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XII *. THE REACTION OF A CARBONYLTUNGSTATE ANION WITH TRIPHENYLTIN CHLORIDE RESULTING IN A PHENYL–TIN BOND CLEAVAGE. X-RAY STRUCTURAL CHARACTERIZATION OF THE NOVEL SALT: $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-}i\text{-}Pr\}W(CO)_3]$

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Summary

The reaction of a highly reduced tricarbonyltungstate species with triphenyltin chloride results in an unprecedented phenyl–tin cleavage and the formation of an unusual substituted carbonyl anion. The X-ray structure of $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-}i\text{-}Pr\}W(CO)_3]$ shows the presence of seven coordinate tungsten bound to three terminal carbonyl groups, two triphenyltin units and a previously unknown isopropoxo-bis(diphenyltin) bidentate ligand. The seven ligating atoms are disposed in an approximate 4:3 piano stool arrangement about the central tungsten atom. Crystal data: Space group $P2_1/c$, a 22.580(10), b 14.162(4), c 23.070(10) Å, β 114.21(4)°, $Z = 4$, V 6728(1) Å^3, ρ(calc) 1.626 g cm^{-3}.

Introduction

For many years it has been established that one of the easiest ways to characterize an unknown mononuclear carbonylmetallate anion is to prepare a triphenyltin derivative by the reaction of the anion with one or more equivalents of Ph_3SnCl. These reactions generally proceed smoothly to provide good yields of $(Ph_3Sn)_xM(CO)_y{}^z$ species where x is generally 1 to 3 and z is usually 0, -1 or -2. It is then usually possible to infer the nature of the initial carbonylmetallate anion by characterizing appropriate triphenyltin derivatives. The latter are generally much less sensitive to polar solvents, oxygen and moisture and more easily obtained as crystalline and analytically pure substances than the original carbonylmetallate species. For example, from the reaction of Ph_3SnCl with a highly reduced carbonyl-

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vanadate ion, produced from the reduction of $V(CO)_6^-$ by sodium metal in liquid ammonia, $Ph_3SnV(CO)_5^{2-}$ and $(Ph_3Sn)_2V(CO)_5^-$ were isolated in excellent yields. From these results, it was correctly inferred that the highly reduced reactant was $V(CO)_5^{3-}$ [2–4]. Similarly, the isolation of triphenyltin derivatives have greatly helped in our characterization of $Na_3M(CO)_4$ (M = Mn and Re) [5], $Na_3M(CO)_3$ (M = Co, Rh and Ir) [6] and $Na_4M(CO)_4$ (M = Cr, Mo and W) [7].

By the same general procedure we hoped to determine the nature of the highly reduced species, "X", produced by the reduction of $W(CO)_3(PMTA)$, PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine, with six equivalents of potassium metal in liquid ammonia. When "X" was treated with three equivalents of Ph_3SnCl, work-up provided $HW(CO)_3(SnPh_3)_3^{2-}$ in 10–12% isolated yields. However, also present in roughly the same amounts was another substance which gave analyses inconsistent with the presence of only triphenyltin groups. For this reason a crystal structure of this other product was determined. This study revealed that a hitherto unprecedented phenyl–tin bond cleavage had occurred during the reaction of "X" with Ph_3SnCl to produce an unusual substituted carbonyl anion containing seven coordinate tungsten. In this paper the results of this structural study are discussed.

Experimental

For general synthetic procedures, starting materials and the synthesis of $[(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]^-$ see the preceding paper in this series [1].

Crystallographic characterization of $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-}i\text{-}Pr\}W(CO)_3]$ *(I)*

Collection and reduction of X-ray data. A summary of crystal and intensity collection data is shown in Table 1. Suitable crystals of $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-}i\text{-}Pr\}W(CO)_3]$ were grown by slow diffusion of isopropanol into a near saturated solution of $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]$ in 1,2-dichloroethane and recovered by decantation of the solvent and drying in a stream of argon. A clear, pale yellow rectangular tablet shaped crystal of dimensions 0.1 × 0.2 × 0.3 mm was selected and wedged inside a 0.2 mm glass capillary tube which was then flame sealed under argon and mounted on a goniometer head. The crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering and indexing programs and by a Delauney reduction calculation. All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package has been described previously [8]. The space group $P2_1/c$ (No. 14) was chosen from the systematic absences observed during data collection ($0k0: k = 2n + 1$, $h0l: l = 2n + 1$) and was verified by successful solution and refinement of the structure. Data was collected on a CAD 4 Nonius diffractometer. Background counts were measured at both ends of the scan range with the use of an ω-2θ scan equal, at each side, to one-fourth of the scan range of the peak. In this manner, the total duration of measuring backgrounds is equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure and showed the crystal to be unstable in the X-ray beam. The three standard reflections showed uniform decay such that after data collection to 20° in θ the observed values of F_0 were 62% of the original. This decay precluded collecting data to higher θ angles and also precluded making an absorption correction. Ideally, we

TABLE 1

SUMMARY OF CRYSTAL AND INTENSITY COLLECTION DATA

Formula	$C_{70}H_{69}NO_4Sn_4W$
Mol.wt.	1647.00
a	22.580(10) Å
b	14.162(4) Å
c	23.070(10) Å
β	114.21(4)°
V	6728(1) $Å^3$
Z	4
d(calc)	1.626 g cm^{-3}
Space group	$P2_1/c$
Temperature	23°C
Radiation	Mo-K_α (0.71073 Å) from monochromator
Linear absorption	33.2 cm^{-1}
2θ limits	0–40°
Final number of variables	347
Unique data used	2997, $F_0^2 \geqslant 2.00\ (F_0^2)$
R [a]	0.079
R_w [a]	0.074
Error in observation [b] of unit weight	1.868
Crystal dimensions	0.1 × 0.2 × 0.3 mm

[a] The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ where $w = 1/\sigma^2(F_o)$. The unweighted residuals are defined as follows: $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$ and $R_w = [(\Sigma w(|F_0|-|F_c|))^2/(\Sigma w|F_o|)^2]^{1/2}$. [b] The error in an observation of unit weight is $[\Sigma w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$ where NO and NV are the number of observations and variables, respectively.

would have preferred to collect a new set of data at low temperature to possibly avoid this difficulty, but equipment for the collection of such data was not available. Since the structure based on these room temperature data seems to be reasonable in all details (e.g., interatomic distances, bond angles, etc.), we are reporting it in its present form. A decay correction was applied to the F_0 values by program CHORTA [8]. The intensities of 6829 ($\pm h$, $+k$, $+l$) reflections were measured at 23°C out to a 2θ of 40° using Mo-K_α monochromatized radiation. The intensity data were processed as described previously [8b]. The net intensity $I = (K/NPI)(C-2B)$, where $K = 20.1166 \times$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count multiplied by a factor to correct for the decay [8b], and B = total background count corrected by the same factor [8b]. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/NPI)^2[C+4B+(pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitudes F_0 are given by $F_0 = (I/Lp)^{1/2}$ where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_0)$ by $\sigma(F_0) = \frac{1}{2}(\sigma(I)/I)F_0$. The data were corrected for Lorentz, polarization and background effects but not for absorption, using a value of 0.04 for p. Of the 6270 unique reflections measured, 2997 have $F_0^2 \geq 2.0\ \sigma(F_0^2)$ and were used in subsequent calculations.

Solution and refinement of the structure. The structure was solved by conventional heavy atom techniques. The W atom was located by Patterson synthesis. Full matrix least-square refinement and difference Fourier calculations were used to

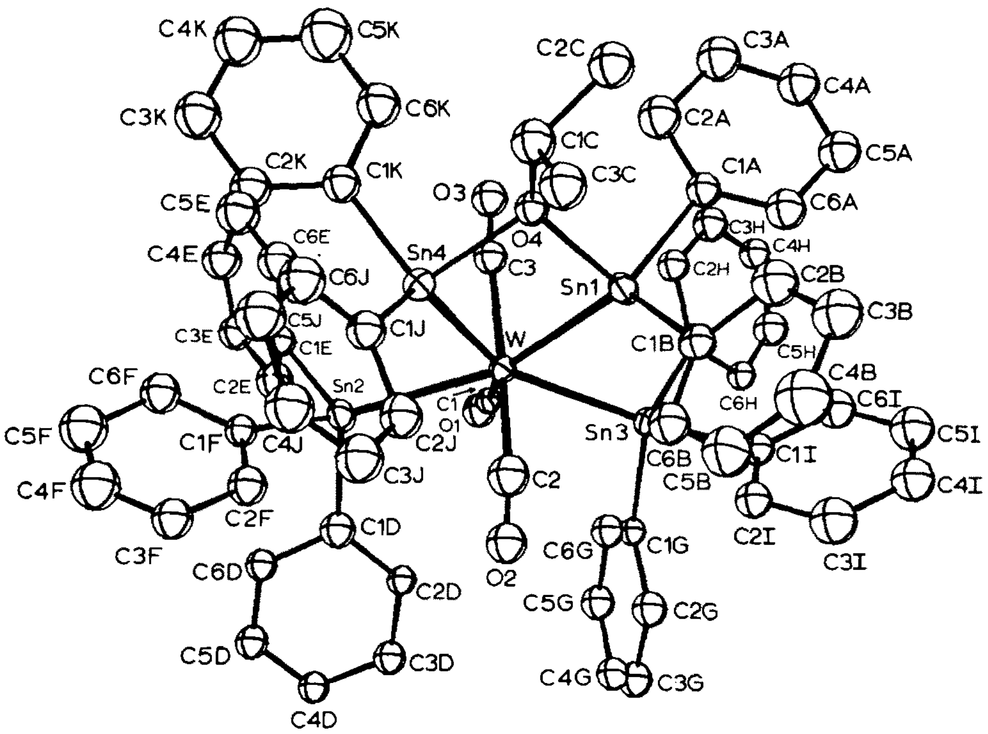

Fig. 1. ORTEP drawing showing the labeling scheme of the anion in [Me$_4$N][(Ph$_3$Sn)$_2$((Ph$_2$Sn)$_2$O-i-Pr)W(CO)$_3$]. Thermal ellipsoids are drawn with 50% probability boundaries.

locate all remaining non-hydrogen atoms. The function minimized was $\Sigma w(|F_0|-|F_c|)^2$, where $w=1/\sigma^2\ (F_0)$. The unweighted and weighted residuals are defined as $R=(\Sigma||F_0|-|F_c||)/\Sigma|F_0|$ and $R_w=[(\Sigma w(|F_0|-|F_c|))^2/(\Sigma w|F_0|)^2]^{1/2}$. The error in

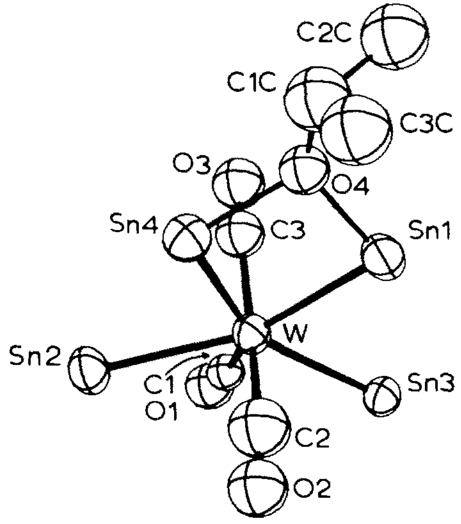

Fig. 2. ORTEP drawing showing the coordination core of [Me$_4$N][(Ph$_3$Sn$_2$)(Ph$_2$Sn)$_2$O-i-Pr)W(CO)$_3$].

the observation of unit weight is $[\Sigma w(|F_0|-|F_c|)^2/(NO-NV)]^{1/2}$ where NO and NV are the number of observations and variables, respectively. The atomic scattering factors were taken from the usual tabulation [9a] and the effects of anomalous dispersion were included in F_c for all atoms using Cromers and Ibers values of $\Delta f'$ and $\Delta f''$ [9b]. The W and Sn atoms were refined anisotropically while all remaining atoms were treated isotropically. Hydrogen atoms were not located in the final difference Fourier maps and therefore were not included and no chemically significant peaks were observed in this map. The final positional and thermal parameters appear in Table 2. The labeling scheme for the molecule is shown in Fig. 1 and an ORTEP drawing of the coordination core is shown in Fig. 2. Selected bond distances and angles are collected in Table 3 *.

Results and discussion

X-Ray structure of $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-}i\text{-}Pr\}W(CO)_3]$ *(I)*

Crystalline salts containing $[(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]^-$ formed methylene chloride or ether solvates which quickly lost solvent and crumbled when removed from the mother liquor. However, it was found that crystals obtained by slow diffusion of isopropyl alcohol into a 1,2-dichloroethane solution of $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]$ were not solvated and retained their crystallinity on drying at room temperature. A single crystal X-ray diffraction study of this material revealed that an isopropyl group had replaced the ethyl group on the doubly bridging oxygen atom (eq. 1).

$$[(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]^- + \text{i-PrOH} \rightarrow [(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-i-Pr}\}W(CO)_3]^- + EtOH \quad (1)$$

It is not known whether this replacement occurred via alkyl or alkoxide exchange. Since the mull and solution infrared spectra of compound I (ν(CO) in CH_3CN: 1945w, 1861m, 1842s), $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]$ and the tetraphenylphosphonium salt [1] are superimposable, it is clear that no gross structural change of the anion resulted from this exchange reaction. The structure of the isopropyl derivative, (I), will now be discussed.

ORTEP drawings of the entire anion showing the labeling scheme and the coordination core of $[(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-i-Pr}\}W(CO)_3]^-$ are shown in Figs. 1 and 2, respectively. Compound I consists of discrete cations and anions with no unusually short interionic contacts. The anion contains a seven coordinate tungsten atom bound to three terminal carbonyl groups, two triphenyltin groups and two diphenyltin units of the unusual bidentate ligand, $(Ph_2Sn)_2O\text{-i-Pr}$. The tungsten atom in the monoanion attains an 18 electron configuration by virtue of its formal charge of -2, while the three coordinate oxygen in the μ-isopropoxo-bis(diphenylstannyl) ligand

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* Supplementary data involving a listing of the observed and calculated structure factor amplitudes, root-mean-square amplitudes of thermal vibration and general temperature factor expressions have been deposited as NAPS Document No. 04068 (16 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017. A copy may be secured by citing the document number, remitting $7.75 for photocopies or $4.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the U.S. and Canada add postage $4.50 for photocopy and $1.00 for microfiche.

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TABLE 2

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-i-Pr}\}W(CO)_3]$ [a]

Atom	x	y	z	$B_{(1,1)}$	$B_{(2,2)}$	$B_{(3,3)}$	$B_{(1,2)}$	$B_{(1,3)}$	$B_{(2,3)}$
W	0.22943(7)	0.4600(1)	0.23546(6)	0.00319(4)	0.0037(1)	0.00192(3)	0.0006(1)	0.00177(5)	0.0005(1)
Sn(1)	0.2722(1)	0.6431(2)	0.26763(10	0.00376(7)	0.0047(2)	0.00242(6)	0.0001(2)	0.00235(9)	−0.0005(2)
Sn(2)	0.2517(1)	0.2781(2)	0.20329(10	0.00415(7)	0.0042(2)	0.00286(6)	0.0008(2)	0.00278(10)	−0.0003(2)
Sn(3)	0.1153(1)	0.5557(2)	0.22146(9)	0.00319(6)	0.0043(2)	0.00221(5)	0.0014(2)	0.00192(9)	0.0007(2)
Sn(4)	0.3585(1)	0.4706(2)	0.25379(10	0.00323(7)	0.0061(2)	0.00265(6)	0.0009(2)	0.00201(10)	0.0002(2)
O(1)	0.1323(9)	0.321(2)	0.2541(8)	6.2(6)					
O(2)	0.1829(10)	0.491(2)	0.0892(9)	7.3(7)					
O(3)	0.2931(9)	0.431(2)	0.3828(9)	6.7(6)					
O(4)	0.3736(8)	0.607(1)	0.2971(8)	5.0(5)					
N	0.145(1)	0.225(2)	0.411(1)	10.0(1)					
C(1)	0.165(1)	0.373(2)	0.244(1)	3.6(7)					
C(2)	0.199(2)	0.483(3)	0.145(2)	8.2(11)					
C(3)	0.275(1)	0.442(2)	0.328(1)	5.7(9)					
C(1C)	0.434(2)	0.658(3)	0.317(2)	8.1(11)					
C(2C)	0.439(2)	0.730(3)	0.374(2)	8.5(11)					
C(3C)	0.437(2)	0.721(3)	0.263(2)	8.7(11)					
C(1A)	0.275(1)	0.713(2)	0.353(1)	5.5(9)					
C(2A)	0.314(2)	0.664(3)	0.414(2)	8.9(12)					
C(3A)	0.309(2)	0.716(3)	0.470(2)	9.3(12)					
C(4A)	0.265(2)	0.788(3)	0.456(2)	8.6(11)					
C(5A)	0.225(2)	0.827(3)	0.401(2)	8.6(11)					
C(6A)	0.231(1)	0.782(3)	0.346(1)	7.6(10)					
C(1B)	0.268(1)	0.757(2)	0.204(1)	5.3(8)					
C(2B)	0.291(2)	0.853(3)	0.232(2)	8.8(12)					
C(3B)	0.288(2)	0.933(3)	0.194(2)	9.5(12)					
C(4B)	0.280(2)	0.911(3)	0.130(2)	11.8(15)					
C(5B)	0.260(2)	0.821(3)	0.104(2)	9.6(12)					
C(6B)	0.255(1)	0.737(3)	0.139(1)	7.3(10)					
C(1D)	0.168(1)	0.221(3)	0.132(1)	6.6(10)					
C(2D)	0.106(1)	0.263(2)	0.103(1)	4.4(8)					
C(3D)	0.054(1)	0.220(2)	0.051(1)	5.6(9)					
C(4D)	0.061(1)	0.129(2)	0.028(1)	5.3(9)					

C(5D)	0.120(1)	0.089(2)	0.055(1)	5.7(9)
C(6D)	0.175(1)	0.134(2)	0.105(1)	5.2(9)
C(1E)	0.275(1)	0.168(2)	0.282(1)	4.7(8)
C(2E)	0.226(2)	0.108(3)	0.270(2)	7.9(11)
C(3E)	0.246(1)	0.034(3)	0.323(1)	7.0(10)
C(4E)	0.302(2)	0.047(3)	0.373(2)	8.9(11)
C(5E)	0.348(2)	0.118(3)	0.390(2)	10.5(13)
C(6E)	0.329(2)	0.192(3)	0.335(2)	8.6(11)
C(1F)	0.321(1)	0.242(2)	0.165(1)	4.8(8)
C(2F)	0.319(1)	0.285(3)	0.111(1)	6.8(10)
C(3F)	0.354(1)	0.254(3)	0.072(1)	7.0(10)
C(4F)	0.385(2)	0.174(3)	0.097(2)	9.9(13)
C(5F)	0.392(2)	0.123(3)	0.151(2)	10.1(13)
C(6F)	0.363(1)	0.163(3)	0.191(1)	7.4(10)
C(1G)	0.031(1)	0.490(2)	0.154(1)	4.1(8)
C(2G)	0.004(1)	0.517(3)	0.087(1)	6.5(10)
C(3G)	−0.050(1)	0.468(3)	0.043(1)	6.6(9)
C(4G)	−0.082(1)	0.402(2)	0.062(1)	5.9(9)
C(5G)	−0.059(1)	0.373(3)	0.125(1)	6.7(10)
C(6G)	−0.002(1)	0.418(2)	0.173(1)	6.1(9)
C(1H)	0.095(1)	0.568(2)	0.306(1)	3.9(8)
C(2H)	0.150(1)	0.564(2)	0.366(1)	5.7(9)
C(3H)	0.132(1)	0.579(3)	0.419(1)	7.0(10)
C(4H)	0.071(1)	0.595(2)	0.415(1)	5.7(9)
C(5H)	0.021(1)	0.600(3)	0.355(1)	7.2(10)
C(6H)	0.032(1)	0.587(2)	0.301(1)	4.7(8)
C(1I)	0.099(1)	0.702(2)	0.185(1)	5.1(8)
C(2I)	0.110(1)	0.723(2)	0.132(1)	6.1(9)
C(3I)	0.098(2)	0.817(3)	0.109(2)	9.8(13)
C(4I)	0.084(2)	0.890(3)	0.143(2)	8.2(11)
C(5I)	0.072(2)	0.867(3)	0.196(2)	9.0(12)
C(6I)	0.083(1)	0.775(3)	0.222(1)	7.6(10)
C(1J)	0.401(1)	0.486(2)	0.189(1)	6.3(10)
C(2J)	0.360(1)	0.522(3)	0.126(1)	7.1(10)
C(3J)	0.390(2)	0.531(3)	0.079(2)	8.6(11)
C(4J)	0.453(2)	0.509(3)	0.096(2)	8.7(12)
C(5J)	0.494(2)	0.482(3)	0.157(2)	9.0(12)
C(6J)	0.467(2)	0.472(3)	0.203(2)	8.7(12)
C(1K)	0.430(1)	0.405(3)	0.325(1)	6.3(10)

TABLE 2 (continued)

Atom	x	y	z	$B_{(1,1)}$	$B_{(2,2)}$	$B_{(3,3)}$	$B_{(1,2)}$	$B_{(1,3)}$	$B_{(2,3)}$
C(2K)	0.460(1)	0.322(3)	0.318(1)	7.5(10)					
C(3K)	0.507(2)	0.271(3)	0.372(2)	9.6(12)					
C(4K)	0.521(2)	0.301(3)	0.434(2)	10.6(13)					
C(5K)	0.487(2)	0.375(3)	0.447(2)	12.6(16)					
C(6K)	0.444(2)	0.432(3)	0.391(2)	8.6(11)					
C(4)	0.150(2)	0.189(3)	0.471(2)	11.5(14)					
C(5)	0.123(2)	0.152(4)	0.359(2)	14.7(18)					
C(6)	0.200(2)	0.260(3)	0.411(2)	11.7(14)					
C(7)	0.095(2)	0.287(4)	0.390(2)	14.8(18)					

[a] The form of the anisotropic thermal parameter is

$$\exp\left[-\left(B_{(1,1)}h^2 + B_{(2,2)}k^2 + B_{(3,3)}l^2 + B_{(1,2)}hk + B_{(1,3)}hl + B_{2,3}kl\right)\right]$$

TABLE 3

SELECTED DISTANCES AND ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS [Me_4N][$(Ph_3Sn)_2((Ph_2Sn)_2O$-i-Pr)$W(CO)_3$]

Distances (Å)			
W-C(1)	1.96(2)	Sn(1)-C(1A)	2.18(2)
W-C(2)	1.95(3)	Sn(1)-C(1B)	2.16(3)
W-C(3)	1.98(3)	Sn(2)-C(1D)	2.09(3)
W-Sn(1)	2.760(2)	Sn(2)-C(1E)	2.28(2)
W-Sn(2)	2.784(2)	Sn(2)-C(1F)	2.15(2)
W-Sn(3)	2.811(2)	Sn(3)-C(1G)	2.12(2)
W-Sn(4)	2.771(2)	Sn(3)-C(1H)	2.19(2)
W-O(4)	3.63(2)	Sn(3)-C(1I)	2.21(3)
C(1)-O(1)	1.15(2)	Sn(4)-C(1J)	2.09(3)
C(2)-O(2)	1.18(3)	Sn(4)-C(1K)	2.00(3)
C(3)-O(3)	1.16(2)	Sn(1)-Sn(4)	3.221(3)
Sn(4)-O(4)	2.14(2)	Sn(1)-Sn(3)	3.482(3)
Sn(1)-O(4)	2.16(2)	Sn(4)-Sn(2)	3.507(3)
C(1C)-O(4)	1.45(3)		

Angles (°)			
Sn(1)-W-Sn(2)	149.29(7)	O(4)-Sn(1)-C(1B)	97.9(7)
Sn(1)-W-Sn(3)	77.36(6)	C(1A)-Sn(1)-C(1B)	105(1)
Sn(1)-W-Sn(4)	71.24(7)	W-Sn(2)-C(1D)	111.1(8)
Sn(1)-W-C(1)	138.7(7)	W-Sn(2)-C(1E)	115.4(6)
Sn(1)-W-C(2)	93.5(9)	W-Sn(2)-C(1F)	125.0(7)
Sn(1)-W-C(3)	82.0(8)	C(1D)-Sn(2)-C(1E)	102(1)
Sn(2)-W-Sn(3)	132.29(7)	C(1D)-Sn(2)-C(1F)	99(1)
Sn(2)-W-Sn(4)	78.29(7)	C(1E)-Sn(2)-C(1F)	101.0(9)
Sn(2)-W-C(1)	70.6(7)	W-Sn(3)-C(1G)	112.3(6)
Sn(2)-W-C(2)	83.8(9)	W-Sn(3)-C(1H)	117.0(6)
Sn(2)-W-C(3)	95.5(8)	W-Sn(3)-C(1I)	119.9(6)
Sn(3)-W-Sn(4)	148.07(8)	C(1G)-Sn(3)-C(1H)	103.6(9)
Sn(3)-W-C(1)	68.6(6)	C(1G)-Sn(3)-C(1I)	99.9(9)
Sn(3)-W-C(2)	83.9(8)	C(1H)-Sn(3)-C(1I)	101.7(9)
Sn(3)-W-C(3)	103.7(7)	W-Sn(4)-O(4)	94.4(4)
Sn(4)-W-C(1)	142.0(6)	W-Sn(4)-C(1J)	130.9(7)
Sn(4)-W-C(2)	92.2(8)	W-Sn(4)-C(1K)	122.7(8)
Sn(4)-W-C(3)	77.9(7)	O(4)-Sn(4)-CJ)	102.1(8)
C(1)-W-C(2)	105(1)	O(4)-Sn(4)-C(1K)	96(1)
C(1)-W-C(3)	84.0(9)	C(1J)-Sn(4)-C(1K)	101(1)
C(2)-W-C(3)	170(1)	W-C(1)-O(1)	173(2)
W-Sn(1)-O(4)	97.1(4)	W-C(2)-O(2)	175(3)
W-Sn(1)-C(1A)	123.1(7)	W-C(3)-O(3)	170(2)
W-Sn(1)-C(1B)	127.3(7)	Sn(1)-O(4)-Sn(4)	96.9(6)
O(4)-Sn(1)-C(1A)	100.7(8)	Sn(1)-O(4)-C(1C)	136(2)
		Sn(4)-O(4)-C(1C)	123(2)

has a + 1 formal charge, which is reasonable for a bound oxonium ion.

Numerous seven coordinate $W(CO)_3(L-L)_2$, (L-L = bidentate ligand) complexes have been prepared and structurally characterized. Among these, pentagonal bipyramidal, monocapped octahedral, monocapped trigonal prismatic and the so called “4 : 3 piano stool” geometries have been recognized. Calculations have shown that energy differences between possible seven coordinate geometries are small and that factors such as metal ion size, electron configuration, ligand character, and crystal packing forces interact in subtle ways to dictate the observed geometry. The theoretical and stereochemical aspects of coordination number seven have been extensively and critically discussed [10–13].

Two useful methods for determining the structural class of a seven coordinate compound involve comparison of the observed interbond angles and dihedral angles between polyhedral faces to those calculated for the idealized geometries. Inspection of Fig. 2 suggests that the coordination geometry could best be described as being a 4 : 3 piano stool or a pentagonal bipyramid. Comparison of interbond angles (Table 4) does not allow a clear choice between these two geometries. However, such a comparison does rule out the possibility of a monocapped octahedral or monocapped trigonal prismatic description.

The more sophisticated dihedral angle analysis (Table 4) also fails to allow a clear choice between the two most obvious possibilities. In this case, the dihedral angles expected for a pentagonal bipyramid are 54.4 and 54.4°, while those observed are

TABLE 4

SUMMARY OF INTERBOND ANGLES (°) FOR SEVEN COORDINATE STRUCTURES [a]

Angle No.	PB	CO	CTP	4:3	$[Me_4N][(Ph_3Sn)_2\{(Ph_2Sn)_2O\text{-i-Pr}\}W(CO)_3]$
1	180.0	160.0	164.0	17.0	170.0
2	144.0	160.0	164.0	153.6	148.1
3	144.0	160.0	144.2	153.6	142.3
4	144.0	130.0	144.2	130.8	142.0
5	144.0	130.0	119.0	130.8	138.7
6	144.0	130.0	119.0	120.0	132.3
7	90.0	108.9	118.8	120.0	105.1
8	90.0	108.9	118.8	108.8	103.7
9	90.0	108.9	99.0	108.8	95.5
10	90.0	83.1	99.0	89.4	93.5
11	90.0	83.1	83.7	89.4	92.2
12	90.0	83.1	83.7	83.1	84.0
13	90.0	82.0	80.3	83.1	83.9
14	90.0	82.0	80.3	83.1	83.8
15	90.0	82.0	78.8	75.5	82.0
16	90.0	82.0	78.6	75.5	78.3
17	72.0	82.0	75.2	75.5	77.9
18	72.0	82.0	75.2	75.5	77.4
19	72.0	70.0	75.0	73.3	71.2
20	72.0	70.0	75.0	73.3	70.6
21	72.0	70.0	71.5	70.0	68.6
δ_1'	54.4	16.2	41.5	20.5	47.5 [b]
δ_2'	54.4	16.2	0	20.5	46.7 [b]
δ_3'	–	16.2	0	0	–

[a] Angles are listed by decreasing size. Abbreviations are PB, pentagonal bipyramid; CO, capped octahedron; CTP, capped trigonal prism; 4:3, the 4:3 piano stool structure. Interbond and dihedral angles of the reference geometries are from ref. 11. [b] Dihedral angles for this compound were calculated from the normalized atomic coordinates as previously described (see ref. 12).

calculated to be 47.5 and 46.7°. However, calculation of a least-squares-plane (Table 5) containing W, C(1), Sn(2), Sn(4), Sn(1) and Sn(3) clearly shows that these atoms are not coplanar as would be the case for a pentagonal bipyramid. This latter circumstance is probably the strongest argument against pentagonal bipyramidal geometry.

For the 4 : 3 case the angles between the triangular and quadrilateral faces as well as the angles across the diagonals of the quadrilateral face should be zero. In fact, the angle between the plane defined by atoms C(3), Sn(1) and Sn(4) and the best least-squares-plane calculated for C(1), C(2), Sn(2) and Sn(3) is 9.9°. In addition the dihedral angles across the diagonals of the quadrilateral face deviate from zero by 6.3°, (C(1)C(2)Sn(2)–C(1)C(2)Sn(3)) and 11.1° (Sn(2)Sn(3)C(2)–Sn(2)Sn(3)C(1).

It is obvious that while it is impossible to precisely fit the compound's geometry to any of the idealized geometries the 4 : 3 piano stool is probably the best description. Other compounds which have been described as 4 : 3 piano stools exhibit trigonal face-quadrilateral face dihedral angles between 4.8 and 9.3° [13]. In these cases, however, the dihedral angles across the diagonals of their quadrilateral faces are much closer to the idealized value ranging from 1.4 to 2.3°.

The W–CO distances are typical of those found in other tungsten carbonyls ranging between 1.95 and 1.98 Å [14–17]. The observed C–O distance and WCO angles are also typical of those found in other systems. Among the four bonding W–Sn distances, those involving the $SnPh_3$ groups were found to be slightly longer than those of the bidentate $(Ph_2Sn)_2O$-i-Pr ligand. Although the W–Sn distances show significant variations among each other [18], they are comparable in magnitude (2.760(2)–2.811(2) Å) to those found in $[CpW(CO)_3]_2SnPh_2$ (2.81 Å) [19]. Within the ten phenyl rings the C–C distances and angles were reasonable, averaging 1.42(3) and 119.8(28) Å. The distances from the Sn atoms to their point of attachment on the phenyl rings are comparable to those in other metal carbonyl-triphenyltin complexes [3,19], but show significant and apparently nonsystematic variations ranging from 2.00(3) to 2.28(2) Å. The Sn(1)–O(4) distance (2.16(3) Å) and Sn(4)–O(4) distance (2.13(2) Å) are similar and compare well to the corresponding distances in compounds such as $[Cl_3SnOH \cdot H_2O]_2 \cdot 3C_4H_8O_2$ (2.05(3) Å [20], $[Cl_3SnOMe \cdot MeOH]_2$ (2.0 Å) [21], $[Cl_3SnOEt \cdot EtOH]_2$ (2.08(1), 2.11(1) Å [22], $[Cy_3SnOAc]$ (2.12 Å) [23], and polymeric $[Me_3SnO(Me)SnMe_3]_x$ (2.26, 2.20 Å) [24].

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TABLE 5

LEAST-SQUARE PLANES[a], SELECTED DISTANCES FROM THE PLANES (Å) AND ANGLES (°) BETWEEN PLANES FOR $[(Ph_3Sn)_2((Ph_2Sn)_2O\text{-}i\text{-}Pr)W(CO)_3]$

Plane No.	*A*	*B*	*C*	*D*	Atom	*X*	*Y*	*Z*	Distance	ESD
1	0.0999	0.1854	−0.9776	−3.3699	Atoms in plane					
					W	2.9529	6.5151	4.9543	0.030	0.001
					C(1)	1.4315	5.2890	5.1251	−0.517	0.024
					Sn(1)	3.6138	9.1075	5.6312	−0.085	0.002
					Sn(2)	3.7601	3.9382	4.2774	0.294	0.002
					Sn(3)	0.5074	7.8702	4.6597	0.325	0.002
					Sn(4)	5.6929	6.6646	5.3400	−0.045	0.002
					Other atoms					
					C(2)	3.1274	6.8444	3.0436	1.976	0.033
					C(3)	3.1126	6.2564	6.9104	−1.915	0.028
					O(4)	5.6243	8.5965	6.2521	−0.586	0.017
					C(1C)	6.8054	9.3216	6.6768	−0.749	0.032
2	−0.4626	−0.2940	−0.8364	−9.0591	Atoms in plane					
					Sn(1)	3.6138	9.1075	5.6312	0.000	0.002
					Sn(4)	5.6929	6.6646	5.3400	0.000	0.002
					C(3)	3.1126	6.2564	6.9104	0.000	0.029
					Other atoms					
					W	2.9529	6.5151	4.9543	1.634	0.001
3	−0.5592	−0.3917	−0.7307	−6.7030	Atoms in plane					
					Sn(2)	3.7601	3.9382	4.2774	−0.068	0.002
					Sn(3)	0.5074	7.8702	4.6597	−0.068	0.002
					C(1)	1.4315	5.2890	5.1251	0.086	0.026
					C(2)	3.1274	6.8444	3.0436	0.049	0.036
3	−0.5592	−0.3917	−0.7307	−6.7030	Other atoms					
					W	2.9529	6.5151	4.9543	−1.120	0.001
4	−0.5177	−0.4273	−0.7412	−6.7999	Atoms in plane					
					C(1)	1.4315	5.2890	5.1251	0.000	0.026
					C(2)	3.1274	6.8444	3.0436	0.000	0.036
					Sn(2)	3.7601	3.9382	4.2774	0.000	0.002

5	−0.5867	−0.3424	−0.7339	−6.4119	Atoms in plane				
					C(1)	1.4315	5.2890	5.1251	0.000	0.026
					C(2)	3.1274	6.8444	3.0436	0.000	0.036
					Sn(3)	0.5074	7.8702	4.6597	0.000	0.002
6	−0.5898	−0.4209	−0.6891	−6.8232	Atoms in plane				
					Sn(2)	3.7601	3.9382	4.2774	0.000	0.002
					Sn(3)	0.5074	7.8702	4.6597	0.000	0.002
					C(2)	3.1274	6.8444	3.0436	0.000	0.036
7	−0.4824	−0.3198	−0.8155	−6.5614	Atoms in plane				
					Sn(2)	3.7601	3.9382	4.2774	0.000	0.002
					Sn(3)	0.5074	7.8702	4.6597	0.000	0.002
					C(1)	1.4315	5.2890	5.1251	0.000	0.026

Plane No.	Plane No.	Dihedral angle
1	2	44.2
1	3	54.2
2	3	9.9
4	5	6.3
4	6	5.1
4	7	7.8
5	6	5.2
5	7	7.7
6	7	11.1

[a] The equation of the plane is of the form: $A^{*}X + B^{*}Y + C^{*}Z - D = 0$ where A, B, C, D are constants and X, Y, Z are orthogonalized coordinates.

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