8.31; B, 3.30; Cl, 10.82; N, 4.27. Found: C, 58.52; H, 8.01; B, 3.35; Cl, 10.24; N, 4.09. Bromo compound **9b** (74%): mp 62–65 °C, $[\alpha]^{30}{}_{546}$ −37.1° (*c* 0.9, $CHCl_3$); 200-MHz NMR ($CDCl_3$) δ 0.75–2.5 (m, pinanediol + other), 3.45 (t, 2, $BrCH_2$), 4.2 (dd, 1, CHOB), 9.20 (br s, 1, NH). Anal. Calcd for $C_{16}H_{27}BBrNO_3$: C, 51.64; H, 7.31; B, 2.91; Br, 21.47; N, 3.76. Found: C, 51.76; H, 7.30; B, 2.98; Br, 21.32; N, 3.82.

Attempted Preparation of 1-Acetamido-4-hydroxybutane-1-boronic Acid. Homologation of (+)-pinanediol 3-(benzyloxy)propane-1-boronate (**7cz**) followed by conversion to the α-acetamido boronic ester **9c** was carried out as described for the halogen compounds in the preceding paragraph, but **9c** was not obtained analytically pure. Treatment with boron trichloride in dichloromethane[2] yielded a residue which was recrystallized from water. The 200-MHz NMR spectrum corresponded to 1-acetamido-2-phenylethane-1-boronic acid (D_2O, no internal ref): δ 1.35 (m, 2, CH_2CHB), 1.46 (m, 2, $CH_2CH_2CH_2$), 2.01 (s, 3, CH_3), 2.46 (t, 1, NCHB), 3.52 (m, 2, OCH_2), 4.724 (s, HOD), with small impurity peaks at δ 1.84 and 1.93. The analysis corresponded approximately to cocrystallization with 2 mol of boric acid. Anal. Calcd for $C_6H_{20}B_3NO_{10}$: C, 24.13; H, 6.75; B, 10.86; N, 4.69. Found: C, 23.42; H, 6.21; B, 10.46; N, 4.59.

((+)-Pinanediyldioxy)borane (10a). A solution of 17.0 g (10 mmol) of (+)-pinanediol in ~25 mL of THF was added dropwise to a solution of 7.6 g (10 mmol) of borane methyl sulfide in 25 mL of THF stirred under argon at 0 °C. The mixture was stirred at 20–25 °C for 2 h and then distilled to yield 78% of **10a**: bp 60–62 °C (0.2 torr); 200-MHz NMR ($CDCl_3$) δ 0.87 (s, 3, CH_3), 1.13 (d, J = 11 Hz, pinanyl CH), 1.30 (s, 3, CH_3), 1.40 (s, 3, CH_3), 1.8–2.4 (m, 5, pinanyl), 4.28 (dd, 1, CHOB), ~4–5 (very broad, visible only in integral, 1, B*H*). Anal. Calcd for $C_{10}H_{17}BO_2$: C, 66.71; H, 9.52; B, 6.00. Found: C, 67.09; H, 9.79; B, 6.17.

{[2-(2-Methoxyethyl)-6,6-dimethylbicyclo[3.1.1]heptane-2,3-diyl]dioxy}borane (10b). This compound was prepared from nopoldiol methyl ether[17] in the same manner as the pinanediol analogue **10a**, yield of **10b** 77%: bp 61–63 °C (0.2 torr); 200-MHz NMR ($CDCl_3$) δ 0.87 (s, 3, CH_3), 1.13 (d, J = 11 Hz, 1), 1.28 (s, 3, CH_3), 1.8–2.4 (m, 7), 3.32 (s, 3, OCH_3), 3.51 (t, 2, OCH_2CH_2), 4.46 (dd, 1, CHOB), ~4–5 (br, visible only in integral, 1, BH). Anal. Calcd for $C_{18}H_{21}BO_3$: C, 64.31; H, 9.45; B, 4.82. Found: C, 64.09; H, 9.46; B, 4.99.

Acknowledgment. We thank the National Institutes of Health for Grant No. GM27109, and the Boeing Corp. for a gift in support of departmental purchase of the Nicolet NT 200-MHz NMR instrument.

Registry No. **1a**, 90084-26-7; **1b**, 84110-34-9; **1c**, 84110-38-3; **1d**, 87190-25-8; **1e**, 78922-83-5; **2a**, 89618-77-9; **2b**, 85167-14-2; **2c**, 85167-12-0; **2d**, 90084-27-8; **2e**, 78902-03-1; **2e**-Br, 90084-28-9; **3e**, 78902-04-2; **4a**, 90084-29-0; **4b**, 87304-49-2; **4c**, 87249-62-5; **4e**, 90084-30-3; **5a**, 90084-31-4; **5b**, 90084-32-5; **6b** (X = Br), 90065-84-2; **6b** (X = Cl), 90191-39-2; **7ay**, 90084-33-6; **7az**, 90084-36-9; **7by**, 90084-34-7; **7bz**, 90084-37-0; **7cy**, 90084-35-8; **7cz**, 90084-38-1; **8a**, 90084-39-2; **8b**, 90084-40-5; **9a**, 90084-41-6; **9b**, 90084-42-7; **10a**, 90084-43-8; **10b**, 90084-44-9; $ClCH_2CH{=}CH_2$, 107-05-1; $BrCH_2CH{=}CH_2$, 106-95-6; $PhCH_2OCH_2CH{=}CH_2$, 14593-43-2; 2-propaneboronic acid, 80041-89-0; potassium (+)-pinanediol borate, 90130-50-0; lithiohexamethyldisilazane, 4039-32-1; (1,2-phenyldioxy)borane, 274-07-7; carbobenzyloxy chloride, 501-53-1.

---

[17] (a) Ray, R.; Matteson, D. S. *Tetrahedron* Lett. **1980**, *21*, 449–450. (b) Ray, R.; Matteson, D. S. *J. Indian Chem. Soc.* **1982**, *59*, 119–123.

Molecular Structure and Chemical Properties of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$, a Chromium Carbonyl Complex Containing Seven Unidentate Ligands

Jiann T. Lin, Gary P. Hagen, and John E. Ellis*

Department of Chemistry, The University of Minnesota, Minneapolis, Minnesota 55455

Received November 7, 1983

The X-ray structure of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ shows the presence of seven-coordinate chromium bound to four terminal carbonyl groups and three triphenyltin units. The anion is of approximate C_{3v} symmetry; a triangular face of tin atoms is capped by a carbon monoxide unit. This is the first structurally characterized chromium carbonyl complex containing seven unidentate ligands and the initial example of a molecule of the general formula $X_3Cr(CO)_4^-$. The crystalline material is triclinic (space group $P\bar{1}$) with cell parameters a = 14.371 (4) Å, b = 20.560 (10) Å, c = 10.730 (5) Å, α = 99.21 (4)°, β = 105.07 (3)°, γ = 83.29 (3)°, V = 3012 (4) Å^3, and Z = 2. Reactions of $(Ph_3Sn)_3Cr(CO)_4^-$ with Ph_3SnLi, MeLi, Ph_3P, and hexamethylphophoramide result in the loss of one triphenyltin group and the formation of moderate to high yields of the six-coordinate anion $(Ph_3Sn)_2Cr(CO)_4^{2-}$.

Introduction

In 1978 we reported that the reaction of $Na_4[Cr(CO)_4]$[1] with excess Ph_3SnCl provided a compound that gave elemental analyses and IR and ^1H NMR spectra consistent with the formulation $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$.[2,3] At that time, trhe anion in this salt was proposed to be the sole example of a molecule containing a chromium atom attached to seven unidentate ligands. Subsequently, other similar seven-coordinate molecules, including $H_2Cr(P(OMe)_3)_5$,[4] $Cr(CN\text{-}t\text{-}Bu)_7^{2+}$,[5] $H(Ph_3Sn)_3Cr(CO)_3^-$,[6] and $H(Ph_3Sn)_2Cr(CO)_4^-$,[3] have been reported. To verify the seven-coordinate nature of the chromium atom in

---

[1] Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 3605.

[2] Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296.

[3] Lin, J. T.; Hagen, G. P.; Ellis, J. E. *Organometallics* **1983**, *2*, 1145.

[4] Van Catledge, F. A.; Ittel, S. D.; Tolman, C. A.; Jerson, J. P. *J. Chem. Soc., Chem. Commun.* **1980**, 254.

[5] Dewan, J. C.; Miali, W. S.; Walton, R. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 133.

[6] Rochfort, G. L.; Ellis, J. E. *J. Organomet. Chem.* **1983**, *250*, 265.

0276-7333/84/2303-1288$01.50/0

Table I. Summary of Crystal Data and Intensity Collection for $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$

(A) Crystal Parameter at 23 °C

space group: $P\bar{1}$

a = 14.371 (4) Å

b = 20.560 (10) Å

c = 10.730 (5) Å

α = 99.21 (4)°

β = 105.07 (3)°

γ = 83.29 (3)°

V = 3012 (4) Å^3

Z = 2

mol wt: 1344.3

ρ(calcd) = 1.482 g/cm^3

cryst dimens: 0.15 × 0.15 × 0.25 mm

(B) Measurement of Intensity Data

radiation: λ(Mo Kα) = 0.710 73 Å

monochromator: graphite

abs coeff = 14.643 cm^{-1}

2θ limits: 0–50°

final no. of variables: 402

unique data used: 8042, $F_o^2 \geq 3.0\sigma(F_o^2)$

R^a = 0.048

$R_w{}^a$ = 0.066

error in observ of unit wt: 1.645

[a] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|)$, and $R_w = (\Sigma w(|F_o| - |F_c|))^2/(\Sigma w(|F_o| - |F_c|))^2/(\Sigma w|F_o|^2]^{1/2}$.

$[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$, a single-crystal X-ray analysis of this material was carried out. In this paper the results of this study and some of the reactivity patterns of this unusual molecule are presented.

Experimental Section

General procedures, solvent and reagent purifications, and the synthesis of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ have been described previously.[3]

Crystal Preparation and Crystallographic Analysis of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ (1). Heptane (3 mL) was layered on and allowed to slowly diffuse through a yellow dichloromethane solution (10 mL) containing 0.10 g of 1. After 1 day well-formed, air-stable yellow crystals had formed. These were washed with isopentane (2 × 10 mL) and dried in vacuo. A clear, pale yellow crystal cut to size of dimensions 0.15 × 0.15 × 0.25 mm was wedged inside a 0.2-mm glass capillary tube that was then flame sealed under argon and mounted on a goniometer head. The crystal was found to belong to the triclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs and by a Delauney reduction calculation.[7] The centrosymmetric space group $P\bar{1}$ (No. 2) was chosen, and this assignment was verified by the successful 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 background 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 no decay with time was noted. The intensities of 11 197 ($\pm h,\pm k,+l$) unique reflections were measured at 23 °C out to 2θ = 50° by using monochromatized Mo Kα radiation. The data were corrected for Lorentz, polarization, absorption, and background effects, using a value of 0.06 for p.[8]

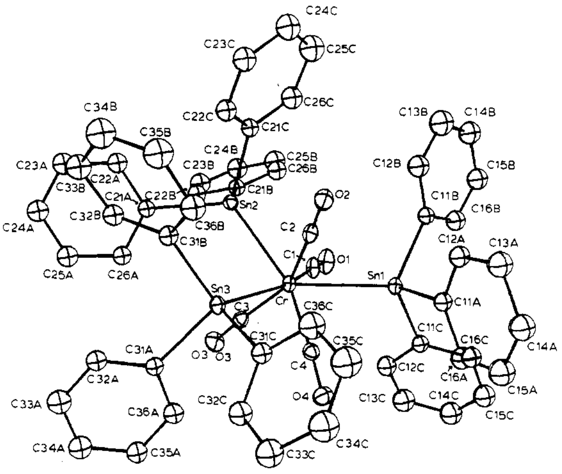


Figure 1. ORTEP drawing of $(Ph_3Sn)_3Cr(CO)_4^-$ showing the labeling scheme for all non-hydrogen atoms. Thermal ellipsoids are drawn with 20% probability boundaries.

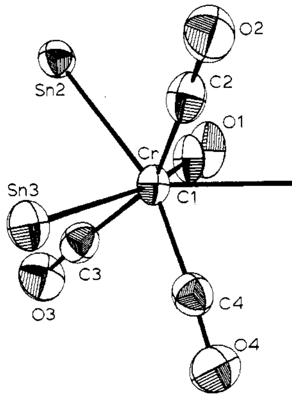


Figure 2. ORTEP drawing showing the coordination core of $(Ph_3Sn)_3Cr(CO)_4^-$.

Of the 11 197 unique reflections 8042 have $F_0^2 \geq 3.0\sigma(F_0^2)$ and were used for the final solution and refinement of the structure. A summary of crystal and intensity collection data is shown in Table I.

Solution and Refinement of the Structure. Conventional heavy-atom techniques were used in solving the structure of 1. The positions of tin atoms were determined from a Patterson map. Subsequent difference Fourier maps and cycles of least-squares refinement revealed the positions of the remaining non-hydrogen atoms.[9] The atomic scattering factors were taken from the usual tabulation.[10] A table of observed and calculated structure factors for 1 is available.[11] Anisotropic thermal parameters were used for the chromium, tin, carbonyl carbon and oxygen, and ethyl carbon atoms; owing to the limited data, isotropic thermal parameters were used for the remainder of the atoms in the compound. Hydrogen atoms in the anion 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 parameters for the atoms in 1 are in Table II, while selected distances and angles with esds are collected in Table III. The labeling scheme for the anion is shown in Figure 1, and an ORTEP drawing of the coordination core is shown in Figure 2. The ellipsoids in the latter were drawn with 20% probability boundaries. The final thermal parameters of all atoms are

---

(7) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described in: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsvele J., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Also: "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978.

(8) The intensity data were processed as described: "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/\mathrm{NPI})(C - 2B)$, where $K = 2.1166x$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$, where p is a factor used to down-weight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2(\sigma(I)/I)F_o$.

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

(10) Cromers, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromers, D. T. *Ibid.*, Table 2.3.1.

(11) See paragraph at end of paper regarding supplementary material.

Table II. Final Positional Parameters and Their Esd's for $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Sn(1)	0.01924 (3)	0.30270 (2)	0.21526 (4)	C(11A)	0.0415 (5)	0.3290 (3)	0.4229 (7)
Sn(2)	0.23159 (3)	0.15637 (2)	−0.00362 (5)	C(12A)	0.0547 (6)	0.2807 (4)	0.5022 (8)
Sn(3)	0.36745 (3)	0.28168 (2)	0.26886 (4)	C(13A)	0.0647 (7)	0.2968 (5)	0.6380 (9)
Cr	0.18107 (7)	0.27448 (5)	0.1281 (1)	C(14A)	0.0611 (7)	0.3653 (5)	0.6902 (9)
O(1)	0.0062 (4)	0.2542 (3)	−0.0945 (5)	C(15A)	0.0485 (7)	0.4127 (5)	0.6112 (10)
O(2)	0.2069 (4)	0.1864 (3)	0.3382 (5)	C(16A)	0.0395 (6)	0.3956 (4)	0.4761 (8)
O(3)	0.2493 (4)	0.3310 (3)	−0.0717 (5)	C(11B)	−0.0735 (5)	0.2222 (3)	0.1639 (7)
O(4)	0.1804 (4)	0.4164 (3)	0.2494 (6)	C(12B)	−0.0427 (7)	0.1595 (5)	0.1940 (9)
N	0.7371 (5)	0.3043 (4)	0.6252 (7)	C(13B)	−0.1062 (8)	0.1084 (6)	0.1663 (12)
C(1)	0.0726 (5)	0.2598 (4)	−0.0082 (7)	C(14B)	−0.2025 (8)	0.1226 (5)	0.1013 (10)
C(2)	0.1957 (5)	0.2198 (3)	0.2575 (6)	C(15B)	−0.2352 (7)	0.1839 (5)	0.0718 (10)
C(3)	0.2256 (5)	0.3082 (3)	0.0048 (7)	C(16B)	−0.1693 (6)	0.2345 (4)	0.1020 (9)
C(4)	0.1794 (5)	0.3614 (3)	0.2058 (7)	C(11C)	−0.0706 (5)	0.3857 (4)	0.1352 (7)
C(11)	0.8097 (8)	0.2632 (6)	0.7156 (13)	C(12C)	−0.0545 (6)	0.4104 (5)	0.0291 (9)
C(12)	0.7688 (13)	0.1980 (6)	0.7317 (14)	C(13C)	−0.1128 (8)	0.4668 (6)	−0.0159 (12)
C(21)	0.6423 (7)	0.3159 (8)	0.6682 (13)	C(14C)	−0.1818 (8)	0.4956 (6)	0.0471 (11)
C(22)	0.6635 (10)	0.3595 (7)	0.8140 (8)	C(15C)	−0.1981 (8)	0.4745 (5)	0.1476 (11)
C(31)	0.7059 (9)	0.2666 (7)	0.4914 (10)	C(16C)	−0.1429 (6)	0.4154 (5)	0.1951 (9)
C(32)	0.7969 (8)	0.2421 (7)	0.4331 (11)	C(21A)	0.3707 (5)	0.1442 (4)	−0.0537 (7)
C(41)	0.7842 (11)	0.3669 (8)	0.6302 (18)	C(22A)	0.4135 (6)	0.0803 (4)	−0.0750 (8)
C(42)	0.7238 (14)	0.4163 (7)	0.5402 (15)	C(23A)	0.4977 (7)	0.0683 (5)	−0.1153 (9)
C(24A)	0.5408 (7)	0.1206 (5)	−0.1409 (9)	C(33A)	0.5964 (7)	0.3573 (5)	0.1323 (10)
C(25A)	0.4977 (6)	0.1844 (4)	−0.1245 (9)	C(34A)	0.5576 (7)	0.4182 (5)	0.0965 (9)
C(26A)	0.4125 (6)	0.1969 (4)	−0.0801 (8)	C(35A)	0.4655 (6)	0.4398 (4)	0.1105 (8)
C(21B)	0.1425 (5)	0.1285 (4)	−0.1983 (7)	C(36A)	0.4129 (6)	0.4006 (4)	0.1560 (8)
C(22B)	0.1856 (6)	0.1231 (4)	−0.3044 (9)	C(31B)	0.4628 (5)	0.1960 (3)	0.3268 (7)
C(23B)	0.1306 (8)	0.1014 (5)	−0.4328 (11)	C(32B)	0.5239 (5)	0.1605 (4)	0.2519 (7)
C(24B)	0.0396 (8)	0.0865 (5)	−0.4539 (11)	C(33B)	0.5845 (7)	0.1056 (5)	0.2911 (9)
C(25B)	−0.0041 (8)	0.0907 (6)	−0.3539 (11)	C(34B)	0.5829 (8)	0.0846 (5)	0.4094 (11)
C(26B)	0.0481 (7)	0.1120 (5)	−0.2222 (9)	C(35B)	0.5255 (8)	0.1183 (5)	0.4841 (11)
C(21C)	0.2327 (5)	0.0746 (4)	0.1021 (7)	C(36B)	0.4636 (6)	0.1754 (5)	0.4442 (9)
C(22C)	0.3124 (6)	0.0597 (4)	0.1995 (8)	C(31C)	0.3725 (5)	0.3408 (4)	0.4574 (7)
C(23C)	−0.3103 (6)	−0.0148 (4)	−0.2829 (9)	C(32C)	0.4243 (6)	0.3979 (4)	0.4903 (9)
C(24C)	0.2279 (7)	−0.0160 (5)	0.2690 (10)	C(33C)	0.4310 (7)	0.4365 (5)	0.6147 (10)
C(25C)	−0.1440 (8)	0.0011 (6)	−0.1727 (11)	C(23C)	0.3878 (8)	0.4156 (6)	0.7041 (11)
C(26C)	0.1459 (7)	0.0449 (5)	0.0861 (9)	C(35C)	0.3366 (8)	0.3603 (6)	0.6729 (12)
C(31A)	0.4522 (5)	0.3386 (3)	0.1914 (7)	C(36C)	0.3281 (7)	0.3207 (5)	0.5447 (10)
C(32A)	0.5446 (5)	0.3176 (4)	0.1790 (8)				

available as supplementary material.[11]

Reactions of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ (1) with Various Nucleophiles. A. (Triphenylstannyl)lithium. A solution of 1, (1.00 g, 0.75 mmol) in 8 mL of THF was added to Ph_3SnLi (0.75 mmol), prepared in situ from Ph_3SnCl, in 10 mL of THF. After 4 h of stirring, a white precipitate formed that was filtered. Recrystallization of this material from CH_3CN–EtOH provided 0.33 g of material identical with that of genuine $[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$.[1,3] This represents a 79% yield, based on available Et_4N^+. Also, the initial filtrate was evaporated to provide a white residue that was dissolved in benzene, filtered, dried, and then recrystallized from CH_2Cl_2–EtOH. This purification provided 0.23 g (44% yield) of product that was identical with bona fide Ph_6Sn_2.[12]

B. Methyllithium. Methyllithium (0.65 mL of a 1.6 M solution in diethyl ether, ca. 1.0 mmol) was added to a solution of 1 (0.71 g, 0.53 mmol) in THF. After 2 h the clear solution was evaporated to dryness and washed with diethyl ether (3 ×10 mL). Treatment of the residue with $[Et_4N]Br$ (0.82 g, 3.9 mmol) in 15 mL of EtOH gave a white precipitate that was recrystallized from CH_3CN–EtOH to give 0.32 g (54%) of product identical with bona fide $[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$.[1,3]

C. Triphenylphosphine. A solution of PPh_3 (0.50 g, 1.9 mmol) and 1 (1.00 g, 0.74 mmol) was refluxed for 48 h in THF, which resulted in the formation of a white crystalline precipitate. This was collected and recrystallized from CH_3CN–EtOH to provide 0.21 g (50% yield based on available Et_4N^+) of genuine $[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$.[3]

Results and Discussion

Table III. Selected Distances and Angles with Esd's for $(Ph_3Sn)_3Cr(CO)_4^-$

(a) Distances (Å)

Cr–Sn(1)	2.695 (1)	C(4)–O(4)	1.151 (7)
Cr–Sn(2)	2.728 (1)	Sn(1)–C(11A)	2.155 (6)
Cr–Sn(3)	2.719 (1)	Sn(1)–C(11B)	2.159 (6)
Cr–C(1)	1.855 (6)	Sn(1)–C(11C)	2.167 (6)
Cr–C(2)	1.879 (6)	Sn(2)–C(21A)	2.178 (6)
Cr–C(3)	1.865 (6)	Sn(2)–C(21B)	2.174 (6)
Cr–C(4)	1.848 (6)	Sn(2)–C(21C)	2.169 (6)
C(1)–O(1)	1.147 (7)	Sn(3)–C(31A)	2.171 (5)
C(2)–O(2)	1.157 (6)	Sn(3)–C(31B)	2.170 (6)
C(3)–O(3)	1.146 (7)	Sn(3)–C(31C)	2.176 (6)

(b) Angles (deg)

Sn(1)–Cr–Sn(2)	125.28 (3)	C(2)–Cr–C(3)	152.2 (2)
Sn(1)–Cr–Sn(3)	127.77 (3)	C(2)–Cr–C(4)	108.4 (2)
Sn(2)–Cr–Sn(3)	89.83 (3)	C(3)–Cr–C(4)	83.5 (2)
Sn(1)–Cr–C(1)	69.7 (2)	Cr–C(1)–O(1)	176.1 (6)
Sn(1)–Cr–C(2)	75.1 (2)	Cr–C(2)–O(2)	178.5 (5)
Sn(1)–Cr–C(3)	132.6 (2)	Cr–C(3)–O(3)	176.8 (5)
Sn(1)–Cr–C(4)	71.9 (2)	Cr–C(4)–O(4)	176.5 (5)
Sn(2)–Cr–C(1)	76.9 (2)	Cr–Sn(1)–C(11A)	115.6 (2)
Sn(2)–Cr–C(2)	80.3 (2)	Cr–Sn(1)–C(11B)	113.0 (2)
Sn(2)–Cr–C(3)	82.6 (2)	Cr–Sn(1)–C(11C)	112.7 (2)
Sn(2)–Cr–C(4)	162.8 (2)	Cr–Sn(2)–C(21A)	118.1 (2)
Sn(3)–Cr–C(1)	162.5 (2)	Cr–Sn(2)–C(21B)	117.2 (2)
Sn(3)–Cr–C(2)	74.8 (2)	Cr–Sn(2)–C(21C)	111.8 (2)
Sn(3)–Cr–C(3)	83.4 (2)	Cr–Sn(3)–C(31A)	114.0 (2)
Sn(3)–Cr–C(4)	78.6 (2)	Cr–Sn(3)–C(31B)	123.5 (2)
C(1)–Cr–C(2)	113.3 (3)	Cr–Sn(3)–C(31C)	110.1 (2)
C(1)–Cr–C(3)	83.6 (2)		
C(1)–Cr–C(4)	111.5 (3)		

Numerous examples of seven-coordinate molybdenum and tungsten carbonyls exist for which there are no known chromium analogues. For example, when this study began, complexes of the type $X_3M(CO)_4^-$ were known only for molybdenum and tungsten.[13] Attempts to prepare the

---

[12] Wittig, G. *Angew. Chem.* **1950**, *62*, 231.

presently unknown anion $I_3Cr(CO)_4^-$ from the reaction of $ICr(CO)_5^-$ with iodine led instead to the formation of the paramagnetic monomer $ICr(CO)_5$,[13b] while corresponding reactions with the analogous molybdenum and tungsten compounds provided good yields of the seven-coordinate anions $I_3M(CO)_4^-$.[13] On this basis, our initial synthesis of compounds of the formula $(Ph_3Sn)_3M(CO)_4^-$ for all three group 6 metals was worthy.[1,3] Except for numerous compounds containing $C_5H_5Cr(CO)_3$ and related units, apparently the only molecules containing seven-coordinate chromium reported prior to this study[1] were $XCr(CO)_2(diars)_2^+$ [14] (X = Br, I; diars = *o*-phenylenebis(dimethylarsine)) and $HCr(CO)_2(dppe)_2^+$ [15] (dppe = 1,2-bis(diphenylphosphino)ethane). In this context, the recently reported tetrahydride $H_4Cr(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), containing eight-coordinate chromium, is of particular interest.[16]

Chemical Properties of $(Ph_3Sn)_3Cr(CO)_4^-$. Tetracarbonyltris(triphenylstannyl)chromate(1−) readily undergoes reactions with a variety of nucleophiles to provide the six-coordinate dianion $(Ph_3Sn)_2Cr(CO)_4^{2-}$ [3] as the only detectable carbonyl-containing product. For example, in the room-temperature reactions of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ (1) with Ph_3SnLi and MeLi, $[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$ was obtained in 79 and 54% isolated yields, respectively. From the former reaction a 44% yield of Ph_6Sn_2 was also isolated, indicating that the reaction proceeds mainly according to eq 1. No attempt was made

$$(Ph_3Sn)_3Cr(CO)_4^- + Ph_3Sn^- \rightarrow {}^1/_2(Ph_3Sn)_2 + (Ph_3Sn)_2Cr(CO)_4^{2-} \quad (1)$$

to determine the fate of the expelled Ph_3Sn group in the reaction of compound 1 with MeLi, but $MeSnPh_3$ was probably formed in this process. Similarly, when 1 is refluxed with excess PPh_3 in THF, a 50% yield of bona fide $[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$ precipitates from solution. In this case the fate of the expelled Ph_3Sn unit is obscure; however, in the absence of added Ph_3P no significant reaction occurs. More well-defined is the solvolysis of compound 1 in hexamethylphosphoramide (HMPA) that rapidly proceeds to completion at room temperature according to eq 2 and can be reversed on addition of excess

$$(Ph_3Sn)_3Cr(CO)_4^- + n\text{HMPA} \rightarrow Ph_3Sn(\text{HMPA})_n^+ + (Ph_3Sn)_2Cr(CO)_4^{2-} \quad (2)$$

THF, a much less basic solvent than HMPA. The pronounced tendency of compound 1 to undergo heterolytic cleavage of one Sn–Cr bond is not surprising in view of its sterically encumbered seven-coordinate nature. In this regard it resembles the related seven-coordinate vanadium compounds $Ph_3SnV(CO)_6$ [17] and $(Ph_3Sn)_2V(CO)_5^-$ [18a] that also tend to lose one triphenylstannyl group in the presence of Lewis bases.

X-ray Structure of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$. ORTEP drawings of the anion showing the labeling scheme and the coordination core of $(Ph_3Sn)_3Cr(CO)_4^-$ are shown in Figures 1 and 2, respectively. The compound consists of discrete cations and anions with no unusually short interionic contacts. The anion contains a seven-coordinate chromium atom bound to four terminal carbonyl groups and three well-separated triphenylstannyl units. In the latter respect this structure differs in a fundamentally important way from that of $(Ph_3PAu)_3V(CO)_5$ [18b] where the bulky Ph_3PAu units are in close proximity to one another due to significant Au–Au bonding interactions. By contrast, the Ph_3Sn units in $(Ph_3Sn)_3Cr(CO)_4^-$ clearly are repelled by one another.

Numerous seven-coordinate complexes have been prepared and structurally characterized during the past decade.[19] They have been described qualitatively or quantitatively[20] in terms of four idealized geometries: pentagonal bipyramid, capped octahedron, capped trigonal prism, or a 4:3 piano stool, where the energy barrier separating one geometry from another is calculated to be very small.[21] Visual inspection of an accurate model of $(Ph_3Sn)_3Cr(CO)_4^-$ indicates that it has approximately C_{3v} symmetry, where the C(2) carbonyl carbon unsymmetrically caps a trigonal face defined by Sn(1), Sn(2), and Sn(3). However, neither qualitative nor quantitative considerations[22] allow a clear choice between capped octahedral, capped trigonal prismatic, or 4:3 piano stool geometries.

Table III summarizes important interatomic distances and angles in the anion. None of the observed distances appear to be unreasonable with respect to those determined for other triphenyltin derivatives of metal carbonyls. For example, the mean Cr–Sn (2.71 (2) Å), Cr–C (1.86 (1) Å), Sn–C (2.169 (7) Å), and C–O (1.150 (5) Å) distances in $(Ph_3Sn)_3Cr(CO)_4^-$ compare favorably with corresponding values reported for $[Et_4N][(Ph_3Sn)_2V(CO)_5]$ (2.77 (1), 1.94 (4), 2.19 (1), and 1.16 (3) Å, respectively,[18] *trans*-$Ph_3SnCr(CO)_4(CNEt_2)$ 2.719 (2), 1.83–1.90, and 2.15–2.16 Å (no C–O distances reported)),[23] and *trans*-$Ph_3SnMn(CO)_4PPh_3$ (2.63 (1), 1.79 (5), 2.17 (4), and 1.15 (6) Å, respectively).[24] The Cr–C and C–O distances are also very similar to those determined for other anionic chromium carbonyl species including $[PPN]_2[Cr_2(CO)_{10}]$,[25] $[Et_4N][HCr_2(CO)_{10}]$,[25] $[PPN][Cr_2(CO)_{10}I]$,[25] and $[Ph_4P][HCr(CO)_5]$.[26] The tetraethylammonium cations are well separated from the anions and show no unusual features. The mean N–C and C–C distances are 1.52 (2) and 1.59 (4) Å, respectively, being in reasonable agreement with previously observed bond lengths in this cation.[18a] Although there is considerable scatter in individual values, the mean N–C–C and C–N–C angles of 111 (3) and 109 (5)° are approximately tetrahedral.

Concluding Remarks. Our study has shown that $(Ph_3Sn)_3Cr(CO)_4^-$ is indeed a seven-coordinate monoanion and the first example of a compound of the general formula $X_3Cr(CO)_4^-$. On the basis of our work, it seems likely that a variety of other compounds of this type should also exist. Since iodine atoms are far smaller than Ph_3Sn groups and I–Cr bonds should not be significantly shorter than Sn–Cr

---

[13] (a) Anker, M. W.; Colton, R.; Tomkins, I. B. *Rev. Pure Appl. Chem.* **1968**, *18*, 23. (b) King, R. B. *Inorg. Chem.* **1964**, *3*, 1039. (c) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1966**, *19*, 1779. (d) Moss, J. R.; Smith, B. J. *S. Afr. J. Chem.* **1983**, *36*, 32.

[14] Lewis, J.; Nyholm, R. S.; Pande, C. S.; Sandhu, S. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1964**, 3009.

[15] Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 2526.

[16] Girolani, G. S.; Salt, J. E.; Wilkinson, G.; Pelt, M. T.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954.

[17] Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 113.

[18] (a) Ellis, J. E.; Hayes, T. G.; Stevens, R. E. *J. Organomet. Chem.* **1981**, *216*, 191. (b) Ellis, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 6106.

[19] Drew, M. g. B. *Prog. Inorg. Chem.* **1977**, *23*, 67. (b) Kepert, D. L. *Ibid.* **1979**, *25*, 41.

[20] (a) Muetterties, E. L.; Guggenberger, *J. Am. Chem. Soc.* **1976**, *15*, 1464. (b) Dreyer, E. V.; Lam, C. T.; Lippard, S. J. *Inorg. Chem.* **1979**, *18*, 1904. (c) Kouba, J. K.; Wreford, S. S. *Ibid.* **1976**, *15*, 1464.

[21] Muetterties, E. L.; Wright, C. M. *Q. Rev.—Chem. Soc.* **1967**, *21*, 109.

[22] Lin, J. T. Ph.D. Thesis, The University of Minnesota, 1983.

[23] Fischer, E. O.; Fischer, H.; Schubert, U.; Pardy, R. B. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 871.

[24] Bryan, R. F. *J. Chem. Soc. A* 1967, 172.

[25] Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7312.

[26] Darensbourg, M. Y.; Bau, R.; Marks, M. W.; Burch, R. R.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.* **1982**, *104*, 6961.

bonds, it seems possible on the basis of steric arguments that the long sought $I_3Cr(CO)_4^-$ may be a viable species and failures to prepare this material previously[13] could be for kinetic and not thermodynamic reasons.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE 82-10496) for continuing support of this research. We also acknowledge the assistance of Professor Louis Pignolet with the crystal structure determination.

Registry No. 1, 67202-54-4; $[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$, 67202-48-6.

Supplementary Material Available: Tables of final thermal parameters and esds for non-hydrogen atoms of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ (1) (Table S-1), bond distances and angles with esds for $(C_2H_5)_4N^+$ in 1 (Table S-2), and final observed and calculated structure factors (Table S-3) (36 pages). Ordering information is given on any current masthead page.

Reactions of Alkylaluminum Reagents with Basic and Acidic Rhodium Compounds. X-ray Crystal and Molecular Structure of $(\eta\text{-}C_5H_5)Rh(PMe_3)_2(Al_2Me_4Cl_2)$, a Rhodium–Lewis Acid Adduct[†]

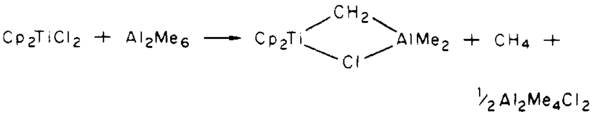
James M. Mayer*[‡] and J. C. Calabrese

E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Received January 6, 1984

A series of alkylaluminum adducts of cyclopentadienylrhodium compounds have been prepared, including $CpRhL_2(AlMe_3)$ (L = PMe_3, PMe_2Ph, PEt_3), $CpRh(PMe_3)_2(AlEt_3)$, $CpRh(C_2H_4)(PMe_3)(AlMe_3)$, and $CpRh(PMe_3)_2(Al_2Me_4Cl_2)$. The crystal and molecular structure at −100 °C of the last complex has been determined: space group $P2_1/n$, a = 15.696 (2) Å, b = 12.664 (2) Å, c = 12.544 (2) Å, β = 108.32 (1)°, V = 2367 (1) Å^3, Z = 4. The final conventional and weighted agreement indices on F_o for 4297 reflections with $F_o^2 > 2\sigma(F_o^2)$ are 0.025 and 0.029. The molecule has a normal "three-legged piano stool" geometry with a short, unbridged rhodium–aluminum bond (2.458 (1) Å). The structure of the $Al_2Me_4Cl_2$ ligand suggests that the complex can be described to some extent as a Rh–$AlMe_2$ cation with a weakly associated $AlMe_2Cl_2$ anion. NMR studies suggest that the trialkylaluminum adducts also have rhodium–aluminum bonds and that the aluminum ligand is extremely labile in solution. The kinetic parameters for dissociation of $AlMe_3$ from $CpRh(PMe_3)_2AlMe_3$ at 15 °C are k = 61 s^{-1}, $\Delta G^\ddagger$ = 14.4 (5) kcal/mol, $\Delta H^\ddagger$ = 18 (3) kcal/mol, and $\Delta S^\ddagger$ = 13 (10) eu. This $\Delta H^\ddagger$ corresponds roughly to the strength of the rhodium–aluminum dative bond. The acidic rhodium compounds $CpRhL(PMe_3)H^+$ react with trimethylaluminum not by deprotonation but by methyl for hydride exchange (making $CpRh(PMe_3)_2Me^+$ from $CpRh(PMe_3)_2H^+$) or methyl anion transfer ($CpRhMe(C_2H_5)PMe_3$ from $CpRh(C_2H_4)PMe_3(H)^+$).

The interactions of Lewis acidic reagents with metal carbonyl compounds have been extensively explored by Shriver and co-workers.[1] However, the chemistry of Lewis acids and metal complexes that do not contain an electronegative element like oxygen has received only sporadic attention.[2] Alkylaluminum reagents are extensively used in industrial processes like Ziegler–Natta polymerization.[3] Organoaluminum compounds have been used in transition-metal chemistry primarily as alkylating agents, although the Lewis acidity of aluminum also appears to be important,[4] as in the formation of "Tebbe's reagent" (eq 1, Cp = η^5-C_5H_5).[4a] We have investigated the reactions



(1)

of alkylaluminum compounds with the very basic rhodium complexes prepared by Werner,[5] in order to study the Lewis acid chemistry of the aluminum reagents.

Most of the examples of alkylaluminum–transition-metal complexes involve bridging carbonyls, alkyls, or hydrides;[6] there is only one firm example of an unbridged transition metal–aluminum bond: $[Cp(CO)_2Fe\text{–}AlPh_3]^-$.[7] The tungstenocene dihydride–trimethylaluminum adduct ($Cp_2WH_2\cdot AlMe_3$) was thought to contain a tungsten–aluminum bond,[8] but a recent crystal structure shows that

---

[†] Contribution No. 3434.

[‡] Present Address: Department of Chemistry, University of Washington, Seattle, WA 98195.

(1) (a) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272–3. (b) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093–5100. (c) Shriver, D. F.; Alich, A. *Coord. Chem. Rev.* **1972**, *8*, 15–20.

(2) (a) Werner, H. *Pure Appl. Chem.* **1982**, *54*, 177–188. (b) Kotz, J. C.; Pedrotty, D. G. *Organomet. Chem. Rev., Sect. A* **1969**, *4*, 479–547. (c) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231–8.

(3) (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (b) Boor, J., Jr. "Ziegler-Natta Catalysis and Polymerizations"; Academic Press: New York, 1979.

(4) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3. (b) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. I. (c) Isobe, K.; deMiguel, A. V.; Maitlis, P. M. *J. Organomet. Chem.* **1983**, *250*, C25–7.

(5) (a) Reference 2a and references therein. (b) Werner, H.; Feser, R.; Buchner, W. *Chem. Ber.* **1979**, *112*, 834–843.

(6) (a) Reference 1c. (b) Hsieh, A. T. T. *Inorg. Chem. Acta* **1975**, *14*, 87–104. (c) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5412. (d) Tebbe, F. N.; Guggenberger, L. J. *J. Chem. Soc., Chem. Commun.* **1973**, 227–8. (e) Forder, R. A.; Prout, K. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2312. (f) Rogers, R. D.; Cook, W. J.; Atwood, J. L. *Inorg. Chem.* **1979**, *18*, 279–282. (g) Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, 235.

(7) Burlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1097–1105.

(8) (a) Brunner, H.; Wailes, P. C.; Kaesz, H. D. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 125–9. (b) Storr, A.; Thomas, B. S. *Can. J. Chem.* **1971**, *49*, 2504–7.

0276-7333/84/2303-1292$01.50/0