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η^2-Coordination of a Sn–H Bond to a Transition Metal. Molecular Structure of (η^5-MeC_5H_4)$(CO)_2Mn(H)SnPh_3$

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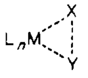
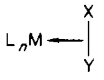
Abstract: (η^5-MeC_5H_4)$(CO)_2Mn(H)SnPh_3$ (**1**) has been prepared by photochemical reaction between $MeCpMn(CO)_3$ and $HSnPh_3$ and thermally reacts with an excess of $HSnPh_3$ to give *trans*-$MeCp(CO)_2Mn(SnPh_3)_2$ (**2**). Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 8.262 (3) Å, b = 10.536 (4) Å, c = 14.755 (6) Å, α = 94.63 (3)°, β = 99.95 (3)°, γ = 110.58 (3)° (Z = 2). The rather high NMR coupling constants $J(^{119}SnMnH)$ = 270 Hz and $J(^{117}SnMnH)$ = 252 Hz of **1** and the structural data, particularly the geometry of the $MeCp(CO)_2Mn$ fragment and the Mn–Sn (2.636 (1) Å), Mn–H (1.37 (4) Å) and Sn–H distance (2.16 (4) Å), show that the stannane is bonded to the metal by a Mn, H, Sn three-center bond. Sn–H interaction in **1** is weaker than Si–H interaction in corresponding silyl complexes, $Cp(CO)_2Mn(H)SiR_3$, which contain η^2-coordinated Si–H bonds.

The recent discovery of a greater number of complexes having "agostic" C–H bonds[1] or η^2-H_2 ligands[2] has focussed attention on three-center two-electron bonds, which seemed to be a domain of early main-group elements or metal clusters. As more and more examples are found, it becomes obvious that such bonds are probably more widespread among transition-metal compounds than commonly assumed. If a metal complex moiety (L_nM) and any two fragments X and Y share two electrons, the bonding situation can be depicted as in A (emphasizing the three-center bond) or as in B (stressing the chemical origin of most of these complexes). Since neither representation implies any information on the electron distribution in a particular complex, the use of either A or B basically depends on the point of view. Considering these complexes as "frozen intermediates" in the oxidative addition of X–Y to L_nM can also be useful; complete oxidative addition would totally cleave the X–Y bond and form both an M–X and an M–Y bond. In the vast majority of transition-metal complexes having three-center two-electron bonds, hydrogen is involved (X = H). The first examples for the participation of main-group 4 elements (E = C, Si, Ge, Sn, Pb) in this type of bonding were already discovered in the early 1970s, when W. A. G. Graham et al. isolated and characterized a number of complexes $Cp(CO)_2Mn(H)SiR_3$.[3] From the very beginning it was realized that some properties of these complexes are different to other hydrido silyl complexes. In the course of time abundant chemical and spectroscopic evidence for the presence of Mn, H, Si three-center bonds in these complexes was gathered, which is discussed elsewhere in detail.[4,5a] Systematic structural and spectroscopic data on $MeCp(CO)LMn(H)SiR_3$ and related complexes showed that the degree to which the H–Si bond is added to the metal fragment depends both on the electronic and steric properties of the metal fragment and on the SiR_3 group.[5] At this point the question arises, whether the three-center interaction is retained when silicon is replaced by its higher homologues. Although chemical behavior is in favor of an η^2-R_3GeH coordination in $Cp(CO)_2Mn(H)GeR_3$,[6] structural data are not available. While an η^2-GeH bond is not unexpected due to the similarity between silicon and germanium, the possibility of a three-center bond involving a SnR_3 group was questionable. In this paper we report the structure of $MeCp(CO)_2Mn(H)SnPh_3$ (**1**), which provides the first example of a metal, hydrogen, tin three-center bond, i.e., of an η^2-coordination of $H–SnR_3$ to a transition metal.



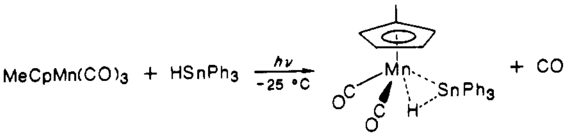
A



B

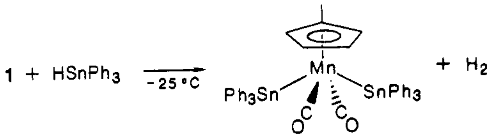
Results and Discussion

$MeCp(CO)_2Mn(H)SnPh_3$ (**1**) is prepared by photochemical reaction of $MeCpMn(CO)_3$ (MeCp = η^5-$CH_3C_5H_4$) with an equimolar amount of $HSnPh_3$ in pentane at low temperatures (eq 1). A nonpolar solvent is essential for the success of the reaction, since **1** thermally reacts with an excess of $HSnPh_3$ in diethyl ether or THF to give the bis-stannyl complex **2** (eq 2). While the reaction conditions for the formation of **1** parallel those of the corresponding SiR_3 and GeR_3 complexes, bis-silyl complexes $MeCp(CO)_2Mn(SiR_3)_2$ can only be prepared photochemically and with SiR_3 = $SiCl_3$ or $SiMeCl_2$.[7]



(1)

1



(2)

2

According to the relative intensities of the ν(CO) bands, the angle between the two CO ligands in **2** must be much larger than 90°, and, therefore, the $SnPh_3$ ligands are in a trans orientation, similar to $MeCp(CO)_2Mn(SiCl_3)_2$.[7b] Contrarily, the equal intensity of the ν(CO) bands of **1** suggest the hydride ligand being cis to SnR_3. **1** is easily deprotonated by sodium hydride in THF (at −10 °C to avoid formation of **2**). On addition of acids to a solution of $Na[MeCp(CO)_2MnSnPh_3]$,[8] only the cis isomer of **1** is reformed. In the case of analogous silyl and germyl complexes

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[8] ν(CO) in THF: 1866 (m), 1764 (m) cm^{-1}. Reactions of $[MeCp(CO)_2MnSnPh_3]^-$ with metal halides are reported in the following: Kunz, E.; Knorr, M.; Willnecker, J.; Schubert, U. *New. J. Chem.* **1988**, *12*, 467.

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Table I. Fractional Atomic Coordinates of **1**

atom	x	y	z
Mn	0.05647 (8)	0.77114 (6)	0.91576 (4)
Sn	−0.13300 (4)	0.75460 (3)	0.74914 (2)
C(1)	0.3188 (6)	0.8030 (5)	0.9855 (4)
C(2)	0.2623 (7)	0.9052 (6)	1.0251 (3)
C(3)	0.2304 (7)	0.9805 (5)	0.9557 (4)
C(4)	0.2662 (6)	0.9267 (5)	0.8749 (4)
C(5)	0.3181 (6)	0.8196 (6)	0.8944 (4)
C(6)	0.3786 (8)	0.7062 (7)	1.0353 (6)
C(7)	−0.0815 (6)	0.7156 (5)	0.9946 (3)
C(8)	−0.0040 (6)	0.5981 (5)	0.8695 (3)
O(7)	−0.1765 (5)	0.6810 (4)	1.0460 (3)
O(8)	−0.0374 (5)	0.4828 (3)	0.8434 (3)
C(10)	−0.2117 (6)	0.9272 (4)	0.7288 (3)
C(11)	−0.0904 (6)	1.0607 (5)	0.7512 (3)
C(12)	−0.1410 (8)	1.1713 (5)	0.7424 (3)
C(13)	−0.3142 (9)	1.1506 (6)	0.7122 (4)
C(14)	−0.4370 (8)	1.0208 (7)	0.6886 (4)
C(20)	0.0147 (5)	0.7444 (4)	0.6443 (3)
C(21)	0.0891 (7)	0.6463 (5)	0.6365 (3)
C(22)	0.1801 (7)	0.6378 (6)	0.5673 (4)
C(23)	0.2000 (7)	0.7282 (7)	0.5057 (4)
C(24)	0.1264 (8)	0.8271 (6)	0.5111 (4)
C(30)	−0.3702 (6)	0.5727 (4)	0.7157 (3)
C(31)	−0.4211 (6)	0.4915 (4)	0.6299 (3)
C(32)	−0.5748 (7)	0.3743 (5)	0.6079 (4)
C(33)	−0.6765 (7)	0.3362 (6)	0.6707 (5)
C(34)	−0.6287 (8)	0.4150 (7)	0.7566 (5)
C(35)	−0.4766 (7)	0.5314 (6)	0.7790 (4)
H(1)	−0.077 (5)	0.812 (4)	0.897 (3)

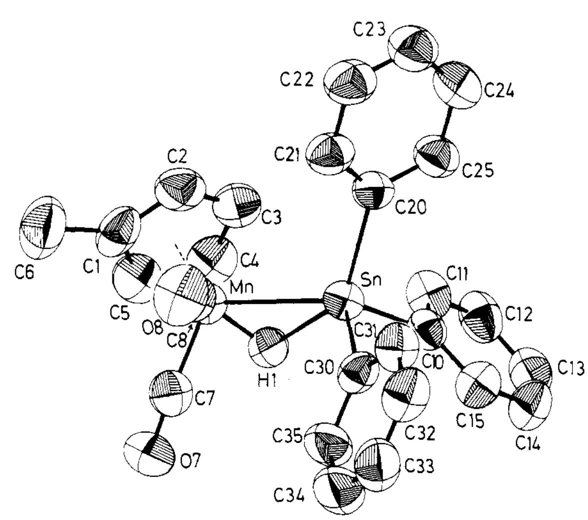

Figure 1. An ORTEP drawing of **1**. Hydrogen atoms at the phenyl rings and the MeCp ligand are omitted for clarity.

Table II. Selected Bond Distances and Bond Angles of **1**

	(a) Bond Distances (Å)		
Mn–Sn	2.636 (1)	Mn–C(7)	1.758 (5)
Mn–C(1)	2.130 (6)	Mn–C(8)	1.756 (5)
Mn–C(2)	2.120 (5)	Mn–H(1)	1.37 (4)
Mn–C(3)	2.133 (5)	Sn–H(1)	2.16 (4)
Mn–C(4)	2.138 (5)	Sn–C(10)	2.161 (4)
Mn–C(5)	2.125 (6)	Sn–C(20)	2.146 (4)
		Sn–C(30)	2.152 (4)
	(b) Bond Angles (deg)		
C(7)–Mn–C(8)	87.9 (2)	Mn–Sn–C(10)	114.9 (1)
C(7)–Mn–Sn	110.6 (2)	Mn–Sn–C(20)	110.5 (1)
C(8)–Mn–Sn	77.8 (2)	Mn–Sn–C(30)	111.7 (1)
C(7)–Mn–H	73 (2)	Mn–Sn–H(1)	31 (1)
C(8)–Mn–H	114 (2)	C(10)–Sn–H(1)	89 (1)
Sn–Mn–H	55 (2)	C(20)–Sn–H(1)	137 (1)
		C(30)–Sn–H(1)	107 (1)

the exclusive formation of the cis isomer on reprotonation of the corresponding anionic complexes was regarded a chemical evidence for Mn, H, Si or Mn, H, Ge interaction.[6,9] Since the trans isomer is sterically more favorable, an electronic factor (formation of the three-center bond) must be responsible for the formation of the cis isomer. Protonation of [Cp(CO)$_2$ReSiPh$_3$]$^-$, in which Si–H interaction is questionable,[10,11] gives both the cis and trans isomer.[10] NMR coupling constants are a valuable analytical tool in the chemistry of metal complexes containing η^2-E–H bonds, because their value is intermediate between ^1J(EH) and ^2J(EMH).[1,2] We have previously shown that the magnitude of J(SiH) can be correlated with the degree of Si–H interaction within a series of complexes MeCp(CO)LMn(H)SiR$_3$ having different ligands L and substituents R.[5a] In alkyltin hydrides ^1J(SnH) is typically 1500–1800 Hz, while ^2J(SnCH) is 50–70 Hz.[12] In *cis*-(CO)$_4$Os(H)SnCl$_3$, in which there should be no interaction between the hydride and SnCl$_3$ ligand J(^{119}SnOsH) = 136 Hz and J(^{117}SnOsH) = 129.5 Hz were observed.[13] The distinctly higher values of J(^{119}SnMnH) = 270 Hz and J(^{117}SnMnH) = 252 Hz in **1** provide spectroscopic evidence for some Sn–H interaction in this compound.

The solid-state structure of **1** closely resembles the structures of analogous silyl compounds[5a] and shows all the structural features which are typical of a three-center bonding situation. In particular, we were able to locate and to refine the position of the hydride ligand, which therefore is reliable within the accuracy of the method (the true Sn–H and Mn–H distances should be somewhat longer, since X-ray structure analyses systematically underestimate E–H distances). Although we do not wish to put too much emphasis on hydrogen parameters derived from X-ray data, the Sn–H distance found in **1** (2.16 (4) Å) is only about 0.45 Å (21%) longer than in methyl-substituted stannanes[14] and is therefore indicative for a bonding interaction between both atoms. For comparison, Si–H distances in the complexes MeCp(CO)$_2$Mn(H)SiR$_3$, containing Mn, H, Si three-center bonds, are 15–20% longer than in tetrahedral silanes.

For an evaluation of the Mn–Sn distance, **1** is better compared with Cp(CO)$_2$Fe-SnPh$_3$[15] than with derivatives of (CO)$_5$Mn–SnR$_3$, because of the stereochemical and electronic similarity of Cp(CO)$_2$Fe and Cp(CO)$_2$Mn fragments.[16] Because the bonding radius of the manganese atom in Cp(CO)$_2$Mn derivatives is at most 0.04 Å larger than that of the iron atom in Cp(CO)$_2$Fe derivatives,[16] the metal–tin distances in **1** and Cp(CO)$_2$Fe–SnPh$_3$ should differ by the same amount, if there would be a "normal" two-center bond between the metal atom and tin in both compounds. However, the Mn–Sn distance in **1** is 0.10 Å longer than the Fe–Sn distance in Cp(CO)$_2$Fe–SnPh$_3$ (2.533 and 2.540 Å, two independent molecules). The relative lengthening of the Mn–Sn bond in **1** must be attributed to the three-center bond.

Apart from the Sn–H and Mn–Sn distances, the geometry of the MeCp(CO)$_2$Mn fragment also suggests a delocalized Mn, H, Sn bond in **1**. The bond angles at the manganese atom, particularly C(7)–Mn–C(8) (87.9 (2)°), are typical of a three-legged piano-stool geometry (Cp(CO)$_2$ML), rather than of a four-legged piano-stool geometry (*cis*-Cp(CO)$_2$MLL′). In the latter complexes the bond angle between the carbonyl ligands typically is in the range of 74–78°, rather independent of M, L, and L′. Therefore in **1** HSnPh$_3$ must be regarded as *one* ligand, i.e., the Sn–H bond occupies one coordination site at the metal. From the geometry of the MeCp(CO)$_2$Mn fragment the direction of the acceptor orbital at the metal can be estimated. It points approximately

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to the center of the Sn–H bond. This, of course, is typical of a three-center bonding situation.

The very similar geometries of **1** and corresponding silyl complexes,[4a] particularly Cp(CO)$_2$Mn(H)SiPh$_3$ (**3**),[3,17] allow a very interesting comparison with respect to the stage in which addition of the silane or stannane to the MeCp(CO)$_2$Mn fragment is arrested.

As the interaction between the metal and the E–H group (E = Si, Sn) becomes stronger, the E–H interaction becomes weaker (i.e., the E–H distance increases and the *J*(EH) coupling constant decreases, compared with the parent R$_3$EH molecule), and both the Mn–E and Mn–H distance decrease.[5a,7b,16] The difference in bond radii between Sn and Si, which is the difference between the mean Si–C distance in **3** (1.88 Å) and the mean Sn–C distance in **1** (2.153 Å), is 0.27 Å. If both complexes would be in the same stage of the oxidative addition, the difference between the Mn–Si and the Mn–Sn distance should be the same. Since this difference is significantly smaller (Mn–Si in **3**, 2.424 (2) Å; Mn–Sn in **1**, 2.636 (1) Å), the relative approach of the tin atom to the metal is closer. This means that oxidative addition of HSnPh$_3$ to the MeCp(CO)$_2$Mn fragment in **1** is in a later stage than that of HSiPh$_3$ in **3**. This interpretation is also supported by a comparison of the NMR coupling constants. The upper limit (^1J(EH), direct E–H bond) is about 1800 Hz for E = Sn and 200 Hz for E = Si. The lower limit (^2J(EMH)) in metal complexes, where ER$_3$ and H are independent ligands, is about 100–150 Hz for E = Sn and 3–20 Hz for E = Si.[4] The fact that *J*(SnMnH) in **1** (136 and 127 Hz, vide supra) is relatively closer to the lower limit, compared with *J*(SiMnH) in MeCp(CO)$_2$Mn(H)SiPh$_3$ (65 Hz[9]), is consistent with a more advanced stage of the oxidative addition in **1**.

Conclusions

We have shown in this paper that a SnR$_3$ moiety can participate in a three-center bond. While numerous examples are known in which a hydride bridges two transition metals,[18] compounds having a hydride bridge between a transition metal and a main-group metal are extremely rare.

Comparison of the NMR and structural data of complexes MeCp(CO)$_2$Mn(H)EPh$_3$, with E = Sn (**1**) and E = Si, indicates that the Mn, H, Sn three-center bond in **1** corresponds to a latter stage of the oxidative addition than the Mn, H, Si three-center bond in MeCp(CO)$_2$Mn(H)SiR$_3$.

Experimental Section

All manipulations were performed under an atmosphere of dry and oxygen-free nitrogen. All solvents were dried by standard methods and saturated with N$_2$. Infrared spectra were taken in a CaF$_2$ solution cell and were recorded on a Perkin-Elmer 283 spectrometer. The ^{1}H NMR spectra were recorded on a Bruker AC 200 spectrometer (200 MHz).

Synthesis of (η^5-CH$_3$C$_5$H$_4$)(CO)$_2$Mn(H)SnPh$_3$ (1). A solution of 2.18 g (10 mmol) of MeCpMn(CO)$_3$ and 3.51 g (10 mmol) of HSnPh$_3$ in 250 mL of pentane was irradiated with a high-pressure mercury lamp (Hereaus TQ 150, 180 W) at −25 °C. During irradiation a slow stream of N$_2$ is bubbled through the solution. The progress of the reaction is monitored IR spectroscopically. Irradiation is stopped, if the intensity of the ν(CO) bands of **1** no longer increases (about 4 h). The reaction mixture is filtered, and the solid is extracted with several portions of pentane. On concentrating the combined filtrates to about 20 mL in vacuo, **1** precipitates as a nearly colorless solid, which is washed with three portions of 5 mL of pentane each: yield 2.16 g (40%); mp 57 °C dec; IR (cm^{-1}, pentane) ν(CO) 1983 (m), 1925 (m); ^{1}H NMR (benzene-d_6, relative internal Me$_4$Si) δ 7.9–7.0 (m, 15 H, Ph), 4.01 (s, 4 H, C$_5$*H*$_4$), 1.40 (s, 3 H, Me), −8.9 (s, 1 H, Mn-*H*, $J(^{119}$SnMnH) = 270 Hz, $J(^{117}$SnMnH) = 252 Hz); ^{119}Sn NMR (C$_6$D$_6$) δ 58.60 ppm. Anal. Calcd for C$_{26}$H$_{23}$MnO$_2$Sn: C, 57.72; H, 4.29 Found: C, 57.33; H, 4.17.

Synthesis of (η^5-CH$_3$C$_5$H$_4$)(CO)$_2$Mn(SnPh$_3$)$_2$ (2). A solution of 0.27 g (0.5 mmol) of **1** and 0.21 g (0.6 mmol) of HSnPh$_3$ in 50 mL of THF is stirred for 30 min at room temperature and then filtered. The filtrate is concentrated to 5 mL at vacuo, and 30 mL of pentane are added. **2** precipitates as a colorless solid: yield 0.40 g (90%); mp 115 °C dec; IR (cm^{-1}, Et$_2$O) 1934 (m), 1886 (vs); ^{1}H NMR (benzene, relative internal Me$_4$Si) δ 4.80 (m), 3.95 (m) (4 H, C$_5$*H*$_4$), 1.08 (s, 3 H, Me); ^{119}Sn NMR (C$_6$D$_6$) δ = 61.08 ppm. Anal. Calcd for C$_{44}$H$_{37}$MnO$_2$Sn$_2$: C, 59.37; H, 4.18. Found: C, 58.94; H, 4.64.

X-ray Structure Analysis of 1. Crystals of **1** were obtained from pentane. A crystal (0.3 × 0.3 × 0.25 mm) was mounted on a Syntex P2$_1$ automatic four circle diffractometer. Mo Kα radiation (λ = 0.71069 A, graphite monochromator) was used for all measurements. Centering and refinement of 25 reflections from different parts of the reciprocal space resulted in the following unit cell dimensions: a = 8.262 (3) Å, b = 10.536 (4) Å, c = 14.755 (6) Å, α = 94.63 (3)°, β = 99.85 (3)°, γ = 110.58 (3)°, and V = 1171 A^3; space group $P\bar{1}$; d(calcd) = 1.53 g/cm^3 (Z = 2).

Diffraction intensities were measured in an ω-scan mode (scan range 0.9°); the scan rate varied as a function of maximum peak intensity from 0.9 to 29.3 cm^{-1}. Background radiation was measured on each side of the reflection center for half of the total scan time. Two reference reflections measured every 40 reflections showed a slow and steady decrease in their intensity. A total of 3677 independent reflections were collected (3° ≤ 2θ ≤ 48°). Intensity data were corrected for Lorentz and polarization effects; a decay correction and an empirical absorption correction was applied (μ = 16.6 cm^{-1}). The structure was solved by the heavy atom method (Syntex XTL). The positions of the aromatic hydrogen atoms were calculated according to the idealized geometry; the remaining hydrogen atoms were located from difference Fourier maps. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms as well as the atomic coordinates and the isotropic temperature factor of the hydride ligand (H1) were refined by full-matrix least squares with all structure factors included. Final R = 0.042 and R_w = 0.038 ($1/w = \sigma(F_o)^2 + 0.000009F_o^2$). The final positional parameters of the non-hydrogen atoms and H1 are listed in Table I. Listings of hydrogen parameters, thermal parameters, bond distances and angles, and observed and calculated structure factors are available as Supplementary Material.

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Registry No. 1, 119337-09-6; **2**, 119337-10-9; MeCpMn(CO)$_3$, 12108-13-3; HSnPh$_3$, 892-20-6.

Supplementary Material Available: Tables of the atomic coordinates and temperature parameters for all atoms and a complete listing of bond distances and angles (8 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any currrent masthead page.

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