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SYNTHESIS OF $BrMe_2Sn$-$Mn(CO)_3(PPh_3)_2$ BY AN UNUSUAL METHYL ELIMINATION REACTION FROM Me_3SnBr IN THE PRESENCE OF $[Mn(CO)_3(PPh_3)_2]^-$ ANION AND ITS CRYSTAL STRUCTURE ANALYSIS

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A reaction of the title anion with Me_3SnBr at reflux temperature in THF gave unexpected $BrMe_2Sn$-$Mn(CO)_3(PPh_3)_2$ in low yield. Its characterization and crystal structure are described.

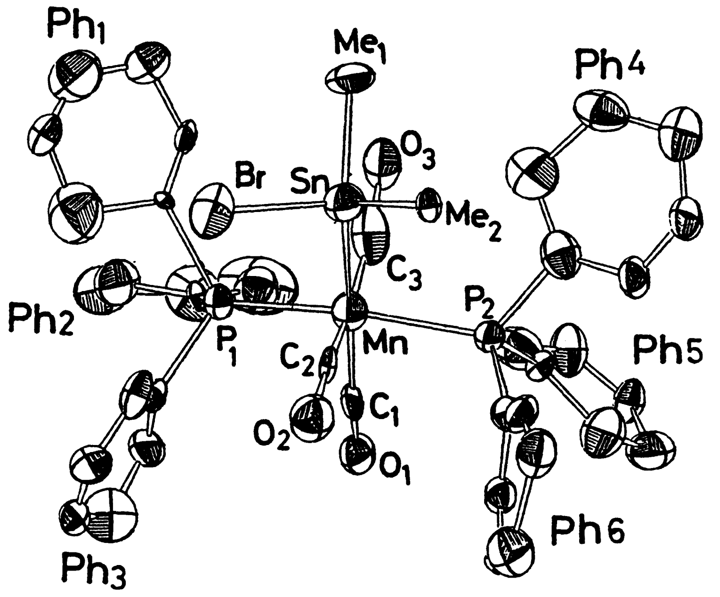
The present study stems from our interest in the structural and dynamical properties of di-substituted metal carbonyl derivatives with triphenylphosphine or triphenylphosphite$^{1)}$ and the synthesis of mer-trans Me_3Sn-$Mn(CO)_3(PPh_3)_2$ was purported to shed further light on this problem.

Metathetical reactions between a metal anion (a sodium salt in most cases) and a metal halide have been most useful and most frequently employed for preparing covalent metal-metal bonds involving Sn and transition elements$^{2-4)}$ (eq.1) among so far devised synthetic procedures.

$$Na^+[ML_x]^- + R_ySnX \longrightarrow L_xM\text{-}SnR_y + NaX \qquad (1)$$

A series of mer-trans R_3Sn-$Mn(CO)_3[P(OPh)_3]_2$ (R_3 = Me_3, Et_3, Ph_3, MePhCl, and Me_2Cl) was synthesized at room temperature from $Na^+[Mn(CO)_3\{P(OPh)_3\}_2]^-$ and R_3SnCl or R_3SnBr in this fashion.$^{1)}$ On the other hand, a mixture of at least two isomers was obtained from previously examined reactions of Me_3SnBr with $Na^+[Mn(CO)_3(PPh_3)_2]^-$ at room temperature in THF; in the preceding paper, these two isomers were supposed to be mer-trans and fac-cis Me_3Sn-$Mn(CO)_3(PPh_3)_2$ on the basis of their IR and ^1H-NMR spectra together with the result of their elemental analyses for this mixture.$^{1,5)}$ When the reaction was conducted at reflux temperature, a small amount of yellow crystals were obtained with the yield of less than 10% and their IR spectrum in CO stretching region and ^1H-NMR spectrum in the methyl proton region were in accord with those of one isomer obtained at room temperature, which was assigned to mer-trans Me_3Sn-$Mn(CO)_3(PPh_3)_2$.[1,5] Later elemental analyses for this yellow crystal, however, showed significant disparity from the expected values for Me_3Sn-$Mn(CO)_3(PPh_3)_2$. (Found; C=53.42; H=4.01%. Calcd. for Me_3Sn-$Mn(CO)_3(PPh_3)_2$; C=60.97; H=4.75%). X-ray structure analysis was performed for elucidation of this crystal.

The crystal belongs to a monoclinic space group with the cell dimensions of: a = 23.751 (5) Å, b = 16.279 (2) Å, c = 10.306 (3) Å, β = 98.03 (2)°, and V = 3945.7 $Å^3$. Observed density (1.45 gcm^{-3}) suggested the presence of four molecules in a unit cell. Systematic absence of (0k0) reflections for k = 2n + 1 indicated that the space group belongs to either $P2_1$ (noncentrosymmetric) or $P2_1/_m$ (centrosymmetric). The statistical treatment of the reflection data indicated that the space group was noncentrosymmetric and two independent molecules should exist in the asymmetric unit. Intensity data were collected on a Philips four-circle diffractometer with graphite-monochromatized Mo Kα radiation. 3735 nonzero reflections with $F_0 > 3\sigma(F_0)$ were adopted for analysis. The structure was solved by the conventional heavy atom method. The positions of two tin atoms were derived from a three-dimensional Patterson map. Consequent minimum function treatment revealed the positions of two manganese atoms, four phosphorous atoms, and two unknown heavy atoms, which possessed almost same peak intensities as those of the manganese atoms and the distances from the tin atoms were approximated to those of the manganese-tin distances. For these reasons, these two heavy atoms were treated as manganese atoms at an early stage of refinement. A Fourier synthesis after several cycles of isotropic refinement on positional and thermal parameters for these atoms revealed three carbonyl groups, two methyl groups, and eighteen phenyl carbon atoms for each molecule. Additional several cycles of isotropic refinement gave R = 0.12. However, we failed to locate any nonhydrogen atoms at around the unknown heavy atoms. A difference Fourier synthesis left significant electron density at the positions of the unknown heavy atoms. Fluorescent X-ray analysis exhibited clearly the presence of bromine atom and the crystal was characterized to be $BrMe_2Sn$-$Mn(CO)_3(PPh_3)_2$. Isotropic refinements produced R = 0.10. Several cycles of anisotropic refinement for all nonhydrogen atoms by the block-diagonal least-squares gave R = 0.081. An ORTEP view of the molecular structure is shown in Fig. 1 along with some bond lengths and bond angles. A view down the P-Mn-P axis for each molecule demonstrated that two triphenylphosphine groups were coordinated to Mn with a fairly distorted



BOND LENGTHS (Å)

Sn-Mn	2.659(6)	C(1)-O(1)	1.183(34)
Sn-Br	2.571(5)	C(2)-O(2)	1.165(36)
Sn-C(Me₁)	2.156(38)	C(3)-O(3)	1.342(52)
Sn-C(Me₂)	2.234(26)	P(1)-C(Ph1)	2.001(24)
Mn-P(1)	2.271(9)	P(1)-C(Ph2)	1.830(28)
Mn-P(2)	2.364(9)	P(1)-C(Ph3)	1.954(29)
Mn-C(1)	1.812(26)	P(2)-C(Ph4)	1.837(38)
Mn-C(2)	1.782(25)	P(2)-C(Ph5)	1.770(24)
Mn-C(3)	1.578(45)	P(2)-C(Ph6)	1.963(34)

BOND ANGLES(°)

Br-Sn-Mn	112.3(2)
C(Me₁)-Sn-Mn	117.3(13)
C(Me₂)-Sn-Mn	122.2(7)
Br-Sn-C(Me₁)	102.7(12)
Br-Sn-C(Me₂)	96.9(7)
C(Me₁)-Sn-C(Me₂)	102.0(13)
Sn-Mn-P(1)	97.9(3)
Sn-Mn-P(2)	93.3(3)
Sn-Mn-C(1)	167.2(8)
Sn-Mn-C(2)	74.8(7)
Sn-Mn-C(3)	82.2(16)
Mn-P(1)-C(Ph1)	117.1(8)
Mn-P(1)-C(Ph2)	117.8(8)
Mn-P(1)-C(Ph3)	112.3(8)
Mn-P(2)-C(Ph4)	121.7(12)
Mn-P(2)-C(Ph5)	113.1(8)
Mn-P(2)-C(Ph6)	113.2(9)
Mn-C(1)-O(1)	174.1(22)
Mn-C(2)-O(2)	167.4(23)
Mn-C(3)-O(3)	172.1(33)
P(1)-Mn-P(2)	168.7(4)
C(2)-Mn-C(3)	156.8(18)

FIG. I. ORTEP view of $BrMe_2Sn\text{-}Mn(CO)_3(PPh_3)_2$ molecule. The drawing and the molecular parameters are referenced to only one molecule in the asymmetric unit.

structure from an exact eclipsed conformation regarding the P-Ph bondings. A schematic molecular projection down the Sn-Mn bond (Fig. 2) displayed that two methyl groups in each independent molecule are asymmetric with respect to the plane which bisects the P-Mn-P bond. Two equatorial carbonyl groups are significantly bent toward the tin-manganese bond.[6)] All bond lengths listed in Fig. 1 are as expected.[6-8)]

The reaction between $Na^+[Mn(CO)_3(PPh_3)_2]^-$ and Me_3SnBr in THF is now clearly demonstrated to involve an unusual methyl elimination pathway. From the reaction

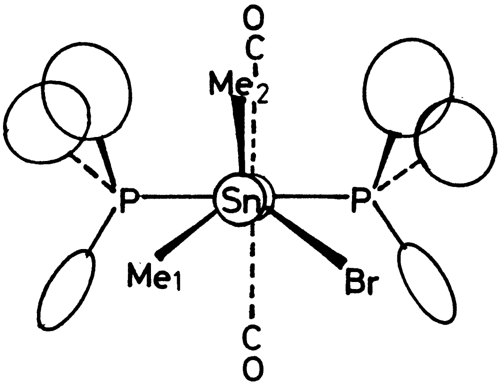


FIG. 2. Schematic drawing of the molecule viewed down the tin-manganese bond.

at room temperature, at least three isomers have been detected so far by IR spectroscopy, whereas two isomers have been so far isolated from the reaction at reflux temperature. The second isomer obtained from the reflux temperature reaction is air-sensitive and exhibits seven terminal CO stretching peaks, suggesting the isomer to be trinuclear. These observations lead us to an idea that the reaction does not proceed in a typical metathetical reaction as shown in eq. 1 . Detailed characterization of other isomers and the analysis of the reaction mechanism are now under investigation.

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