Sn}(\text{tbd})_2$	1.92	-1.48	2.62	0.75	45
$(\text{CO})_4\text{Fe}=\text{Sn}(\text{tbd})_2^b$	1.30	-2.10	2.03	0.16	76
Sn(bpd) ₂ (R = R' = CF ₃)					
$(\text{CO})_5\text{Cr}=\text{Sn}(\text{bpd})_2$	1.99	-1.61	2.60	0.94	75
$(\text{CO})_5\text{Mo}=\text{Sn}(\text{bpd})_2$	2.03	-1.57	2.45	0.79	75
$(\text{CO})_5\text{W}=\text{Sn}(\text{bpd})_2$	2.13	-1.47	2.56	0.90	75
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{Sn}(\text{bpd})_2$	1.89	-1.71	2.77	1.11	45
$(\text{CO})_4\text{Fe}=\text{Sn}(\text{bpd})_2^b$	1.20	-2.40	1.95	0.29	76
Sn(dpd) ₂ (R = R' = Ph)					
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{Sn}(\text{dpd})_2$	1.96		2.55		45
$(\text{CO})_4\text{Fe}=\text{Sn}(\text{dpd})_2$	1.29		1.81		76
Sn(chtd) ₂ (chtd = 2-Hydroxycyclohepta-2,4,6-trienonate)					
$\text{MeC}_5\text{H}_4(\text{CO})_2\text{Mn}=\text{Sn}(\text{chtd})_2$	1.88		2.26		45

^a $\Delta(\delta) = \delta(\text{complex}) - \delta(\text{ligand})$; $\Delta(\Delta E^Q) = \Delta E^Q(\text{complex}) - \Delta E^Q(\text{ligand})$. ^b Measured in frozen pyridine solution. ^c Key to the ligands in Table 8.

TABLE 12. ^{57}Fe Mössbauer Data of Type II and Type II' Complexes^a

compound ^{b,c}	δ , mm/s	ΔE^A , mm/s	T, K	ref
$(\text{CO})_4\text{FeSnCl}_2\text{py}$	-0.24	2.45	77	76
$(\text{CO})_4\text{FeSnBr}_2\text{py}$	-0.20	2.62	77	76
$(\text{CO})_4\text{FeSn}(\text{pd})_2\text{py}$	-0.39	2.09	77	76
$(\text{CO})_4\text{FeSn}(\text{tbd})_2\text{py}$	-0.31	2.03	77	76
$(\text{CO})_4\text{FeSn}(\text{bpd})_2\text{py}$	-0.36	1.86	77	76
$(\text{CO})_4\text{FeSn}(\text{pbd})_2\text{py}$	-0.15	2.36	77	76
$(\text{CO})_4\text{FeSn}(\text{dpd})_2\text{py}$	-0.28	2.06	77	76
$(\text{CO})_4\text{FeSn}(\eta^1\text{-C}_5\text{H}_4\text{Me})_2\text{py}$	-0.08	2.36	77	67
$(\text{CO})_4\text{FeSn}(\text{oepr})$	-0.081	2.27	95	49

^a Rel to iron metal. ^b Pyridine adducts measured in frozen pyridine solution. ^c Key to the ligands in Table 8.

complexes $[(\text{CO})_4\text{FeSnX}_2]_2$ upon base addition is reflected in the ^{57}Fe Mössbauer data. Whereas the geometry at the tin atom does not change, rehybridization takes place at the iron atom from an octahedral coordination in the dimer to a trigonal-bipyramidal coordination in the monomeric species upon addition of a strong base such as pyridine.⁷⁶ The ^{57}Fe Mössbauer spectra of the dimers consist of a single rather broad line with a very small quadrupole splitting resulting from only a small deviation from the octahedral geometry. On going to frozen pyridine solutions, the QS values increase dramatically, thus indicating an increase of the electric field gradient at the Fe nucleus and the

TABLE 13. ^{119}Sn NMR Chemical Shifts of Tin Ylide Complexes (Relative to SnMe_4 , ppm)

L (^{119}Sn chem shift)	^{119}Sn chem shift						ref
	$(\text{CO})_5\text{Cr}=\text{L}$	$(\text{CO})_5\text{W}=\text{L}$	$(\text{CO})_3\text{Ni}=\text{L}$	$(\text{PPh}_3)_2\text{PtL}_2$	PtL_3	PdL_3	
$\text{Sn}(\text{SCH}_2\text{CH}_2)\text{NBU-}t$ (68.9)	622.8						24
$\text{Sn}(\text{OH})_2\cdot\text{THF}$	9.5	-198					50
$\text{Sn}(\text{OSiMe}_3)_2^a$ (-220)	74.2 ^{a,c}		35.3, 24.0 ^b				46
$\text{Sn}(\text{OSiPh}_3)_2^a$ (-339.5)		-303 ^d					46
		-202 ^e					
$\text{Sn}(\text{OBU-}n)_2$ (-93)			79.3 ^a				46
$\text{Sn}(\text{acac})_2$ (-702)				-601 ^f			32
$\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (770)					815 ^g	885	17
$\text{SnCl}_2\cdot\text{THF}$	193	-54.6 ^h					50
$\text{SnCl}_2\cdot\text{THF}_x$ (-238)	55	-209.0 ⁱ					50
$\text{SnCl}_2\cdot\text{PEt}_3$ (-47.5)	228.5	-5.8 ^k					50
$\text{SnCl}_2\cdot\text{P}(\text{Bu-}n)_3$ (-48)	269	9.5 ^l					50
$\text{SnCl}_2\cdot\text{P}(\text{Bu-}t)_3$ (21)		2.9 ^m					50
$\text{SnCl}_2\cdot\text{PPh}_3$	238	-15.1					50
$\text{SnBr}_2\cdot\text{THF}$ (-70.6)		2.6 ⁿ					50
$\text{SnBr}_2\cdot\text{THF}_x$		-217.6 ^o					50

^a Dimeric. ^b $(\text{CO})_3\text{Ni}=\text{L}\cdot\text{L}$. ^c Further signals at 61.5 and 44.4 ppm. ^d In THF/ C_6D_6 , $J(^{183}\text{W}, ^{119}\text{Sn}) = 1660$ Hz. ^e In C_6D_6 . ^f $J(^{195}\text{Pt}, ^{119}\text{Sn}) = 12891$ Hz, $J(^{117}\text{Sn}, ^{119}\text{Sn}) = 4517$ Hz. ^g $J(^{195}\text{Pt}, ^{119}/^{117}\text{Sn}) = 27847/26654$ Hz. ^h $J(^{183}\text{W}, ^{119}\text{Sn}) = 1440$. ⁱ $J(^{183}\text{W}, ^{119}\text{Sn}) = 1595$. ^j $J(^{183}\text{W}, ^{119}\text{Sn}) = 1350$. ^k $J(^{183}\text{W}, ^{119}\text{Sn}) = 1490$. ^l $J(^{183}\text{W}, ^{119}\text{Sn}) = 1470$. ^m $J(^{183}\text{W}, ^{119}\text{Sn}) = 1440$. ⁿ $J(^{183}\text{W}, ^{119}\text{Sn}) = 1440$. ^o $J(^{183}\text{W}, ^{119}\text{Sn}) = 1610$.

formation of the type II species. Similar parameters were recorded for complexes of the type $(\text{CO})_5\text{FeL}$ where L represents a neutral Lewis base in the axial position of the trigonal bipyramid.⁹³

This change in ^{57}Fe Mössbauer parameters upon addition of base was observed for different ligands X at the tin atom such as $\eta^1\text{-C}_5\text{H}_4\text{Me}$, halogens, or β -keto enolates, where an additional coordination of the β -carbonyl oxygen atom at the tin nucleus may be operative.⁶⁷

C. ^{119}Sn NMR Studies

The carbene carbon atoms are among the most deshielded carbon atoms, with ^{13}C NMR shifts up to 450 ppm.⁹⁴ Investigations with the isostructural tin congeners using ^{119}Sn NMR studies, until now, have not been done.

Recently, however, similar studies have been started by duMont et al. on some type II complexes, and the ^{119}Sn NMR data are collected in Table 13.⁵⁰ In contrast to the carbene chemistry, most of the tin(II) compounds functioning as ligands in the complexes are quite stable in the free state. This allows one to determine the chemical shift differences on complex formation expressed by $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$. Similarly, ^{31}P NMR shift differences for various phosphine complexes are well documented in a review.⁹⁵

The first results clearly demonstrate that the coordination of a given ylide causes a downfield shift that strongly depends upon the nature of the transition-metal moiety. A dramatic shift occurs in the case of $\text{Cr}(\text{CO})_5$ (270–550 ppm) and only a moderate one for $\text{W}(\text{CO})_5$. This correlates well with effects found at Sn(IV) transition-metal complexes of the type $\text{M}(\text{CO})_5\text{SnMe}_3$ on going from Mn to Re.⁹⁶

The number of base molecules coordinated at the tin(II) atom has great influence too. Thus, addition of excess THF to $\text{M}(\text{CO})_5\text{SnCl}_2\cdot\text{THF}$ ($\text{M} = \text{Cr}, \text{W}$) induces a dramatic upfield shift of about 150 ppm. On going to tungsten complexes, this shift is also accompanied by an increase of $J(^{119}\text{Sn}, ^{183}\text{W})$.⁵⁰

At present, the small amount of data does not permit one to draw any conclusion from the ^{119}Sn NMR shifts concerning the nature of the metal–ligand bond, but

TABLE 14. Selected IR Data of Some Type I and Type II Complexes Containing the $(\text{CO})_5\text{M}$ ($\text{M} = \text{Cr}, \text{W}$) Moiety (cm^{-1})

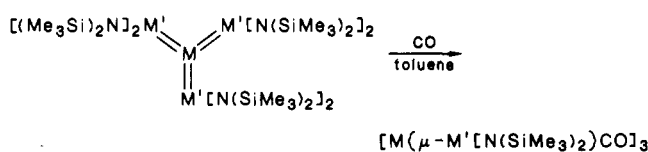
complex	A_1^2	B_1	A_1^1	E	ref
$(\text{CO})_5\text{Cr}=\text{GeCl}_2$	2075		1985	1960	57
$(\text{CO})_5\text{Cr}=\text{GeCl}_2\cdot\text{THF}$	2060	1950	1935	1910	43
$(\text{CO})_5\text{Cr}=\text{Ge}(\text{mes})_2$	2075		1995	1945	59
$(\text{CO})_5\text{Cr}=\text{Ge}(\text{mes})_2\cdot\text{py}$	2065		1945	1925	59
$(\text{CO})_5\text{Cr}=\text{Ge}(\text{Smes})_2$	2060		1990	1955	14
$(\text{CO})_5\text{Cr}=\text{Ge}(\text{Smes})_2\cdot\text{py}$	2055		1975	1930	14
$(\text{CO})_5\text{Cr}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$	2053		1948		11
$(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{C}_6\text{H}_5$	2060	1976	1947	1938	98
$(\text{CO})_5\text{CrC}(\text{OMe})\text{C}_6\text{H}_5\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$	2032		1866	1894	98
$(\text{CO})_5\text{W}=\text{GeCl}_2\cdot\text{THF}$	2075	1950	1930	1905	43, 56
$(\text{CO})_5\text{W}=\text{SnCl}_2\cdot\text{THF}$	2090	1987	1950	1915	35
$(\text{CO})_5\text{W}=\text{SnCl}_2\cdot\text{P}(\text{Bu-}t)_3$	2073	1984	1940	1919	49
$(\text{CO})_5\text{W}=\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$	2072		1962	1953	42
$(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{C}_6\text{H}_5$	2070	1969	1945	1934	98
$(\text{CO})_5\text{WC}(\text{OMe})\text{C}_6\text{H}_5\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$	2049		1869	1897	98

this method may be considered to be an excellent probe for the coordination of a tin(II) compound at transition-metal moieties.

D. IR Spectroscopy

It is commonly accepted that the position of the $\nu(\text{CO})$ frequencies of a given $\text{M}(\text{CO})_5\text{L}$ complex reflects the σ -donor/ π -acceptor ability of the coordinated ligand L. With few exceptions (CS, PF_3) this has been found to be increased if compared with that of carbon monoxide.⁹⁷ In order to locate the position of the $\text{M}'\text{XY}$ ligands with respect to their σ -donor/ π -acceptor ratios, the $\nu(\text{CO})$ frequencies of some selected complexes bearing various carbene, germylene, or stannylyne ligands or the related ylides have been collected in Table 14 for comparison. In the octahedral ligand arrangement, a local C_{4v} symmetry for the $\text{M}(\text{CO})_5$ moiety is assumed, which gives rise to three IR-active $\nu(\text{CO})$ vibrations ($2A_1 + E$). Severe deviations from the local symmetry probably by asymmetric ligands L create an additional band (B_1) in the IR spectrum.

The position of the A_1^1 band at lower wavenumbers, representing the vibration of the CO group opposite to the ligand L, serves as a rough gauge for the π -bonding ability of this ligand.

SCHEME 17^a

^aM = Pd, Pt. M' = Ge, Sn.

The A_1^1 bands in type I as well as type II complexes are found close to the position of the related bands in carbene complexes, which indicates that these ligands are at least as strong π acceptors as carbenes and back-donation of transition-metal d electrons into empty np or nd levels of the divalent group 14 element should occur. A comparison of type I and type II complexes with the same $(\text{CO})_5\text{M}=\text{M}'\text{X}_2$ unit indicates that the actual carbene congeners are slightly better π acceptors than the corresponding ylide ligands. In contrast, the vibrations of the complex containing the ylide ligand $\text{C}(\text{OMe})\text{Ph}\leftarrow\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$, which has no vacant orbitals for back-donation, are shifted by about 70 cm^{-1} to lower frequencies.

Similar results are obtained for related transition-metal fragments containing terminal CO groups, thus indicating the soft nature of the ligands with the divalent group 14 element as the donor atoms.

VII. Chemical Reactions

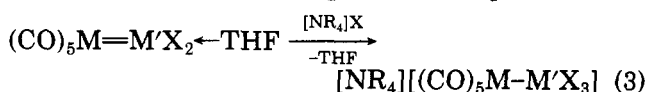
In contrast to the very extended chemistry involving the transition metal bonded carbene ligand, little attention has been focused in the last years on the chemical reactions of homologous systems.

In order to avoid overlap with the previous chapters, no reactions will be considered in this section in which a given type I or type II ligand at the transition-metal moiety is only modified or an interconversion between both types has occurred. With this prerequisite, the reactions to be described are restricted to only a few examples.

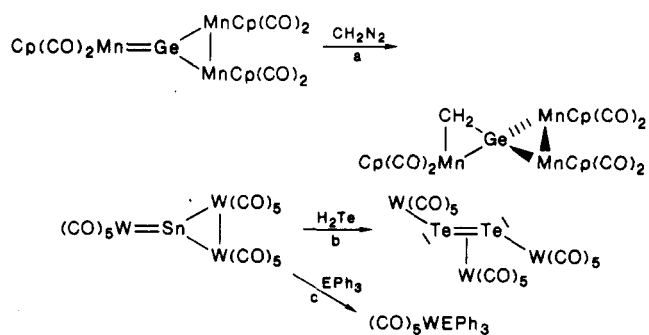
At first it appears quite surprising that there is no reaction described in the literature where the divalent group 14 ligand is replaced by other neutral donor systems like phosphines or amines, etc. This indicates a strong bond between the transition metal and the group 14 elements.

Recently, however, Lappert has shown that the action of CO on $\text{M}[\text{M}'\text{[N(SiMe}_3\text{)}_2\text{]}_2\text{]}_3$ occurs with loss of two of the three ligands and trimerization of the remaining fragment with CO uptake to give an interesting cluster complex as shown in Scheme 17.⁹⁹ The formerly terminal ligand $\text{M}'\text{[N(SiMe}_3\text{)}_2\text{]}_2$ now has become bridging, and one CO group coordinates at the transition metal in a terminal manner.

Replacement reactions at the $\text{M}'\text{XY}\leftarrow\text{B}$ ligand also take place with other than neutral donor systems. Thus, treatment of the type II compounds $(\text{CO})_5\text{M}=\text{M}'\text{XY}\leftarrow\text{THF}$ ($\text{X} = \text{Y} = \text{Cl, Br, I}$; $\text{M} = \text{Cr, Mo, W}$; $\text{M}' = \text{Ge, Sn}$) with ammonium halides replaces the coordinated THF molecule to give anionic species:³⁶



These anions had been prepared earlier directly from $(\text{CO})_6\text{M}$ and $[\text{AsR}_4]\text{M}'\text{X}_3$ ($\text{M} = \text{Cr, Mo}$; $\text{X} = \text{Cl, Br, I}$).¹⁰⁰

SCHEME 18^a

^aE = P, As, Sb. Reference key: (a) 59; (b) 26; (c) 26.

Interestingly, no complexes have been described where the entering halide anion is different from that in the complex, resulting in $-\text{M}'\text{X}_2\text{Y}$ ligands. Transition-metal compounds with $\text{M}'\text{X}_3$ ligands are well-known for $\text{M}' = \text{Si, Ge, and Sn}$ and will not be considered in this paper.

The reverse reaction, the abstraction of a halide ion to form a type I species, has not been observed. This route is well-known in carbene chemistry and opened the way to recently described transition-metal complexes with the CF_2 ligand.¹⁰¹

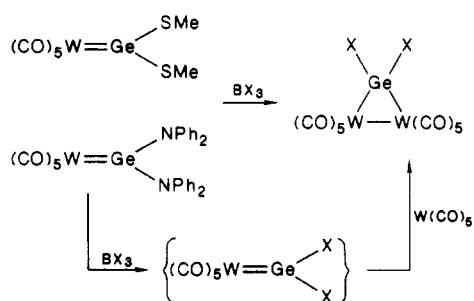
Very little interest has yet been focused on the reactivity of the double bond between the transition metal and the heavier main-group group 14 element. This is in contrast to the extended chemistry of the related metal-metal or metal-carbon double bond systems, which are, for instance, capable of alkylidene addition via the diazomethane method as developed by Herrmann et al.¹⁰²

Recently, a similar methylidene addition to the manganese-germanium double bond has been applied by the same laboratory, resulting in a novel μ -methylene complex as depicted in Scheme 18.⁵⁹ The addition of the diazomethane proceeds with concomitant nitrogen elimination, forming the μ, η^2 -germylidene complex in about 90% yield. This is also the first example of a metallacyclopropane containing two different group 14 elements. No studies concerning the general application of this synthetic concept to other type I complexes have been done.

The action of the Lewis base H_2Te (prepared in situ from Al_2Te_3 and HCl) on $(\text{CO})_5\text{W}=\text{Sn}[\text{W}(\text{CO})_5]_2$ replaces the tin atom by the Te_2 unit by simultaneous cleavage of the W-W bond. The transition from a "closed" to an "open" structure can be rationalized by the replacement of the four-electron-donor tin by the six-electron-donor Te_2 , making the metal-metal bond unnecessary.²⁶ Further studies of the chemistry of this type of compound are to be expected in the future.

Another example of a double-bond reaction is the conversion of some tungsten carbonyl stabilized germylenes into a "trimetallacyclopropanes" by boron halides as depicted in Scheme 19.¹⁰³ The resulting μ -germylene complexes have been obtained in 22–80% yield. With the homologous chromium complex, the terminally bonded GeX_2 ligand is formed as mentioned earlier.⁴³

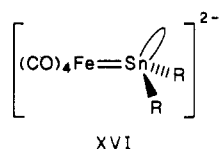
It was supposed that initially a dihalogen germylene complex forms that adds a $(\text{CO})_5\text{W}$ moiety obtained by a concurrent reaction involving ligand extrusion from the starting material by the BX_3 species. The proposed

SCHEME 19^a

^a X = Cl, Br.

reaction mechanism resembles the preparative route to dimetallacyclopropane complexes starting from Fischer-type carbene complexes and electronically unsaturated palladium or platinum compounds as described by Stone et al.¹⁰⁴

The monomeric type II complexes $(\text{CO})_4\text{Fe}=\text{SnR}_2\leftarrow\text{B}$ derived from the dimers $[(\text{CO})_4\text{FeSnR}_2]_2$ by addition of a base such as THF, pyridine, or 4-picoline *N*-oxide undergo two-electron reduction by sodium hydride or sodium amalgam to produce the anions XVI. These ions may be considered as type II species where the base is formally replaced by a pair of electrons.



XVI

An sp^3 hybridization rather than sp^2 at the tin atom is suggested. The solid shows variable base content, but the base is always coordinated to the cation. A formal one-electron reduction at each metal is derived from the Mössbauer and IR data.¹⁰⁵

VIII. Summary and Conclusion

In the last 15 years of research, about 200 different transition-metal complexes have been synthesized with ligands based on the Lewis base behavior of divalent Ge, Sn, and Pb compounds, and new discoveries in this area are constantly appearing.

Among this material about 30 complexes are found in which the group 14 element achieves the less favorable coordination number 3 (type I species), as in the analogous carbene complexes.

This series has been enriched recently by new species in which not only the formal "double bond" is formed to a transition metal but also the two remaining single bonds as found in the compounds with the $M'M_3$ core, having a "naked" group 14 element coordinated to three transition metals. At present, this type of compounds is restricted to $M = \text{Mn}$ or W and $M' = \text{Ge}$ and Sn , and no complexes with different metals M in the same molecule have been described.

The chemistry of the type I complexes differs markedly from the behavior of their carbene analogues despite many structural similarities. The most striking feature is that no stabilizing effect occurs by introducing a heteroatom in the X or Y position of $M'XY$ that would then be capable of π back-donation. This is common for the Fischer-type carbene complexes and necessary to saturate the carbene carbon atom. The stability of the heavier carbene complex congeners ap-

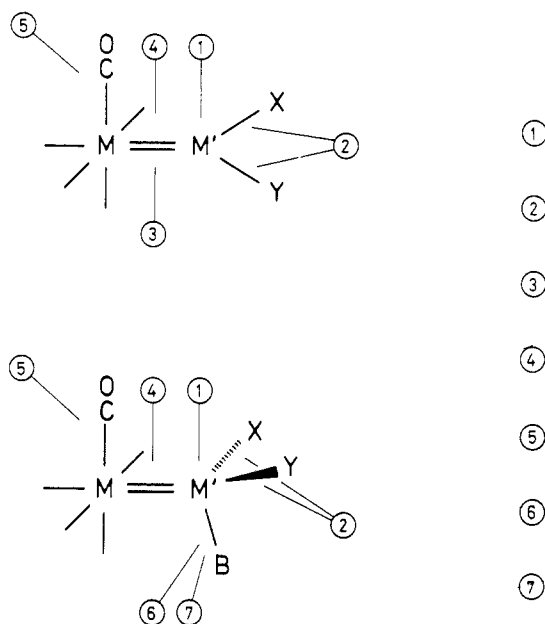


Figure 5. Outline of reactions of type I and type II species. Key: (1) base addition; (2) ligand substitution; (3) addition of unsaturated molecules to the double bond; (4) liberation of $M'XY$ or $M'XY\leftarrow B$; (5) CO substitution; (6) base substitution; (7) two-electron reduction.

parently is only achieved by steric effects with sufficiently bulky X or Y ligands. The steric crowding around the M' atom often prevents the attack of a base molecule from forming the more saturated type II species, and only a few compounds exist where both type I and type II are available having the same $L_nM=M'XY$ unit. In the Ge series, these are compounds with $X = Y = \text{C}_6\text{H}_2\text{Me}_3$, NPh_2 , SMe , and $\text{SC}_6\text{H}_2\text{Me}_3$ and in some cases Cl and Br; in the Sn series only the ligand $\text{Sn}[\text{W}(\text{CO})_5]_2$ participates in this manner. The reverse reaction, the loss of the base from the type II complex, has never been observed even with those compounds where the corresponding type I complex is well-known.

The second main difference from carbene chemistry is in the reaction with hard Lewis acids like BX_3 , which does not lead to carbyne-like germylyne or stannylyne complexes with a transition metal- M' triple bond; only an exchange of ligands is observed. Recently, it has been shown that similar triple bonds may be discussed, for instance, in the complex



in which a linear array of the metal atoms has been established.⁶⁴ The chemical reactions that can be carried out with the title complexes are outline in Figure 5.

It is obvious that no extensive substitution chemistry of either type of complex exists (5, Figure 5), although the substitution-prone $(\text{CO})_5\text{M}$ or $(\text{CO})_4\text{Fe}$ groups predominate as transition-metal fragments. This is probably a consequence of the weaker back-bonding capacities of the new ligands, keeping the CO groups more strongly bonded.

There is little doubt that the future will constantly bring us new results in this area of chemistry, and it is hoped that this comprehensive review will stimulate new or "old" investigators to make progress on this subject. Further research is needed in the area of

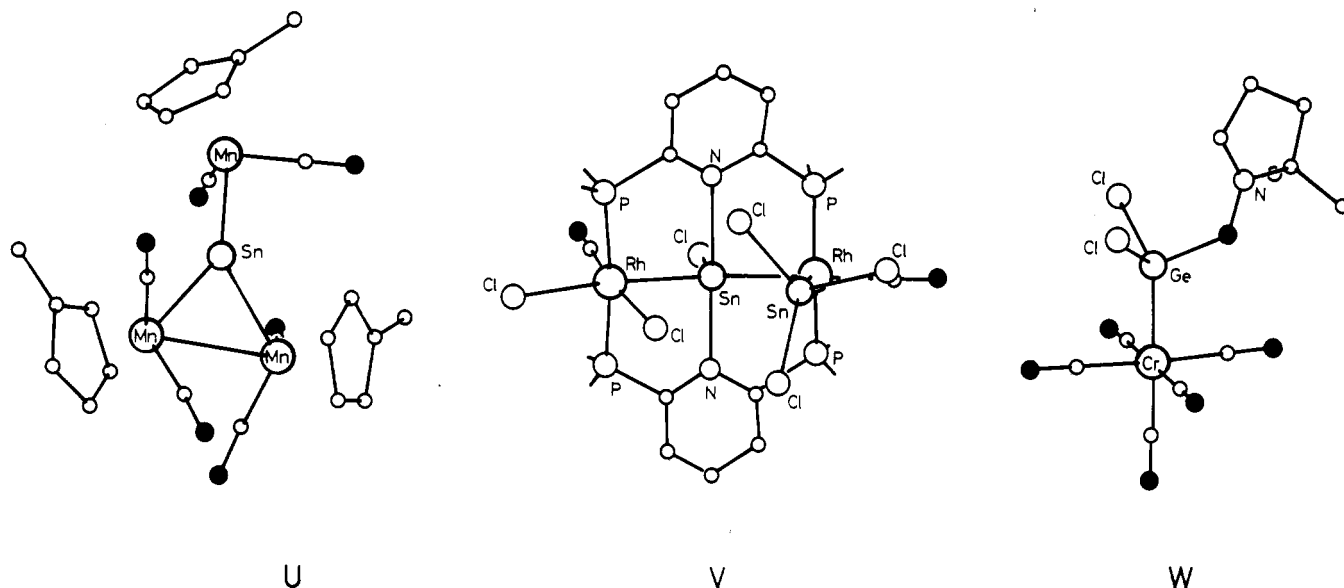
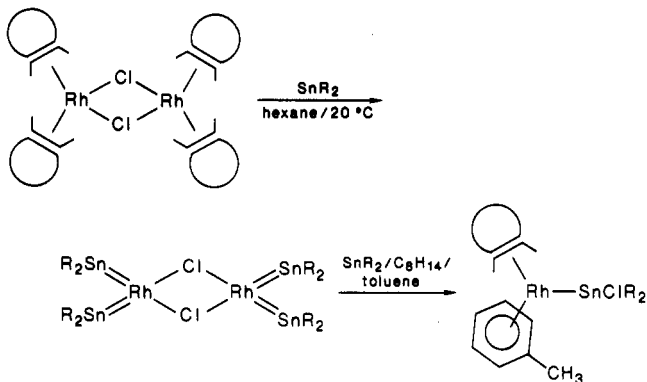


Figure 6. Structures of the complexes: $(C_5H_4Me)(CO)_2Mn=Sn[Mn(CO)_2(C_5H_4Me)]_2$ (U), 107; $Rh_2Sn_2Cl_6(CO)_2[C_5H_5N(PPh_2)_2]$ (V), 108; $(CO)_5Cr=GeCl_2\leftarrow ON=CHCH_2CH_2C(CH_3)_2$ (W), 111. The phenyl groups of V are omitted for clarity.

SCHEME 20^a

^a R = N(SiMe₃)₂. = η-C₈H₁₄.

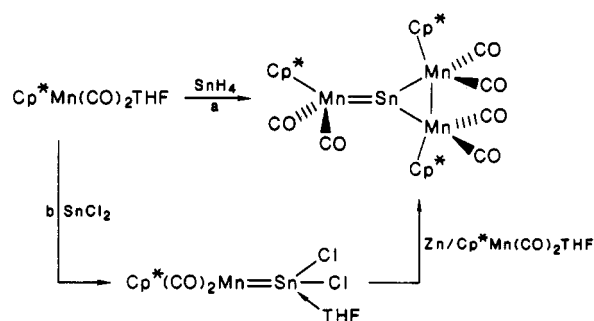
chemical reactivity of the title compounds as well as in the area of spectroscopy, to get more insight into the nature of the interesting M=M' double bond.

IX. Addendum

Since this review was completed, several significant new papers have appeared dealing with the syntheses and reactions of additional type I and type II compounds mainly from the research groups of M. F. Lappert, W. A. Herrmann, J. Satgé, and A. Tzschach. They are briefly noted here and the most important features will be discussed.

(1) The reaction of $[Rh(\eta-C_8H_{14})_2(\mu-Cl)]_2$ with the stannylene $Sn[N(SiMe_3)_2]_2$ results in the replacement of all weakly bonded cyclooctene molecules as depicted in Scheme 20 (see Section IIIB). With cyclooctene in toluene solution, $Sn[N(SiMe_3)_2]_2$ insertion into the Rh-Cl bond occurs and the 18-electron species $Rh(\eta-C_8H_{14})(\eta^6-C_7H_9)SnCl[N(SiMe_3)_2]_2$ is formed.¹⁰⁶

(2) New results have also been obtained in the chemistry of naked tin atoms coordinated at transition metals. Thus, the first complex having an SnMn₃ skeleton is described as shown in Scheme 21. This complex is either available by the hydride method via

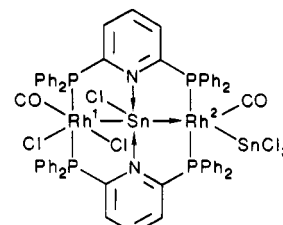
SCHEME 21^a

^a Cp* = C₅H₄Me.

pathway a or in two steps following pathway b with the new tin ylide complex $Cp^*(CO)_2Mn=SnCl_2\leftarrow THF$ as an isolable intermediate. Zinc dust dehalogenation in the presence of further $Cp^*(CO)_2MnTHF$ results in an overall yield of the complex of about 60%. A structure determination (structure U, Figure 6) confirms that the tin atom is trigonal planar, coordinated like that in $(CO)_5W=Sn[W_2(CO)_{10}]$.

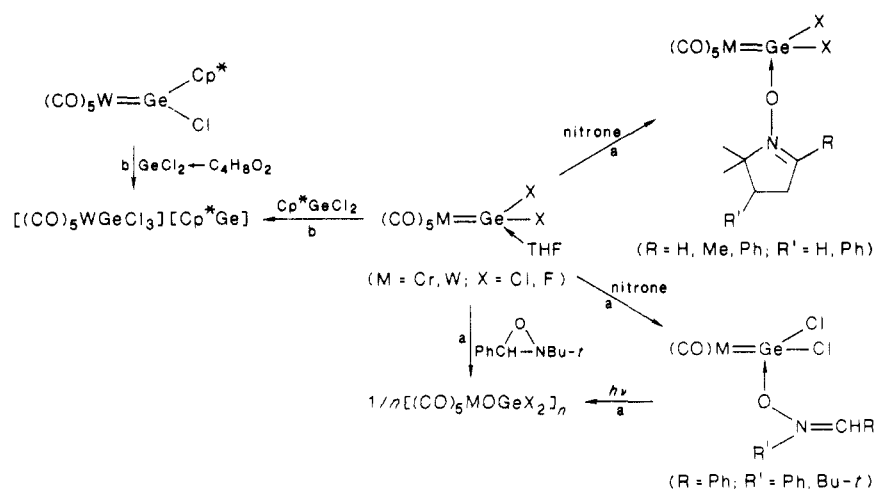
The complex $Cp^*(CO)_2Mn(\mu-Sn)Mn(CO)_2Cp^*$ with a linear coordinated tin atom probably acts as an intermediate during the reduction procedure.¹⁰⁷ The ylide complex $Cp^*(CO)_2Mn=SnCl_2\leftarrow THF$ described in this paper is probably identical with compound 166 in Table 6 formulated without a coordinating THF molecule.⁴⁵

(3) The unusual complex XVII produced by the reaction of $SnCl_2$ with $Rh_2(CO)_2Cl_2[\mu-(Ph_2P)_2py]_2$ can also



XVII

be regarded as a type II' complex similar to those described in Sections IIC and IVC. For electron counting,

SCHEME 22^a

^aCp* = C₅Me₅. Reference key: (a) 111; (b) 112.

Rh(1) is a six-coordinate, 18-electron Rh(III) center and the central tin atom acts as a two-electron donor toward the five-coordinate Rh(2) atom, consistent with a Rh(I) formulation.

According to the structure determination both Rh-Sn distances are almost identical and consistent with single bonds. The environment at the central tin atom is best described as square pyramidal with Cl at the apex.¹⁰⁸

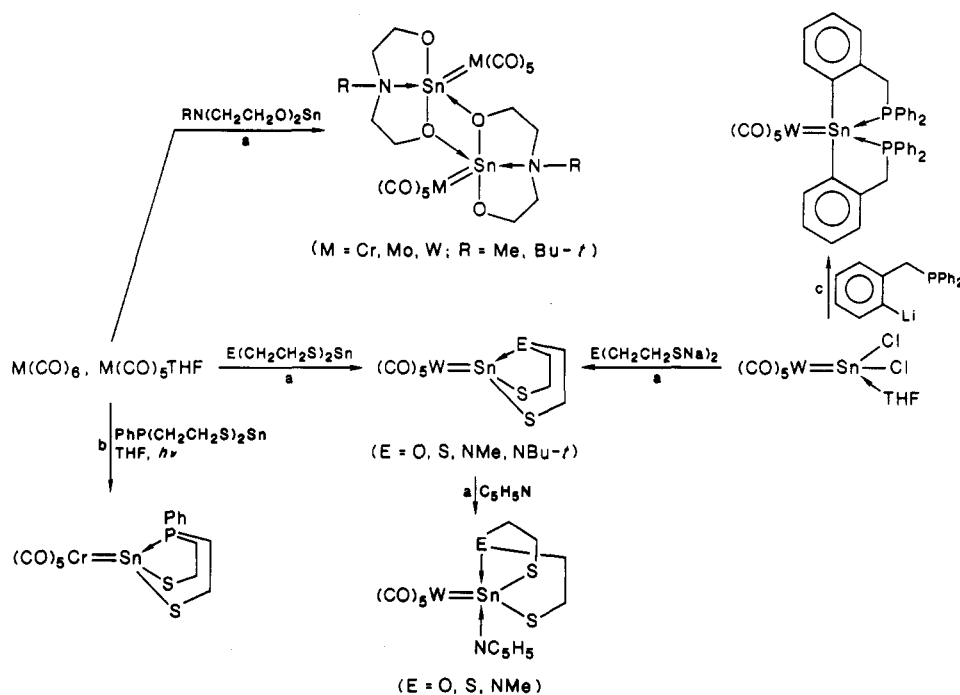
(4) New results have also been reported in the field of tin and germanium metalloporphyrins. Thus, (tptp)M'Fe(CO)₄ (M' = Ge, Sn; tptp = *meso*-tetra-*p*-tolylporphyrin) can reversibly be reduced in two single-electron-transfer steps occurring in a range of potentials between -1.0 and -1.45 V. It is proposed that the site of reduction is at the porphyrin π ring system.¹⁰⁹ A new type II' complex, (CO)₄Fe=Sn(Pc), has been obtained by the reduction of PcSnCl₂ (Pc = phthalocyaninato dianion) with Na₂Fe(CO)₄ in THF.¹¹⁰ The ⁵⁷Fe Mössbauer data (δ -0.10 mm s⁻¹; Δ 2.26 mm s⁻¹) are closely related to those of (CO)₄Fe=Sn(oep) (Table 12). The ¹¹⁹Sn data (δ 1.32 mm s⁻¹; Δ 1.37 mm s⁻¹) are marked by a decrease in the δ value relative to the free ligand while the Δ value is almost unaffected (see Table 11).

(5) New stable type II germanium ylide complexes have been prepared by exchange of THF in (CO)₅M=GeX₂←THF by various nitrones according to method C in Chapter III (Scheme 22). However, reactions with the isomeric oxaziridines produce only unstable adducts that rapidly decompose to the polymeric 1/*n*-[X₂GeOM(CO)₅]_{*n*} and the corresponding imines. The structure of (CO)₅Cr=GeCl₂←ON=CHCH₂CH₂C(CH₃)₂ (structure W, Figure 6) exhibits a M=M' distance of 239.1 pm that is only slightly longer than that of a type I complex with the same (CO)₅Cr=Ge core [e.g., (CO)₅Cr=Ge(SC₉H₁₁)₂ with 236.7 pm; see Table 1]. The Ge-O distance, M'←B, is with 189.3 pm comparable with that in the Ni complex L (Table 1) and somewhat longer than a normal covalent Ge-O bond. For the first time, the ylide ligand F₂Ge←THF appears in the starting material and the preparation follows the method B outlined in Chapter III.¹¹¹ A further replacement reaction of the THF molecule is described by Jutzi et al. Thus, the ylide complex (CO)₅W=GeCl₂←THF reacts with Cp*GeCl (Cp* = C₅Me₅) with

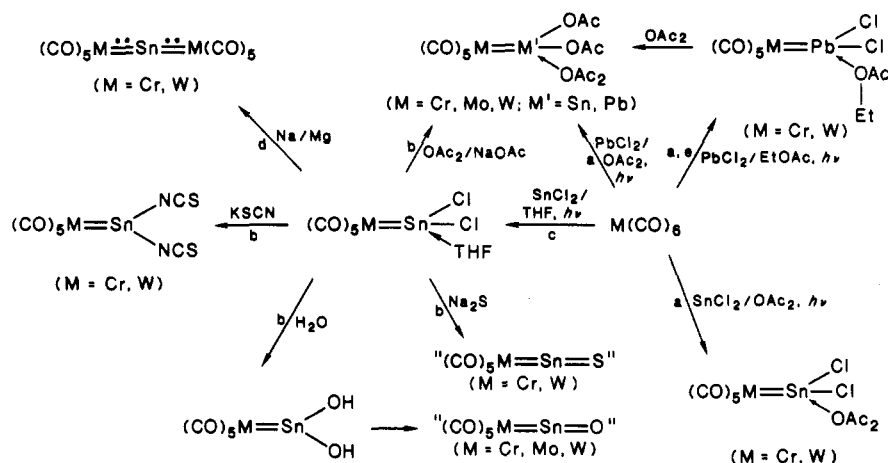
abstraction of a Cl⁻ ion to give the ionic compound [(CO)₅WGeCl₃][Cp*Ge]. This compound, containing the pyramidally arranged cation [Cp*Ge]⁺, forms also by the action of the ylide GeCl₂←dioxane on the previously described complex (CO)₅W=GeCp*Cl (17, Table 5).¹¹²

(6) A broad chemistry has also developed concerning the "tail-stabilized" ylide ligands E(CH₂CH₂X)₂Sn (E = O, S, NR, PR; X = O, S) and was presented recently by the research group of A. Tzschach. The first sample in this series was described earlier (151, Table 6) and was confirmed by an X-ray structure determination (structure N, Figure 3). As outlined in Scheme 23, monomeric type II complexes are only formed if X = S, whereas in the case of X = O new dimeric species are obtained in which the tin atoms attain the coordination number 5 (type II' species).^{113,114} The ¹¹⁹Sn NMR spectra of all these compounds exhibit dramatic low-field shifts with respect to the uncomplexed ligands, more so with the (CO)₅Cr fragment than with the (CO)₅W fragment. A similar trend was found with other tin ylide ligands as shown in Table 13. The action of pyridine on the monomeric compounds, (CO)₅W=Sn(SCH₂CH₂)₂E, gives stable 1:1 adducts of the type II'.^{113,114} An interesting ligand-exchange reaction at the coordinated tin atom resulting in a further type II' complex, (CO)₅W=Sn(C₆H₄CH₂PPh₂-*o*)₂, was described by the same group.¹¹⁵ The monomeric compound forms in 60% yield according to pathway c in Scheme 23; from ¹³C, ¹¹⁹Sn, ³¹P NMR, and ¹¹⁹Sn Mössbauer studies a structure with a trigonal-bipyramidal tin atom was deduced in which the phosphorus atoms occupy equatorial positions.

(7) A series of new tin and lead ylide complexes of type II has been synthesized by a group of Russian workers. Unfortunately all contributions from this group have appeared in journals that are not usually available for the majority of chemists involved in this field of chemistry. The photochemically induced replacement of a CO group by the M'Cl₂ moiety according to method B (chapter III) was carried out in acetic anhydride (OAc₂) or ethyl acetate instead of THF as the solvent. With SnCl₂, the OAc₂ only acts as a coordinating base similar to THF, whereas in the lead derivatives the chloro atoms were concomitantly re-

SCHEME 23^a

^a Reference key: (a) 113; (b) 114; (c) 115.

SCHEME 24^a

^a Reference key: (a) 116; (b) 119, 120; (c) 122; (d) 118; (e) 117.

placed by the OAc group, resulting in the new $(\text{CO})_5\text{M}=\text{Pb}(\text{OAc})_2\leftarrow\text{OAc}_2$ complexes (M = Cr, W). The different reaction modes were explained by an enhanced reactivity of the $\text{M}'\text{Cl}_2$ moiety in the coordinated state toward nucleophilic agents in the order $\text{PbCl}_2 > \text{SnCl}_2 > \text{GeCl}_2$; the reverse order for the cleavage of the $\text{M}'\text{-Cl}$ is found in the noncoordinated state. It was also demonstrated that the $(\text{CO})_5\text{M}=\text{M}'\text{XY}\leftarrow\text{B}$ derivatives in Scheme 24 are unstable toward the action of potential donor systems. On heating the compounds in acetone disproportionation occurs with formation of the hexacarbonyls and with triphenylphosphine the ylide ligands are replaced to give the $(\text{CO})_5\text{MPPh}_3$ compounds.^{116,117}

Earlier reports by the same group were also made dealing with some nucleophilic substitution reactions starting from the $(\text{CO})_5\text{M}=\text{SnCl}_2\leftarrow\text{THF}$ complexes. Thus, reduction with a suspension of sodium or magnesium in THF generates the yellow compounds $(\text{CO})_5\text{M}=\text{Sn}=\text{M}(\text{CO})_5$ (M = Cr, W; yields about

45%),¹¹⁸ in which a linear array of metal atoms was deduced by IR spectroscopy.¹¹⁹ The synthesis of the rather striking compounds containing the CO analogue $\text{Sn}=\text{O}$ ("stannacarbonyl") and $\text{Sn}=\text{S}$ ("stannathio-carbonyl") ligands have been described, too. The tin monosulfide complexes were obtained by treating a THF solution of the ylide complexes with NaS_2 (1 h). For the preparation of the tin monoxide species an ethereal solution was treated with H_2O to give first the type I complexes $(\text{CO})_5\text{M}=\text{M}'(\text{OH})_2$. Dehydration over CaCl_2 in a desiccator (24 h) and exposure to a vacuum (5 h) at 50–60 °C followed. Nothing was reported about the nature of the compounds but it was noticed that after a certain storage time the solubility was lost, probably due to oligomerization processes.^{119,120} A similar dihydroxystannylene complex, $\text{Cp}(\text{CO})_2\text{Mn}=\text{Sn}(\text{OH})_2$, was described after hydrolysis of $\text{Cp}(\text{CO})_2\text{Mn}=\text{SnCl}_2\leftarrow\text{THF}$. Upon storage, condensation of the hydroxyl groups to form polymeric units occurs.¹²¹ With KSCN in acetone solution (1 h) conver-

sion of the ylide complexes into the type I complexes $(CO)_5M=M'(NCS)_2$ was reported. In the case of the tungsten derivative a mixture with the isomeric species $(CO)_5W=Sn(SCN)_2$ was obtained.^{119,120} The structures of the new compounds mentioned in Scheme 24 were only confirmed by IR spectroscopy and analysis. A review including some of the tin complexes and other divalent tin species is given in ref 123.

X. Acknowledgment

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