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Tin-Bridged Metal–Metal Bonds from the Photolysis of Bis(metal carbonyl)- and Chloro(metal carbonyl)dimethylstannanes

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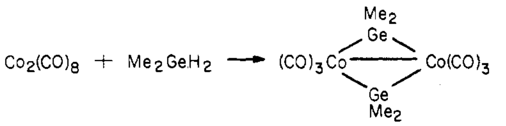
Photolysis of $Me_2Sn(m_2)$ (m = metal carbonyl) proceeds with loss of one CO and ring closure to give M–M bonds bridged by CO and Me_2Sn. Upon similar treatment, $Me_2Sn(Cl)m$ gives complexes with M–M bonds bridged by two Me_2Sn groups. The lack of significant structural or NMR effects in the Me_2Sn group upon the drastic reduction of the m–Sn–m angle on going from the open chain to the bridged structure is discussed in terms of bent metal–tin bonds in the bridged complexes. The new Sn-bridged complexes prepared in this work are $(\mu\text{-CO})(\mu\text{-}Me_2Sn)Fe_2(CO)_2Cp_2$, $(\mu\text{-CO})(\mu\text{-}Me_2Sn)Co_2(CO)_6$, $(\mu\text{-}Me_2Sn)_2Mn_2(CO)_8$, and $(\mu\text{-}Me_2Sn)_2Co_2(CO)_6$.

Introduction

Complexes containing bonds between transition metals and the heavier main group 4 elements have attracted considerable attention.[1] Complexes containing the R_2E (R = alkyl, etc., E = Si, Ge, Sn, Pb) group are especially interesting as this group is isoelectronic with the carbene R_2C. Transition metal complexes with both bridging and terminal carbenes are known,[2,3] although the terminal mode of bonding is by far the most common. Conversely, terminal bonding for the heavier congeners is rare;[4,5] and the preferred mode of complexation has the R_2E group bridging two metal centers. In the latter case, metal–metal bonds may or may not be present.[1]

Several methods have been used to prepare complexes with Si-, Ge-, or Sn-bridged metal–metal bonds, for example, eq 1–3.[6-8]



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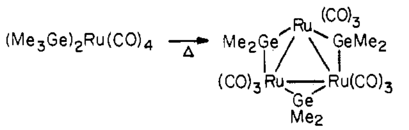

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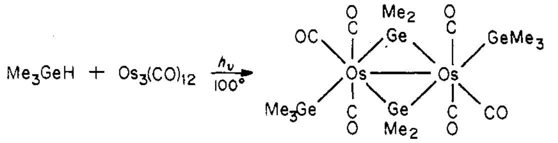

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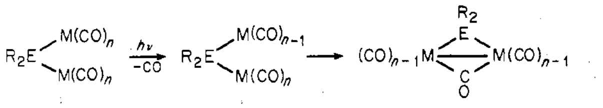
Job and Curtis[9] and Cleland et al.[10] have reported the photolytic conversion of R_2E(metal carbonyl)$_2$ (**1**) to complexes containing R_2E-bridged metal–metal bonds via eq 4.



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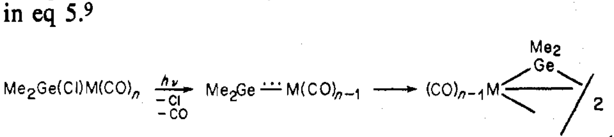
1 **2** **3**

The coordinatively unsaturated intermediate, **2**, regains the 18-electron count around each metal upon formation of structure **3**.

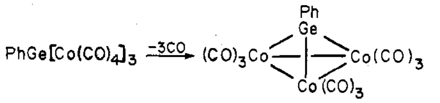
Similarly it was found that compounds **4** yielded dinuclear complexes with two bridging Me_2Ge groups as rationalized in eq 5.[9]



4 **5**

(5)

Tin has been reported to bridge metal–metal bonds more reluctantly than Ge, possibly due to the increased size of the tin atom. Thus, Ball et al.[11] observed the reaction shown in eq 6, but Patmore and Graham[12] reported that the corresponding tin derivative $BuSn[Co(CO)_4]_3$ does not lose carbon monoxide.



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In view of the differences exhibited by germanium and tin in their propensity to bridge metal–metal bonds, we have extended our earlier investigations[9] to include tin in order to test the generality of the photolytic reactions typified by eq 4 and 5. In addition, the behavior of the $^{117-119}Sn\text{–}CH_3$ nuclear hyperfine coupling constants on bridge formation was of interest.

Experimental Section

All operations involving air-sensitive materials were performed under a N_2 atmosphere using standard Schlenk-ware techniques. Room-temperature NMR spectra were recorded on Varian T-60 or T-60A instruments.

Mass spectra were obtained by direct insert on an AEI MS902 instrument operating with an ionization energy of 70 eV. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Metal carbonyl anions were prepared in THF solution by sodium amalgam reduction of the corresponding dimers. All chromatographic separations were carried out on a 2.5 × 100 cm column packed with Florisil (100–200 mesh) under N_2 atmosphere. Photolyses were conducted with a Hanovia, 500-W, medium-pressure Hg lamp in a fused-silica reactor.

Photolysis of $Me_2Sn[Mo(CO)_3Cp]_2$. A 3.0-g (4.7-mmol) sample of $Me_2Sn[Mo(CO)_3Cp]_2$[13] in 500 ml of benzene was photolyzed for 80 min. Solvent was pumped off from the resulting red solution, and a portion of the oily, red-black residue was chromatographed. Extensive tailing and decomposition on the column were noted, and only unreacted starting material and $Cp_2Mo_2(CO)_6$ could be eluted in a pure state. Addition of petroleum ether (bp 90–100°) to a methylene chloride solution of the remaining portion of the crude photolysis mixture caused $Cp_2Mo_2(CO)_6$ to precipitate. From the mother liquor, only unreacted starting material could be crystallized.

Photolysis of $Me_2SnCl[Mo(CO)_3Cp]$. (Dimethylchlorostannyl)cyclopentadienylmolybdenum tricarbonyl was prepared by a modification of the method of Patil and Graham.[13] The $CpMo(CO)_3^-$ anion solution was added dropwise *to* a solution of Me_2SnCl_2 in THF (reverse addition of reagents). This solution can be worked up immediately to give the product. Reverse addition eliminates the overnight equilibration step and increases the yield from 50% to 74%.

A 0.6-g sample of $Me_2SnCl[Mo(CO)_3Cp]$ in 100 ml of cyclohexane was photolyzed for 38 min to produce a brown precipitate and a pale brown solution. Only $Cp_2Mo_2(CO)_6$ could be isolated from either the solid or solution.

Photolysis of $Me_2Sn[Fe(CO)_2Cp]_2$. A 1.25-g amount of bis(cyclopentadienyldicarbonylferrio)dimethylstannane[14] in 100 ml of cyclohexane was subjected to photolysis for 52 min, giving a dark, red-purple solution. After filtration and concentration under vacuum, the filtrate was chromatographed using CH_2Cl_2 as eluent. Yellow,

Table I. Photolysis Products of Dimethylstannylenemetal Carbonyls

	J(Sn–C–H), Hz				*J*(Sn–C–H), Hz		
Reactant	^{117}Sn	^{119}Sn	τ(Me)	Product	^{117}Sn	^{119}Sn	τ(Me)
$Me_2Sn[Fe(CO)_2Cp]_2$	35.8	37.3	9.36	$(\mu\text{-}CO)(\mu\text{-}Me_2Sn)Fe_2(CO)_2Cp_2$	40.8[a] 36.0[b] 37.6[c]	42.4[a] 38.1[b] 40.4[c]	8.92[a] 9.02[b] 8.98[c]
$Me_2Sn[Mn(CO)_5]_2$	34.8	36.8	9.54	No reaction			
$Me_2Sn(Cl)Mn(CO)_5$	43.9	45.8	9.17	$(\mu\text{-}Me_2Sn)_2Mn_2(CO)_8$	41.2	43.6	9.02
$Me_2Sn[Co(CO)_4]_2$	43.2	45.7	8.92	$(\mu\text{-}Me_2Sn)_2Co_2(CO)_6$[d] $(\mu\text{-}CO)(\mu\text{-}Me_2Sn)Co_2(CO)_6$[e]	41.6	43.6	9.31
$Me_2Sn[Mo(CO)_3Cp]_2$	35.8	37.4	9.02	$Cp_2Mo_2(CO)_6$			
$Me_2Sn(Cl)Mo(CO)_3Cp$	46.4	47.7	9.08	$Cp_2Mo_2(CO)_6$			

[a] Low-field resonance of cis isomer. [b] High-field resonance of cis isomer. [c] Resonance of trans isomer. [d] Obtained at 25°. [e] Obtained at −50°.

red, and purple bands are eluted in order. The yellow and red bands were shown to be due to unreacted $Me_2Sn[Fe(CO)_2Cp]_2$ and $Cp_2Fe_2(CO)_4$, respectively. The purple fraction yielded dark purple crystals of μ-carbonyl-μ-(dimethylstannylene)-bis(cyclopentadienylcarbonyliron)(*Fe–Fe*), $(\mu\text{-}CO)(\mu\text{-}Me_2Sn)[Fe(CO)Cp]_2$, mp 178° dec. A parent ion at *m/e* 476 and peaks due to consecutive loss of three carbonyls were observed in the mass spectrum. Anal. Calcd for $C_{15}H_{16}Fe_2O_3Sn$: C, 37.88; H, 3.37. Found: C, 37.77; H, 3.44.

Photolysis of $Me_2Sn[Mn(CO)_5]_2$. A 1.0-g (1.86-mmol) amount of bis(pentacarbonylmanganio)dimethylstannane[15] in 100 ml of cyclohexane was irradiated for 18 hr, after which time the initially yellow solution had turned red. Only unreacted $Me_2Sn[Mn(CO)_5]_2$ and traces of $Mn_2(CO)_{10}$ could be isolated from this solution.

Photolysis of $Me_2SnCl[Mn(CO)_5]$. Reverse addition of $Mn(CO)_5^-$ to Me_2SnCl_2 decreased the reaction time to 30 min and increased the yield to 80%, compared to 50–60% in a previous report.[16] A 1.1-g (1.74-mmol) sample in 100 ml of cyclohexane was photolyzed for 65 min, giving a red solution. Removal of solvent, followed by chromatography of the residue, gave a yellow-orange fraction with petroleum ether (bp 30–60°) as eluent. Recrystallization of this fraction from cyclohexane gave pure bis-μ-(dimethylstannylene)-bis(tetracarbonylmanganese)(*Mn–Mn*), which shrinks at 148°, sublimes near 160°, and melts with decomposition near 200°. The parent ion was observed at *m/e* 632, and the fragmentation pattern is consistent with the proposed structure. Anal. Calcd for $C_{12}H_{12}Mn_2O_8Sn_2$: C, 22.83; H, 1.90. Found: C, 23.08; H, 2.12.

Photolysis of $Me_2Sn[Co(CO)_4]_2$. Bis(tetracarbonylcobaltio)dimethylstannane was prepared by adding Me_2SnCl_2 (0.68 g, 3.0 mmol) to 6.0 mmol of $NaCo(CO)_4$ in THF at room temperature. After stirring of the mixture for 15 min, the THF was pumped off and the residue extracted with CH_2Cl_2. Addition of petroleum ether (bp 30–60°) to the CH_2Cl_2 solution, followed by cooling to −78°, gave yellow needles of the product in 53% yield. The product is identical with that prepared by Patmore and Graham[17] from methanolic $Co(CO)_4^-$ and by Hieber and Breu from $Hg[Co(CO)_4]_2$.[18]

A 0.6-g (1.22-mmol) sample of $Me_2Sn[Co(CO)_4]_2$ in 100 ml of petroleum ether (bp 30–60°) gave a dark yellow-orange solution after 100 min of photolysis. Concentration of the solution under vacuum and cooling to −78°° afforded a yellow powder which was recrystallized from petroleum ether (bp 30–60°) at −78° to give pure $(\mu\text{-}Me_2Sn)_2[Co(CO)_3]_2$, mp 133–134°; parent ion at *m/e* 586. Anal. Calcd for $C_{10}H_{12}Co_2O_6Sn_2$: C, 20.54; H, 2.06. Found: C, 20.45; H, 2.13.

The filtrate from the initial photolysis showed bridging carbonyl bands in the ir spectrum at 1861, 1858, and 1835 cm^{-1}. The first two are assigned to $Co_4(CO)_{12}$ and $Co_2(CO)_8$ by comparison with authentic samples and by isolating these compounds from solution by chromatography. The 1835-cm^{-1} band is due to $(\mu\text{-}CO)(\mu\text{-}Me_2Sn)[Co(CO)_3]_2$, as shown below.

A repeat photolysis of $Me_2Sn[Co(CO)_4]$ in petroleum ether (bp 30–60°) at −50° for 50 min gave a red solution which deposited $Co_2(CO)_8$ on cooling to −78°. Further concentration of the solution at −30° (vacuum) and cooling to −78° gave yellow-brown crystals mixed with a yellow-red oil. Chromatography with petroleum ether (30–60°) eluent of the combined solid and oil afforded $(\mu\text{-}Me_2Sn)_2[Co(CO)_3]_2$. Methylene chloride eluent washed down a yellow fraction from which μ-carbonyl-μ-(dimethylstannylene)-bis(tricarbonylcobalt)(*Co–Co*), $(\mu\text{-}CO)(\mu\text{-}Me_2Sn)[Co(CO)_3]_2$, could be crystallized at −78°. This compound melts below 0° and is exceedingly unstable. A parent ion was observed at *m/e* 464, along with peaks due to successive loss of seven carbonyls. Due to its instability, the sample could not be freed of traces of $(\mu\text{-}Me_2Sn)_2[Co(CO)_3]_2$ and hence could not be satisfactorily analyzed.

Reaction of $NaFe(CO)_2Cp$ and Me_2SnBr_2. A THF solution of $NaFe(CO)_2Cp$ (2.3 mmol) was slowly added to 0.75 g (2.4 mmol) of Me_2SnBr_2 in THF at −65°. The mixture was allowed to stand at −78° overnight, and the THF was then pumped off at ca. −30°. The residue was dissolved in cold petroleum ether (bp 30–60°), and the solution was then filtered and cooled to −78° to give red crystals. These were shown to be $Me(Br)Sn[Fe(CO)_2Cp]_2$, mp 127–129°, ν_{CO} 2000 (m), 1988 (s), 1952 (s), 1940 (sh) cm^{-1}. The NMR spectrum in C_6D_6 showed peaks at τ 5.77 (Cp) and 8.62 (Me) in a ratio of 10:3. The parent ion at *m/e* 568 was observed. Anal. Calcd for $C_{15}H_{13}BrFe_2O_4Sn$: C, 31.69; H, 2.29. Found: C, 31.72; H, 2.37.

The mother liquor from the above crystallization deposited a mixture of red and yellow crystals upon concentration and cooling to −78°. An NMR spectrum of a solution of this mixture showed resonances at τ 5.96 (Cp), 9.12 (Me), and 9.73 (Me) in addition to those due to $MeBrSn[Fe(CO)_2Cp]_2$. The τ 5.96 and 9.12 peaks had an area ratio of 5:6 as required for $Me_2Sn(Br)Fe(CO)_2Cp$, and the resonance of added Me_3SnBr was superimposable on the τ 9.73 peak. Continued attempts to crystallize these substances fractionally led to a continual decrease in the proportion of $Me_2Sn(Br)Fe(CO)_2Cp$ and corresponding increase in the amount of $Me(Br)Sn[Fe(CO)_2Cp]_2$.

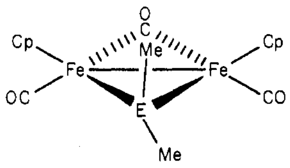
Results and Discussion

Table I summarizes the results obtained upon photolysis of the (metal carbonyl)-substituted stannanes. For the most part, the reactions parallel those of the corresponding germanes[9] (eq 4 and 5). Several differences are noted, however. Photolysis of $Me_2Sn[Mn(CO)_5]_2$ for 18 hr gave only traces of $Mn_2(CO)_{10}$ and most of the reactant was recovered. In contrast, $Me_2Ge[Mn(CO)_5]_2$ was completely converted to $(Me_2Ge)Mn_2(CO)_9$ after 1 hr of photolysis.

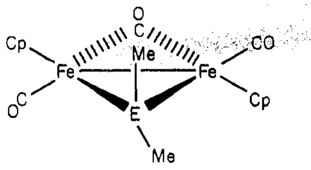
Both $Me_2Ge[Mo(CO)_3Cp]_2$ and $Me_2Sn[Mo(CO)_3Cp]_2$ gave only $Cp_2Mo_2(CO)_6$ upon photolysis in benzene solution. A low yield of $(Me_2Ge)_2Mo_2(CO)_4Cp_2$ was obtained from $Me_2Ge(Cl)Mo(CO)_3Cp$, but $Me_2Sn(Cl)Mo(CO)_3Cp$ gave only $Cp_2Mo_2(CO)_6$.

In the photolysis of $Me_2Ge[Co(CO)_4]_2$, only $(\mu\text{-}CO)(\mu\text{-}Me_2Ge)[Co(CO)_3]_2$ was produced. However, photolysis of $Me_2Sn[Co(CO)_4]_2$ gave both $(\mu\text{-}Me_2Sn)_2[Co(CO)_3]_2$ and $(\mu\text{-}CO)(\mu\text{-}Me_2Sn)[Co(CO)_3]_2$ at −50°. Only the former could be isolated when the photolysis was conducted at room temperature, but it is probable that some of the latter also forms but decomposes at the higher temperature as evidenced by the bridging carbonyl band at 1835 cm^{-1} in the photolysis mixture.

Both the tin and germanium[9] complexes $(\mu\text{-}CO)(\mu\text{-}Me_2E)[Fe(CO)Cp]_2$ (E = Ge, Sn) exist in solution at room temperature as an equilibrium mixture of cis and trans isomers, **6a** and **6b**. Adams et al.[19] have investigated the rate of cis $\rightleftharpoons$ trans interconversion of the germanium compound by variable-temperature NMR techniques. They postulated that the methyl groups exchange sites by a concerted bridge-opening mechanism with an activation energy of about 21 kcal/mol. We have been unable to obtain corresponding rate



6a



6b

data for the tin derivative due to the onset of decomposition near 120° (the methyl resonances of the germanium compound coalesce near 150°).

The compound (μ-Me$_2$Sn)$_2$[Co(CO)$_3$]$_2$ is also fluxional. Adams et al.[20] have reported an activation energy for methyl site exchange of 12.5 ± 0.5 kcal/mol.

Upon going from the open-chain reactants, m–Sn–m, to the cyclic or bridged products, $\overline{\text{m–Sn–m}}$, the m–Sn–m angle decreases from 106–130 to about 70°.[21,22] One might expect a large change in the ^{117,119}Sn–C–H coupling constants to accompany this large change in angle. However, as Table I shows, the coupling constant is rather insensitive to the m–Sn–m angle, and furthermore no general trends are apparent. As structural data show,[21,22] the Me–Sn–Me angle in dimethylstannylenemetal complexes varies between 104 and 109° and no trend with m–Sn–m angle is apparent. Thus, the *apparent* strain from the highly acute m–Sn–m angles found in tin-bridged metal–metal bonds is not manifested in the bonding within the Me$_2$Sn group itself. This in turn suggests that the major electron density in the tin–metal bonds in the bridged species does not lie along the tin–metal axis. Triplett and Curtis[23] have suggested a bonding model based on the MO calculations of Teo et al.[24] This model (see Figure 2 in ref 23) considers the R$_2$Sn (or any group with a filled σ-donor orbital and empty π-acceptor orbital, e.g., CO, R$_2$Si, R$_2$P$^+$, etc.) as a bridging carbenoid ligand. The empty p orbital (or π^* for CO) forms bonding combinations of symmetry 1b$_{3u}$ and b$_{2g}$ which places electron density outside the internuclear axis.

We have been unable to prepare pure di*methyl*germylene or -stannylene complexes of the type, Me$_2$E(m)(m'), where m and m' are different metal carbonyl moieties. Apparently, facile redistribution reactions occur which lead to scrambling of the methyl groups as well as the metal groups. For example, addition of 1 molar equiv of CpFe(CO)$_2^-$ to Me$_2$SnBr$_2$ in THF at −65°, followed by work-up at −30°, gave Me(Br)Sn[Fe(CO)$_2$Cp]$_2$. The spectroscopic identification of Me$_2$Sn(Br)Fe(CO)$_2$Cp and Me$_3$SnBr in the reaction mixture suggests the redistribution reaction eq 7 occurs rapidly even at low

$$2\text{Me}_2\text{Sn(Br)Fe(CO)}_2\text{Cp} \rightarrow \text{Me(Br)Sn[Fe(CO)}_2\text{Cp]}_2 + \text{Me}_3\text{SnBr} \quad (7)$$

temperatures. Other workers have observed similar redistribution reactions of methyl groups when tin is bonded to a transition element.[21a,25] In contrast, di*phenyl*stannylene complexes, Ph$_2$Sn(m)(m'), are readily prepared.[26]

Registry No. Me$_2$Sn[Mo(CO)$_3$Cp]$_2$, 12194-19-3; Me$_2$SnCl[Mo(CO)$_3$Cp], 12083-78-2; Me$_2$Sn[Fe(CO)$_2$Cp]$_2$, 12091-98-4; Me$_2$SnCl[Mn(CO)$_5$], 17501-04-1; Me$_2$Sn[Co(CO)$_4$]$_2$, 15708-78-8; NaFe(CO)$_2$Cp, 12152-20-4; Me$_2$SnBr$_2$, 2767-47-7; Cp$_2$Mo$_2$(CO)$_6$, 12091-64-4; (μ-CO)(μ-Me$_2$Sn)[Fe(CO)Cp]$_2$, 57428-46-3; (μ-Me$_2$Sn)$_2$Mn$_2$(CO)$_8$, 57428-45-2; (μ-Me$_2$Sn)$_2$[Co(CO)$_3$]$_2$, 54678-21-6; (μ-CO)(μ-Me$_2$Sn)[Co(CO)$_3$]$_2$, 57396-27-7; Me(Br)Sn[Fe(CO)$_2$Cp]$_2$, 57396-28-8; Me$_2$Sn(Br)Fe(CO)$_2$Cp, 57396-29-9.

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