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SIX- AND SEVEN-COORDINATE MAIN GROUP IV METAL DERIVATIVES OF PENTACARBONYLVANADATE(3—) ION. STRUCTURAL CHARACTERIZATION OF TETRAETHYLAMMONIUM BIS(TRIPHENYLSTANNYL)-PENTACARBONYLVANADATE

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Summary

Organotin and triphenyllead derivatives $(Ph_3Sn)_2V(CO)_5^-$, $((C_6H_{11})_3Sn)$-$(Ph_3Sn)V(CO)_5^-$, $(Me_3Sn)(Ph_3Sn)V(CO)_5^-$ and $(Ph_3Pb)_2V(CO)_5^-$ containing seven-coordinate vanadium have been isolated as tetraethylammonium salts in 40—80% yields from the reactions of appropriate organometal halides with $Ph_3EV(CO)_5^{2-}$ (E = Sn, Pb). The latter have been prepared by the reduction of $[Et_4N][(Ph_3E)_2V(CO)_5]$ and are the first reported organotin and -lead metal carbonyl derivatives which contain a transition metal in a formal negative oxidation state. The crystal structure of $[Et_4N][(Ph_3Sn)_2V(CO)_5]$, which is synthesized in low yields (ca. 15%) from the photolysis of $[Et_4N][V(CO)_6]$ in the presence of Ph_6Sn_2, has been determined by single crystal X-ray diffraction techniques. The anion contains two Sn—V bonds with a Sn—V—Sn angle of 137.9(1)°. Its geometry is discussed in terms of three possible seven-coordination environments.

Introduction

The remarkable thermal, solvolytic and air stabilities exhibited by many organometal Group IV-metal carbonyl compounds have made these compounds important and useful in the derivatization of numerous extremely sensitive monomeric metal carbonyl anions. Hein was the first to prepare heterobimetallic compounds containing Main Group IV and transition metals. Examples include $(Ph_3Pb)_2Fe(CO)_4$ (from Ph_3PbOH and $Ca(HFe(CO)_4)_2$) [1] and $Ph_3SnCo(CO)_4$ (from Ph_3SnOH and $NaCo(CO)_4$) [2]. Gorsich first demonstrated that oxygen- and moisture-stable Ph_3EM (E = Sn, Pb; M = $Mn(CO)_5$, C_5H_5Fe-$(CO)_2$) species were easily prepared in high yields from Ph_3ECl and M^- [3].

Our research group later found that similar derivatives were extremely useful in the characterization of previously unknown highly reduced carbonyl anions,

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including $Na_3M(CO)_4$ (M = Mn and Re) [4], $Na_3M(CO)_3$ (M = Co, Rh and Ir) [5], $Na_4M(CO)_4$ (M = Cr, Mo and W) [6] and $Na_3V(CO)_5$ [7]. The preparation of stable derivatives of the vanadium carbonyl anion was especially important since $Na_3V(CO)_5$ proved to be thermally unstable [7,8]. In this paper we discuss syntheses and some chemical properties of organotin and triphenyllead derivatives of $V(CO)_5^{3-}$ and report on the structural characterization of a key compound in this series, tetraethylammonium bis(triphenylstannyl)pentacarbonylvanadate. Portions of the results in this paper have been the subject of a preliminary communication [7].

Experimental

General procedures and starting materials

All synthetic procedures, except where noted, were carried out in standard taper glassware under prepurified argon or nitrogen, or in a Vacuum Atmospheres Corporation drybox under continually recirculating nitrogen. Tank argon or nitrogen was scrubbed by concentrated H_2SO_4, deoxygenated by a 1.5 meter column of activated copper catalyst (BASF), and dried by a second 1.5 meter column of molecular sieves (Linde) and $Mg(ClO_4)_2$.

Solutions were transferred via stainless steel cannulae where possible, or in syringes with nylon stopcocks. Infrared solution spectra were recorded in 0.1 mm sealed NaCl cells, equipped with steel stopcocks to exclude air. Nujol and Fluorolube mulls of air sensitive compounds were prepared in the drybox between polished NaCl disks. Spectra were recorded on a Perkin—Elmer 283 grating spectrophotometer. NMR samples, sealed into 5 mm Pyrex tubes, were run on either a Varian T60 or FT80 spectrometer. Microanalyses were performed by Galbraith Laboratory.

Since several of the compounds described are highly susceptible to oxidation in solution, special care was taken in deoxygenating solvents. Tetrahydrofuran (THF), diethyl ether, benzene, toluene, heptane, and isopentane were distilled from alkali metal-benzophenone ketyls immediately before use where necessary. Dichloromethane, ethanol and acetone were dried over 4A molecular sieves (Linde) and saturated with nitrogen. Solvents used for recording the NMR spectra were degassed by freeze—thawing three times (or until no effervescence was noted at the melting point).

The following solid reactants were purchased from commercial sources and used without further purification except the customary degassing: bis(diglyme)-sodium hexacarbonylvanadate, tetraethylammonium bromide, hexaphenylditin, triphenyllead chloride, triphenyltin chloride, tricyclohexyltin bromide, and trimethyltin chloride. Tetraethylammonium salts of bis(triphenylplumbyl)-pentacarbonylvanadate were prepared from $Na_3V(CO)_5$ by previously reported methods [7,8] in addition to those mentioned below. Tetraethylammonium hexacarbonylvanadate was prepared as described previously [25].

Synthetic procedures

$[Et_4N]_2[Ph_3PbV(CO)_5]$ (I). Sodium amalgam (5 ml, 0.8% Na) was added to a solution of $[Et_4N][(Ph_3Pb)_2V(CO)_5]$ [7] (0.80 g, 0.67 mmol) in THF (20 ml) and stirred for 15 minutes at room temperature. During this time the solution

darkened due to the formation of lead metal, and yellow crystals precipitated. Infrared spectra in the ν(CO) region indicated that all reactant was consumed during this period. After removal of excess Na-Hg, excess tetraethylammonium bromide (2.1 g, 10 mmol) in ethanol (20 ml) was added which caused additional precipitation of product. The solid was collected on a medium porosity fritted disc, dried and dissolved in 60 ml of acetone at 0°C to provide a thermally unstable and extremely air-sensitive solution. Acetone was removed from the filtrate in vacuo at —20°C until ca. 5 ml remained. Dropwise addition of heptane (60 ml) provided a dark crystalline solid. Rapid recrystallization from cold (0°C) acetone/THF (60/180 ml) gave 0.19 g (32% yield) of yellow crystalline and analytically pure I. Attempts to characterize this slightly soluble material by ^{1}H NMR spectroscopy were unsuccessful due to its thermal instability in solution. Anal. Found: C, 52.88; H, 6.45; N, 3.15. Calcd. for $C_{39}H_{55}N_2O_5PbV$: C, 52.63; H, 6.23; N, 3.15% (decomposes slowly without melting above 50°C).

$[Et_4N]_2[Ph_3SnV(CO)_5]$ (II). Method 1: Excess lithium wire (0.067 g, 9.7 mmol) and Ph_3SnCl (0.75 g, 1.95 mmol) were magnetically stirred in 25 ml THF for 12 h under a nitrogen atmosphere to prepare the usual deep green-black solution of Ph_3SnLi [9]. This solution was filtered into a flask containing $[Et_4N][(Ph_3Sn)_2V(CO)_5]$ [7] (0.89 g, 0.87 mmol) and stirred until infrared spectra indicated all reactant was consumed (ca. 3 h). Addition of excess tetraethylammonium bromide (2.0 g) in 45 ml THF/ethanol (5/40 V/V) precipitated yellow II. Dissolution of this solid in 80 ml acetone followed by filtration (medium porosity fritted disc) and evaporation of the solution gave yellow crystals of II contaminated with Et_4NBr. By triturating this mixture with ethanol (3 X 10 ml) the analytically pure sample of II was obtained (0.31 g; 44% yield). Anal. Found: C, 58.86; H, 6.75; N, 3.62; Sn, 14.96. Calcd. for $C_{39}H_{55}N_2O_5SnV$: C, 58.43; H, 6.87; N, 3.50; Sn, 14.86%. (Slowly darkens above 210°C; melts with decomposition 224—225°C.)

Method 2: Reduction of $[Et_4N][(Ph_3Sn)_2V(CO)_5]$ (1.39 g, 1.36 mmol) by 0.8% sodium-amalgam (5 ml) in THF (40 ml) also provided II. After 72 h only ν(CO) bands consistent with $Ph_3SnV(CO)_5^{2-}$ were observed. Excess tetraethylammonium bromide (2.0 g) in ethanol (20 ml) was added to completely precipitate the product. This was dissolved in acetone and purified as in method 1 to provide 0.91 g (84% yield) of yellow crystalline II. Salts obtained by both methods had identical infrared spectra.

$[Et_4N][(C_6H_{11})_3Sn)(Ph_3Sn)V(CO)_5]$(III). A slurry of II (0.40 g, 0.50 mmol) in acetone (50 ml) was stirred with a suspension of $(C_6H_{11})_3SnBr$ in THF (20 ml). As the yellow crystalline II slowly dissolved a white precipitate of Et_4NBr formed. After 6 h all but 10 ml of solvent mixture was removed. Addition of water (50 ml) caused a yellow precipitate to form. This solid was collected on a coarse frit, washed with water (15 X 10 ml) and dried in vacuo. The product was dissolved in THF (20 ml). After removal of all but 5 ml of THF from the clear yellow solution, ether (~100 ml) was slowly added whereupon finely divided crystalline III formed. Recrystallization of III from THF/heptane (5/40 ml) followed by washing with ether (2 X 20 ml) provided 0.90 g (44% yield) of analytically pure III. Anal. Found: C, 56.72; H, 6.93; N, 1.37. Calcd. for $C_{49}H_{68}NO_5Sn_2V$: C, 56.59; H, 6.55; N, 1.35%. (Decomposes without melting above 180°C.) III is practically insoluble in water, hydrocarbons and diethyl ether, but dis-

solves in most polar organic solvents to provide oxygen-sensitive yellow-orange solutions.

$[\mathrm{Et_4N}][(\mathrm{Me_3Sn})(\mathrm{Ph_3Sn})\mathrm{V(CO)_5}]$ (IV). A mixture of II (0.40 g, 0.50 mmol) and $\mathrm{Me_3SnCl}$ (0.10 g, 0.50 mmol) was stirred for 12 h in THF. After removal of solvent in vacuo, the resulting solid was triturated with ethanol (4 × 20 ml) and then dissolved in acetone (20 ml). Slow concentration of the yellow solution provided product. Recrystallization of the product from acetone/ether followed by washing the product with isopentane (2 × 10 ml) provided 0.16 g (38% yield) of analytically pure yellow crystalline IV. Anal. Found: C, 49.27; H, 5.51; N, 1.54. Calcd. for $\mathrm{C_{34}H_{44}NO_5Sn_2V}$: C, 48.90; H, 5.32; N, 1.68%. (Decomposes slowly without melting above 100°C). The solubility properties of IV are very similar to those of III (vide supra).

$[\mathrm{Et_4N}][(\mathrm{Ph_3E})_2\mathrm{V(CO)_5}]$ (E = Sn(V), M = Pb(VI)). Method 1: A mixture of II (0.40 g, 0.50 mmol) and $\mathrm{Ph_3SnCl}$ (0.20 g, 0.50 mmol) was stirred for 6 h in THF. Removal of solvent and subsequent work up as for IV provided 0.39 g (76% yield) of V which had an infrared spectrum identical to that of genuine $[\mathrm{Et_4N}][(\mathrm{Ph_3Sn})_2\mathrm{V(CO)_5}]$ prepared from $\mathrm{V(CO)_5}^{3-}$ [7]. The reaction of I and $\mathrm{Ph_3PbCl}$ is performed and worked up in the same manner as shown above and provides 70—80% yields of VI, identical to genuine $[\mathrm{Et_4N}][(\mathrm{Ph_3Pb})_2\mathrm{V(CO)_5}]$ prepared previously [7].

Method 2 (E = Sn): A solution 1.50 g (4.3 mmol) $[\mathrm{Et_4N}][\mathrm{V(CO)_6}]$ and 6.0 g (8.6 mmol) $\mathrm{Ph_6Sn_2}$ in THF (150 ml) was photolyzed at room temperature under a partial vacuum (ca. 300 mmHg) to promote removal of carbon monoxide. Photolyses were conducted in a borosilicate reaction vessel similar to Ace Glass Model 6515. A high pressure Hanovia quartz mercury vapor lamp (450 W, Model 679 A-36) inside a cooled quartz photochemical immersion well (Ace Glass Model 6515-25) served as the radiation source. The use of a Pyrex filter did not improve product yield. Reaction progress was monitored by infrared spectroscopy. Photolysis was stopped after 1.5 h when the product band at 1983 $\mathrm{cm^{-1}}$ discontinued growing. After filtering off a very slightly soluble red-brown metal carbonyl-containing solid which was not further characterized, all but 40 ml solvent was removed in vacuo. Addition of 100 ml ethanol followed by cooling in ice caused precipitation of most unreacted $\mathrm{Ph_6Sn_2}$. Three acetone/ether recrystallizations separated unreacted $[\mathrm{Et_4N}][\mathrm{V(CO)_6}]$ from the less soluble product and provided 0.60 g (14% yield) of orange crystalline $[\mathrm{Et_4N}][(\mathrm{Ph_3Sn})_2\mathrm{V(CO)_5}]$ which had an infrared spectrum superimposable with that of the genuine substance [7].

X-Ray crystallographic study of $[\mathrm{Et_4N}][(\mathrm{Ph_3Sn})_2\mathrm{V(CO)_5}]$ (V)

Crystals of V were grown via a vapor diffusion of THF/xylene over a period of two weeks. A suitable crystal of dimensions 0.10 × 0.25 × 0.40 mm was selected and used in the structural determination. The salt crystallizes with four formula species in a monoclinic unit cell. The space group was determined to be $P2_1/n$ from the systematic absences in the data. The single independent anion ideally conforms to C_1 —1 point symmetry. The unit cell dimensions were determined by least-squares refinement of the angular settings of 15 peaks with 2θ values between 15 and 25° centered on the diffractometer and are $a = 10.428(2)$ Å, $b = 20.962(5)$ Å, $c = 21.146(3)$ Å, $\alpha = 90.000(-)°$, $\beta =$

(Continued on p. 199)

TABLE 1

INFRARED-ACTIVE CARBONYL STRETCHING FREQUENCIES AND ^{1}H NMR DATA FOR ORGANOTIN AND LEAD DERIVATIVES OF $V(CO)_5^{3-}$

Compound		ν(CO) (cm^{-1})	NMR (acetone-d_6, δ (ppm))
$[Et_4N]_2[Ph_3PbV(CO)_5]$	Nujol [a, b]	1934m, 1825(sh), 1779s(broad)	[b]
$[Et_4N]_2[Ph_3SnV(CO)_5]$	Nujol [a]	1923m, 1819m, 1771s, 1727s	1.33 (t of t, 24 H, -CH_3), 3.46 (q, 16 H, -CH_2-), 7.28, 7.60 (m, 15 H, phenyl)
	CH_3CN	1927m, 1782s, 1750(sh)	
$[Et_4N][(C_6H_{11})_3Sn)(Ph_3Sn)V(CO)_5]$	THF	1971m, 1864s(br)	1.35 (t of t, 12 H, -CH_3), 1.76 (m, 33 H, cyclohexyl), 3.45 (q, 8 H, -CH_2), 7.17, 7.63 (m, 15 H, phenyl)
$[Et_4N][(Me_3Sn)(Ph_3Sn)V(CO)_5]$	THF	1974m, 1877s(br)	0.39 (s, 9 H, Sn—CH_3), 1.36 (t of t, 12 H, -CH_3), 3.49 (q, 8 H, -CH_2-), 7.19, 7.61 (m, 15 H, phenyl)

[a] Nujol mull. [b] Thermal instability precluded obtaining reproducible solution spectra.

TABLE 2

ATOMIC AND GROUP PARAMETERS FOR [TEA][$(Ph_3Sn)_2V(CO)_5$]

Positional parameters [a]

	x/a	*y/b*	*z/c*
V	0.2740(3)	0.1474(2)	0.2285(1)
O(2)	0.0402(16)	0.2392(7)	0.2212(8)
O(1)	0.3481(20)	0.2406(8)	0.1256(9)
O(3)	0.4880(12)	0.0551(6)	0.2876(6)
O(4)	0.4518(14)	0.2436(8)	0.3047(9)
O(5)	0.0516(14)	0.0529(8)	0.1870(7)
CC(2)	0.1290(20)	0.2059(10)	0.2251(9)
CC(1)	0.3196(24)	0.2022(9)	0.1620(12)
CC(3)	0.4038(20)	0.0884(9)	0.2649(8)
CC(4)	0.3859(20)	0.2073(9)	0.2756(10)
CC(5)	0.1332(20)	0.0853(8)	0.2027(8)
N(1)	—0.2657(12)	0.3950(7)	0.1824(6)
C(1)	—0.1833(22)	0.3478(10)	0.2246(11)
C(2)	—0.2643(34)	0.3021(13)	0.2658(14)
C(3)	—0.3557(21)	0.4362(12)	0.2188(12)
C(4)	—0.2696(25)	0.4794(11)	0.2682(12)
C(5)	—0.3660(21)	0.3564(12)	0.1401(11)
C(6)	—0.3064(28)	0.3075(14)	0.0938(13)
C(7)	—0.1699(23)	0.4303(10)	0.1443(11)
C(8)	—0.2363(29)	0.4840(13)	0.0991(12)
Sn(1)	0.1985(1)	0.1204(1)	0.3470(1)
Sn(2)	0.3590(1)	0.0808(1)	0.1266(1)
C(11)	0.1823(11)	0.0186(4)	0.3702(6)
C(12)	0.2244(10)	—0.0300(6)	0.3326(4)
C(13)	0.2207(11)	—0.0930(5)	0.3529(6)
C(14)	0.1748(11)	—0.1075(4)	0.4107(6)
C(15)	0.1327(11)	—0.0589(6)	0.4483(4)
C(16)	0.1364(11)	0.0041(5)	0.4281(5)
H(12)	0.2574(15)	—0.0196(8)	0.2910(5)
H(13)	0.2510(16)	—0.1280(6)	0.3258(8)
H(14)	0.1721(17)	—0.1528(5)	0.4253(9)
H(15)	0.0997(16)	—0.0693(9)	0.4900(5)
H(16)	0.1061(16)	0.0391(4)	0.4552(7)
C(21)	0.0113(11)	0.1532(6)	0.3712(6)
C(22)	—0.0002(13)	0.1897(6)	0.4252(5)
C(23)	—0.1214(16)	0.2076(6)	0.4410(5)
C(24)	—0.2311(12)	0.1890(7)	0.4027(8)
C(25)	—0.2196(12)	0.1525(7)	0.3487(7)
C(26)	—0.0984(15)	0.1346(6)	0.3329(6)
H(22)	0.0787(16)	0.2030(9)	0.4527(8)
H(23)	—0.1296(24)	0.2338(8)	0.4799(7)
H(24)	—0.3182(14)	0.2019(10)	0.4141(11)
H(25)	—0.2986(15)	0.1391(10)	0.3212(10)
H(26)	—0.0902(22)	0.1084(8)	0.2940(7)
C(31)	0.3371(12)	0.1492(7)	0.4262(5)
C(32)	0.3499(12)	0.2121(6)	0.4465(6)
C(33)	0.4428(13)	0.2282(5)	0.4957(6)
C(34)	0.5228(11)	0.1813(7)	0.5245(5)
C(35)	0.5100(12)	0.1184(6)	0.5041(6)
C(36)	0.4172(13)	0.1023(5)	0.4550(6)
H(32)	0.2923(17)	0.2458(8)	0.4258(9)
H(33)	0.4520(19)	0.2735(6)	0.5103(9)
H(34)	0.5896(15)	0.1929(10)	0.5598(7)
H(35)	0.5676(17)	0.0847(8)	0.5248(9)
H(36)	0.4080(20)	0.0571(6)	0.4403(9)
C(41)	0.2409(18)	0.0911(9)	0.0364(7)

TABLE 2 (continued)

	x/a	y/b	z/c
C(42)	0.1893(23)	0.0352(7)	0.0092(8)
C(43)	0.1106(23)	0.0377(7)	−0.0478(9)
C(44)	0.0834(18)	0.0960(9)	−0.0775(7)
C(45)	0.1350(20)	0.1518(7)	−0.0502(8)
C(46)	0.2137(19)	0.1494(7)	0.0068(8)
H(42)	0.2089(34)	−0.0067(8)	0.0305(12)
H(43)	0.0735(39)	−0.0025(8)	−0.0674(13)
H(44)	0.0268(26)	0.0977(12)	−0.1184(9)
H(45)	0.1154(30)	0.1938(8)	−0.0715(12)
H(46)	0.2508(30)	0.1896(9)	0.0264(12)
C(51)	0.5537(10)	0.1090(7)	0.1068(7)
C(52)	0.5912(13)	0.1046(8)	0.0456(6)
C(53)	0.7174(15)	0.1183(8)	0.0346(5)
C(54)	0.8063(10)	0.1365(7)	0.0847(8)
C(55)	0.7688(12)	0.1410(7)	0.1458(6)
C(56)	0.6425(14)	0.1272(7)	0.1569(5)
H(52)	0.5273(18)	0.0915(11)	0.0096(7)
H(53)	0.7444(21)	0.1151(11)	−0.0094(6)
H(54)	0.8971(11)	0.1464(10)	0.0768(11)
H(55)	0.8327(17)	0.1541(10)	0.1819(8)
H(56)	0.6156(20)	0.1304(10)	0.2008(6)
C(61)	0.3748(14)	−0.0226(5)	0.1385(6)
C(62)	0.2781(11)	−0.0590(7)	0.1614(6)
C(63)	0.2901(13)	−0.1250(7)	0.1650(6)
C(64)	0.3989(16)	−0.1546(5)	0.1456(6)
C(65)	0.4957(12)	−0.1182(7)	0.1227(6)
C(66)	0.4836(11)	−0.0522(7)	0.1191(5)
H(62)	0.1998(14)	−0.0378(10)	0.1754(8)
H(63)	0.2205(18)	−0.1512(9)	0.1815(8)
H(64)	0.4076(23)	−0.2020(5)	0.1482(9)
H(65)	0.5740(14)	−0.1395(11)	0.1087(8)
H(66)	0.5532(15)	−0.0260(10)	0.1026(8)

B. Thermal parameters $^{a, b}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.058(2)	0.048(2)	0.047(2)	0.009(1)	0.001(1)	−0.001(1)
O(2)	0.113(14)	0.079(12)	0.153(15)	0.045(10)	−0.051(12)	−0.002(11)
O(1)	0.225(21)	0.073(13)	0.143(16)	0.010(13)	0.099(15)	0.036(12)
O(3)	0.062(10)	0.076(11)	0.092(11)	0.024(8)	−0.001(8)	0.016(9)
O(4)	0.071(12)	0.108(14)	0.205(20)	−0.036(10)	−0.007(12)	−0.057(13)
O(5)	0.076(12)	0.109(14)	0.114(13)	0.005(10)	−0.006(10)	−0.044(11)
CC(2)	0.076(17)	0.063(17)	0.068(15)	−0.001(13)	−0.002(13)	0.015(12)
CC(1)	0.134(23)	0.027(14)	0.135(22)	0.007(14)	0.064(18)	−0.018(14)
CC(3)	0.085(17)	0.049(14)	0.041(12)	−0.013(12)	0.031(11)	−0.026(11)
CC(4)	0.078(17)	0.044(15)	0.095(17)	−0.021(12)	−0.018(14)	−0.002(13)
CC(5)	0.090(17)	0.032(13)	0.039(12)	0.033(13)	0.014(11)	−0.007(10)
N(1)	0.044(11)	0.105(15)	0.062(11)	−0.007(10)	−0.030(9)	0.028(11)
C(1)	0.128(24)	0.092(20)	0.116(22)	0.005(17)	−0.040(18)	0.010(17)
C(2)	0.276(41)	0.099(24)	0.139(27)	−0.058(24)	0.045(26)	0.026(20)
C(3)	0.080(20)	0.132(25)	0.146(25)	0.045(17)	0.021(18)	−0.030(20)
C(4)	0.158(26)	0.091(22)	0.117(23)	0.018(18)	0.044(20)	0.000(17)
C(5)	0.089(21)	0.183(31)	0.104(22)	−0.024(19)	−0.012(17)	−0.007(20)
C(6)	0.187(33)	0.168(31)	0.129(26)	−0.018(25)	−0.011(23)	−0.067(23)
C(7)	0.144(25)	0.072(20)	0.142(25)	−0.020(17)	0.068(20)	−0.006(17)
C(8)	0.211(33)	0.137(27)	0.099(22)	−0.004(24)	0.029(21)	0.053(20)
Sn(1)	0.052(0)	0.051(0)	0.042(0)	0.002(0)	0.001(0)	−0.002(0)
Sn(2)	0.057(1)	0.054(1)	0.042(0)	0.007(0)	0.002(0)	−0.001(0)

TABLE 2 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(11)	0.057(12)	0.046(13)	0.056(16)	0.000(12)	−0.006(7)	0.001(5)
C(12)	0.062(17)	0.051(15)	0.060(33)	−0.006(16)	0.001(8)	−0.005(8)
C(13)	0.059(14)	0.048(12)	0.085(51)	−0.002(12)	0.003(10)	−0.006(10)
C(14)	0.059(7)	0.049(6)	0.077(46)	−0.003(5)	−0.013(11)	0.009(6)
C(15)	0.070(10)	0.060(8)	0.055(19)	−0.014(8)	−0.009(6)	0.004(6)
C(16)	0.064(7)	0.053(6)	0.059(9)	−0.008(6)	0.001(5)	−0.006(6)
H(12)	0.077(26)	0.066(19)	0.063(37)	−0.021(22)	0.008(9)	−0.013(11)
H(13)	0.065(23)	0.053(13)	0.125(72)	−0.008(17)	0.020(17)	−0.022(17)
H(14)	0.062(12)	0.053(6)	0.105(65)	−0.006(8)	−0.021(18)	0.019(7)
H(15)	0.091(23)	0.081(21)	0.054(13)	−0.035(19)	−0.008(7)	0.003(9)
H(16)	0.075(10)	0.063(9)	0.079(18)	−0.018(7)	0.016(11)	−0.020(9)
C(21)	0.074(10)	0.060(16)	0.048(27)	0.013(8)	0.015(15)	0.012(19)
C(22)	0.095(11)	0.099(14)	0.035(34)	0.026(10)	0.022(14)	0.013(16)
C(23)	0.110(14)	0.101(19)	0.068(39)	0.037(15)	0.047(19)	0.026(23)
C(24)	0.084(13)	0.082(24)	0.120(51)	0.027(12)	0.042(24)	0.051(28)
C(25)	0.072(14)	0.099(33)	0.137(47)	0.000(14)	0.010(17)	0.017(25)
C(26)	0.076(13)	0.079(25)	0.098(32)	−0.004(14)	0.008(14)	−0.008(20)
H(22)	0.117(13)	0.161(28)	0.027(40)	0.027(17)	0.013(14)	−0.008(11)
H(23)	0.154(26)	0.153(37)	0.080(46)	0.050(27)	0.069(22)	0.008(29)
H(24)	0.092(15)	0.096(36)	0.169(72)	0.038(17)	0.062(32)	0.077(39)
H(25)	0.077(19)	0.161(57)	0.201(66)	−0.017(22)	−0.008(14)	0.000(34)
H(26)	0.096(23)	0.117(36)	0.131(37)	−0.019(24)	0.001(12)	−0.050(20)
C(31)	0.088(7)	0.090(8)	0.069(6)	0.010(6)	−0.018(4)	−0.028(6)
C(32)	0.088(7)	0.090(8)	0.069(6)	0.010(6)	−0.018(4)	−0.028(6)
C(33)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
C(34)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
C(35)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
C(36)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
H(32)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
H(33)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
H(34)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
H(35)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
H(36)	0.089(7)	0.090(8)	0.069(6)	−0.018(6)	0.010(4)	−0.027(6)
C(41)	0.173(20)	0.109(21)	0.087(10)	0.003(10)	−0.062(11)	0.003(8)
C(42)	0.354(28)	0.108(22)	0.129(12)	−0.010(12)	−0.149(14)	0.009(9)
C(43)	0.381(42)	0.112(21)	0.137(15)	−0.031(17)	−0.164(22)	0.019(10)
C(44)	0.182(25)	0.110(20)	0.090(11)	−0.004(11)	−0.067(13)	0.006(8)
C(45)	0.245(21)	0.108(20)	0.104(10)	−0.004(14)	−0.097(11)	0.006(8)
C(46)	0.262(19)	0.111(20)	0.109(10)	−0.018(14)	−0.106(10)	0.013(8)
H(42)	0.635(50)	0.109(23)	0.193(22)	−0.028(17)	−0.283(27)	0.017(12)
H(43)	0.708(80)	0.121(21)	0.216(30)	−0.083(30)	−0.324(43)	0.045(14)
H(44)	0.187(29)	0.113(19)	0.092(11)	−0.009(12)	−0.070(15)	0.009(8)
H(45)	0.446(47)	0.109(20)	0.150(17)	−0.017(22)	−0.193(24)	0.012(12)
H(46)	0.503(36)	0.119(19)	0.168(17)	−0.061(21)	−0.225(20)	0.034(10)
C(51)	0.060(11)	0.098(19)	0.069(18)	0.006(13)	0.006(12)	0.013(18)
C(52)	0.090(20)	0.171(31)	0.073(20)	−0.041(25)	0.018(19)	−0.005(26)
C(53)	0.096(24)	0.167(42)	0.092(26)	−0.044(31)	0.036(24)	−0.029(34)
C(54)	0.063(15)	0.096(29)	0.098(34)	0.005(20)	0.018(16)	0.003(30)
C(55)	0.064(9)	0.116(19)	0.079(35)	−0.002(10)	0.000(10)	0.027(24)
C(56)	0.066(8)	0.114(14)	0.069(27)	−0.004(9)	0.006(8)	0.014(18)
H(52)	0.130(30)	0.281(44)	0.072(26)	−0.108(35)	0.020(23)	−0.009(29)
H(53)	0.144(38)	0.270(68)	0.110(32)	−0.115(48)	0.066(34)	−0.073(46)
H(54)	0.065(16)	0.096(32)	0.125(46)	0.004(22)	0.025(19)	0.000(38)
H(55)	0.084(10)	0.188(33)	0.082(46)	−0.041(16)	−0.011(13)	0.047(32)
H(56)	0.092(11)	0.180(20)	0.071(34)	−0.046(14)	0.014(8)	0.000(19)
C(61)	0.077(20)	0.063(12)	0.050(11)	0.013(10)	−0.014(10)	0.003(9)
C(62)	0.096(30)	0.061(11)	0.058(13)	0.009(7)	0.001(13)	0.003(10)
C(63)	0.149(48)	0.061(11)	0.071(20)	0.010(6)	0.027(26)	0.004(12)
C(64)	0.156(51)	0.067(14)	0.053(20)	0.033(9)	0.005(27)	0.009(14)

TABLE 2 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(65)	0.105(30)	0.082(21)	0.054(19)	0.037(15)	—0.025(18)	—0.006(18)
C(66)	0.078(18)	0.079(19)	0.065(16)	0.017(12)	—0.018(11)	—0.012(15)
H(62)	0.094(31)	0.067(12)	0.074(13)	0.001(7)	0.008(12)	—0.008(11)
H(63)	0.199(66)	0.064(12)	0.110(32)	—0.008(13)	0.074(39)	—0.009(15)
H(64)	0.217(75)	0.068(14)	0.059(25)	0.044(11)	0.024(40)	0.013(17)
H(65)	0.109(31)	0.104(31)	0.068(26)	0.049(21)	—0.037(20)	—0.024(26)
H(66)	0.078(16)	0.094(27)	0.099(24)	0.005(14)	—0.004(13)	—0.036(22)

C. Librational parameters [c]

Phenyl 1		Phenyl 2	
E1	0.054	E1	0.050
E2	—0.003	E2	—0.003
E3	—0.002	E3	0.007
E4	0.005	E4	0.020
E5	—0.004	E5	—0.001
E6	—0.005	E6	0.014
D1	0.00°	D1	8.9°
D2	0.00°	D2	0.00°
D3	6.3°	D3	5.3°
Phenyl 3		Phenyl 4	
E1	0.083	E1	0.122
E2	—0.004	E2	0.054
E3	0.014	E3	0.040
E4	0.002	E4	0.006
E5	—0.028	E5	—0.042
E6	0.017	E6	—0.005
D1	0.00°	D1	0.00°
D2	0.00°	D2	19.6°
D3	0.00°	D3	0.00°
Phenyl 5		Phenyl 6	
E1	0.074	E1	0.062
E2	—0.009	E2	0.000
E3	—0.007	E3	0.004
E4	0.022	E4	0.021
E5	—0.002	E5	—0.004
E6	—0.005	E6	0.000
D1	11.9°	D1	0.00°
D2	0.00°	D2	0.00°
D3	0.00°	D3	7.9°

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[a] The estimated standard deviation of the least significant figure is given in parentheses. [b] The anisotropic temperature factors are of the form: $\exp(-(1/2\ \Sigma U_{ij}t_it_j))$ [15]. [c] $E1 = (1/3)(T_{11} + T_{22} + T_{33})$; $E2 = T_{33} - E1$; $E3 = 1/2(T_{11} - T_{22})$; $E4 = T_{12}$; $E5 = T_{13}$; $E6 = T_{23}$; Di = liberation angle in direction i.

95.67(1)°, $\gamma = 90.000(—)°$, $V = 4560(2)$ Å^3, and $\rho_{calc} = 1.49$ g/cm^3. The lattice lengths were verified by axial rotation photography.

A total of 4606 data were measured over the scan range $2\theta = 3—40°$ on a Syntex $P\bar{1}$ automated diffractometer controlled by a 4K NOVA computer and equipped with a scintillation counter, a pulse height analyzer adjusted to admit 90% of the Mo $K\alpha$ ($\lambda\alpha_1 = 0.070900$ Å, $\lambda\alpha_2 = 0.71359$ Å) radiation, and a crys-

(Continued on p. 202)

TABLE 3. INTERATOMIC DISTANCES AND ANGLES FOR [TEA](Ph$_3$Sn)$_2$V(CO)$_5$]

A. Interatomic bonding distances (Å) [a]

N—C(1)	1.54(1)	C(1)—C(2)	1.59(2)
N—C(3)	1.54(1)	C(3)—C(4)	1.59(2)
N—C(5)	1.54(1)	C(5)—C(6)	1.59(2)
N—C(7)	1.54(1)	C(7)—C(8)	1.59(2)
Ave.	1.54	Ave.	1.59
V—CC(1)	1.92(2)	CC(1)—O(1)	1.17(2)
V—CC(2)	1.94(2)	CC(2)—O(2)	1.16(2)
V—CC(3)	1.94(2)	CC(3)—O(3)	1.18(2)
V—CC(4)	1.92(2)	CC(4)—O(4)	1.16(2)
V—CC(5)	1.99(2)	CC(5)—O(5)	1.11(2)
Ave.	1.94	Ave.	1.16
Sn(1)—C(11)	2.203(9)	V—Sn(1)	2.757(3)
Sn(1)—C(21)	2.179(10)	V—Sn(2)	2.785(3)
Sn(1)—C(31)	2.186(9)		
Sn(2)—C(41)	2.175(11)	Ave.	2.771
Sn(2)—C(51)	2.195(10)		
Sn(2)—C(61)	2.188(10)		
Ave.	2.188		

B. Interatomic bond angles (deg) [a]

N—C(1)—C(2)	114(2)	C(1)—N—C(3)	114(2)
N—C(3)—C(4)	109(2)	C(1)—N—C(5)	108(2)
N—C(5)—C(6)	114(2)	C(1)—N—C(7)	105(2)
N—C(7)—C(8)	113(2)	C(3)—N—C(5)	100(2)
		C(3)—N—C(7)	117(2)
Ave.	112	C(5)—N—C(7)	113(2)
		Ave.	110
Sn(2)—V—CC(1)	66.9(6)		
Sn(2)—V—CC(3)	73.9(5)	Sn(2)—V—CC(2)	126.4(6)
Sn(2)—V—CC(5)	75.1(5)	Sn(2)—V—CC(4)	120.3(7)
		Sn(2)—V—Sn(1)	137.9(1)
Ave.	72.0		
		Ave.	128.2
C(11)—Sn(1)—C(21)	99.4(5)	V—Sn(1)—C(11)	116.0(3)
C(11)—Sn(1)—C(31)	99.0(5)	V—Sn(1)—C(21)	119.4(3)
C(21)—Sn(1)—C(31)	105.6(5)	V—Sn(1)—C(31)	114.6(5)
C(41)—Sn(2)—C(51)	105.0(7)	V—Sn(2)—C(41)	115.7(6)
C(41)—Sn(2)—C(61)	103.1(6)	V—Sn(2)—C(51)	112.6(4)
C(51)—Sn(2)—C(61)	103.2(6)	V—Sn(2)—C(61)	115.7(4)
Ave.	102.6	Ave.	115.7
CC(1)—V—CC(3)	117.2(8)	Sn(1)—V—CC(2)	82.6(6)
CC(1)—V—CC(5)	114.8(9)	Sn(1)—V—CC(4)	82.9(6)
CC(3)—V—CC(5)	99.2(7)	CC(2)—V—CC(4)	92.1(8)
Ave.	110.4	Ave.	85.9
V—CC(1)—O(1)	173(2)	Sn(1)—V—CC(2)	82.6(6)
V—CC(2)—O(2)	177(2)	Sn(1)—V—CC(3)	76.1(5)
V—CC(3)—O(3)	176(2)	Sn(1)—V—CC(4)	82.9(6)
V—CC(4)—O(4)	179(2)	Sn(1)—V—CC(5)	81.2(5)
V—CC(5)—O(5)	177(2)		
		Ave.	80.7
Ave.	176		

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[a] The estimated standard deviation of the least significant figure is given in parentheses.

TABLE 4

PLANES AND ANGLES BETWEEN PLANES FOR THE VANADIUM COORDINATION GEOMETRY [a, b]

A. C_{2v} geometry

Plane I, through V, Sn(1), Sn(2), CC(1), and O(1)

$$-0.909363X - 0.038778Y - 0.4141937Z + 4.325029 = 0$$

Plane II, through V, Sn(1), Mid3—4, Mid2—5 [c]

$$0.057321X - 0.979539Y - 0.1929177Z + 3.805348 = 0$$

Perpendicular distances (Å) of atoms from designated planes

	I	II
V	0.05	−0.01
Sn(1)	−0.02	0.00
Sn(2)	−0.01	1.83
CC(1)	−0.01	−0.78
O(1)	−0.01	−1.41
CC(2)	1.35	−1.26
O(2)	2.21	−1.98
CC(3)	−1.38	−1.34
O(3)	2.50	−2.18
CC(4)	−1.37	1.10
O(4)	−2.28	1.74
CC(5)	1.60	1.27
O(5)	2.50	1.96

The angle between the normals of the two planes is 86.23°.

B. C_{3v} geometry

Plane I, same as Plane I for C_{2v}

Plane II, through V, Sn(2), CC(2), O(2), CC(4), and O(4)

$$0.665288X + 0.74172Y - 0.085097Z - 3.365684 = 0$$

Plane III, through V, Sn(2), CC(3), O(3), CC(5), and O(5)

$$-0.353282X + 0.716726Y - 0.6012457Z + 1.604086 = 0$$

Perpendicular distance (Å) of atoms from designated planes

	I	II	III
V	0.05	0.10	0.09
Sn(2)	−0.01	−0.02	−0.01
Sn(1)	−0.02	−1.22	−1.45
CC(1)	−0.01	1.43	1.45
O(1)	−0.01	2.35	2.41
CC(2)	1.35	0.03	1.50
O(2)	2.21	−0.06	2.41
CC(3)	−1.38	1.65	0.00
O(3)	2.50	2.55	−0.04
CC(4)	−1.37	−0.01	−1.68
O(4)	−2.28	−0.04	−2.75
CC(5)	1.60	−1.74	−0.01
O(5)	2.50	−2.77	−0.03

Angle (deg.) between normals to designated planes

	I	II	III
II	126.8	—	—
III	57.1	69.6	—

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[a] Only the immediate coordination sphere atoms were included in the calculation. [b] The equations of the planes are given in an orthogonal angstrom coordinate system (X, Y, Z) which is related to the fractional unit cell coordinate system (x, y, z) as follows:

$$X = xa + yb\cos\gamma + zc\cos\beta;\ Y = yb\sin\gamma + zc\cos\mu;\ Z = zc\cos\sigma$$

Where $\cos\mu = (\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma$, and $\sin^2\sigma = 1 - \cos^2\beta - \cos^2\mu$; all atoms were assigned unit weights. [c] In order to generate this plane in the correct orientation, the midpoints between CC(2) and CC(5), and CC(3) and CC(4) were used.

tal graphite monochromator set at a Bragg 2θ angle of 12.2°. A variable rate $\theta - 2\theta$ scan technique was employed. Two standard reflections, measured after every 48 reflections, showed no decay in intensity. The data was reduced, corrected for Lorentz polarization and background effects [10], and merged [11] to yield 4459 independent reflections of which 2658 were considered observed with $I > 2\sigma(I)$. No absorption corrections were applied.

An initial Patterson map [12] gave the location of one of the tin atoms. Application of standard Fourier, difference Fourier, and block-diagonal least-squares techniques [13] led to the location of all the non-hydrogen atoms. The phenyl rings were idealized [14] and were refined as rigid groups while allowing for libration about the tin—carbon bond [15]. The carbon—carbon bond lengths of the cation were constrained to be equal by the use of slack constraints [15b], as were the nitrogen—carbon bond lengths of the cation. Block-diagonal least squares refinement of this model via the conjugate gradient method [15c] converged to $R_1(F) = [(\Sigma||F_0| - |F_c|)/(\Sigma|F_0|] = 0.083$ and $R_2(F^2) = [(\Sigma||F_0^2| - |F_c^2||)/(\Sigma|F_0^2|)] = 0.113$ with no shift over error ratio, Δ/σ, greater than 0.75 and with only two of the 299 parameters being between 0.50 and 0.75. No significant correlation between parameters was observed. The function minimized was $\Sigma_h [w_h{}^2 |F_c|_{0h} a'_{hi}(|F_0^2|_h - |F_c^2|_{0h})]$ where $w_h = 1/\sigma_h^2$ and $a'_{hi} = \cos \alpha_{0h}(\partial Ac/\partial ui)_{0h} + \sin \alpha(\partial Ba/\partial ui)_{0h}$ [15d].

The final atomic and group parameters with their estimated standard deviations are given in Table 2. Interatomic distances and angles with estimated standard deviations are given in Table 3. Planes and angles between planes for vanadium coordination geometry are in Table 4 *.

Results and discussion

Reduction of $(Ph_3E)_2V(CO)_5^-$ ($E = Sn, Pb$)

We have previously shown [16] that sodium amalgam reduction of $Ph_3SnV(CO)_{6-n}L_n$ ($L = PR_3$, $n = 0$—2) provides $V(CO)_{6-n}L_n{}^-$ almost quantitatively by the following equation:

$$Ph_3SnV(CO)_{6-n}L_n + Na \xrightarrow[Hg]{THF} Na^+V(CO)_{6-n}L_n{}^- + 1/2(Ph_3Sn)_2$$

It was therefore of interest to examine whether this procedure could be used to obtain previously unknown $Ph_3EV(CO)_5{}^{2-}$ ($E = Sn, Pb$) by the reduction of corresponding $(Ph_3E)_2V(CO)_5{}^-$. Rapid reduction of $(Ph_3Pb)_2V(CO)_5{}^-$ by sodium amalgam occurred at room temperature in THF and provided ca. 30% yields of thermally unstable $(Et_4N)_2[Ph_3PbV(CO)_5]$ (I) characterized by elemental analyses, infrared spectroscopy (Table 1) and its reaction with Ph_3PbCl to provide high yields (ca. 80%) of starting material. This route to $Ph_3PbV(CO)_5{}^{2-}$ is important as we have been unable to synthesize this material directly from $Na_3V(CO)_5$ [7].

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* Supplementary data involving a listing of the observed and calculated structure factors have been deposited as NAPS Document No. 03834 (15 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 $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the U.S. and Canada add postage of $3.00 for photocopy and $1.00 for microfiche.

Sodium amalgam reduction of $(Ph_3Sn)_2V(CO)_5^-$ provides significantly better yields (ca. 80—90%) of $[Et_4N]_2[Ph_3SnV(CO)_5]$ but the reduction requires much longer reaction times (ca. 72 h) at room temperature. High yields of hexaphenylditin are also isolated from this reduction in accord with our previous results [16]. Somewhat faster reductions occur when $(Ph_3Sn)_2V(CO)_5^-$ is treated with Ph_3SnLi but the yield (40—50%) is lower. This latter reaction also generates considerable amounts of hexaphenylditin. Both of these reductions are summarized in the following scheme:

$$(Ph_3Sn)_2V(CO)_5^- \xrightarrow[Na/Hg]{Ph_3SnLi} (Ph_3Sn)V(CO)_5^{2-} + (Ph_3Sn)_2$$

Solution infrared spectra of $Ph_3SnV(CO)_5^{2-}$ show the characteristic three-band pattern in the carbonyl stretching frequency region expected for a largely unperturbed anion of C_{4v} local symmetry. For example, the shapes and relative intensities of the $\nu(CO)$ absorptions for $Ph_3SnB(CO)_5^{2-}$ (Table 1) are very similar to those of the isoelectronic species $Ph_3SnCr(CO)_5^-$ ($\nu(CO)$: 2019m, 1900vs, 1883(sh) cm^{-1} as Et_4N^+ salt in THF) [18] and $Ph_3SnMn(CO)_5$ ($\nu(CO)$: 2097m, 2026w, 2001vs cm^{-1} in THF) [19] as well as that of a related vanadium(—1) species, $Ph_3PV(CO)_5^-$ ($\nu(CO)$: 1965m, 1858w, 1823vs cm^{-1} as Et_4N^+ salt in THF) [20]. It should be noted that four band $\nu(CO)$ patterns of formally C_{4v} $M(CO)_5L^z$-species are also observed in the infrared, especially in mull and solution spectra of salts where there is some degree of ion pairing. This sometimes results in significant structural perturbation of the $M(CO)_5L^z$-unit (see, for example, reported $\nu(CO)$ values in ref. 21).

Reactions of $Ph_3EV(CO)_5^{2-}$ (E = Sn, Pb)

Since these species are the first compounds containing an organotin or -lead group bound to a transition metal in a formally negative oxidation state, it is not surprising that they are very oxygen sensitive in solution. Oxygen and a variety of other oxidizing agents such as tropylium ion rapidly convert $Ph_3EV(CO)_5^{2-}$ into a mixture of $(Ph_3E)_2V(CO)_5^-$, $V(CO)_6^-$ and dark uncharacterized decomposition material. We have no evidence for the formation of the unknown dimers $[Ph_3EV(CO)_5]_2^{2-}$ in these reactions.

Similarities in the reactivity patterns of $Ph_3SnV(CO)_5^{2-}$ and $C_5H_5V(CO)_3^{2-}$ are expected since each dianion contains octahedral vanadium in a —1 formal oxidation state. Infrared spectra of these dianions suggest that the vanadium in $Ph_3EV(CO)_5^{2-}$ (E = Sn, $\nu(CO)$: 1927m, 1783s, 1750(sh) cm^{-1} as Et_4N^+ salt in CH_3CN) should be less basic than that in $C_5H_5V(CO)_3^{2-}$ ($\nu(CO)$: 1742s, 1619s cm^{-1} as Na^+ salt in HMPA) [17]. Although $Ph_3SnV(CO)_5^{2-}$ and $C_5H_5V(CO)_3^{2-}$ do react with one additional equivalent of Ph_3SnCl to yield the termally stable anions $(Ph_3Sn)_2V(CO)_5^-$ and $Ph_3SnV(CO)_3C_5H_5^-$ [17], respectively, $Ph_3SnV(CO)_5^{2-}$ appears to form less stable with most electrophiles. (Only the previously cited reactions of the thermally unstable $Ph_3PbV(CO)_5^{2-}$ with Ph_3PbCl and oxygen have been examined.) For example, $C_5H_5V(CO)_3^{2-}$ readily protonates to yield $C_5H_5V(CO)_3H^-$ and/or $[C_5H_5V(CO)_3]_2H^-$ which may be isolated as PPN^+ salts [22]. However, the reaction of glacial acetic acid with $[Et_4N]_2[Ph_3SnV(CO)_5]$ in THF at room temperature yield an orange-red soluble species, possibly $H(Ph_3Sn)V(CO)_5^-$ ($\nu(CO)$: 1997s, 1884s(br) cm^{-1}, attempts to observe a high-field resonance characteristic of a metal hydride in the ^{1}H NMR spectrum of the product were not successful). This product decomposes to $(Ph_3Sn)_2V(CO)_5^-$, $V(CO)_6^-$ and $Ph_3SnV(CO)_5^{2-}$ on work up. Alkylating agents such as MeI, Me_3O^+ and $MeOSO_2F$ also react with $Ph_3SnV(CO)_5^{2-}$, but all attempts to isolate products resulted in decomposition. By contrast, high yields of $C_5H_5V(CO)_3CH_3^-$ have been prepared by treatment of $C_5H_5V(CO)_3^{2-}$ with CH_3I [22]. We have not examined the reactions of other alkylating agents with $Ph_3SnV(CO)_5^{2-}$. Such a study, especially with regard to organic products, could provide useful comparisons with $C_5H_5V(CO)_3^{2-}$ chemistry. The problem with $Ph_3SnV(CO)_5^{2-}$ is not that it is unreactive, but rather that the products are unstable. This circumstance is one more indication that vanadium carbonyl species do not tend to form stable seven-coordinate species (for exceptions see ref. 23).

More success was obtained when $Ph_3SnV(CO)_5^{2-}$ was treated with Me_3SnCl and $(C_6H_{11})_3SnBr$. In these cases approximately 40% yields of mixed seven-coordinate $(Ph_3Sn(R_3Sn)V(CO)_5^-$ were isolated as tetraethylammonium salts. On this basis of the similarity of the infrared spectra of these mixed organotin derivatives with that of $(Ph_3Sn)_2V(CO)_5^-$, it is expected that these have similar structures and contain seven-coordinate vanadium.

Synthesis of $(Ph_3Sn)_2V(CO)_5^-$ by photolysis

In view of Faltynek and Wrighton's report [24] that $(Ph_3Sn)_2Mn(CO)_4^-$ could be obtained in nearly quantitative yields by the photolysis of $Mn(CO)_5^-$ in the presence of excess Ph_6Sn_2, we investigated the possibility that this method could be used for the synthesis of $(Ph_3Sn)_2V(CO)_5^-$ directly from $V(CO)_6^-$. All of our attempts to produce reasonable yields of the desired product were unsuccessful. As indicated in the Experimental section, approximately 15% conversion of $V(CO)_6^-$ to $(Ph_3Sn)_2V(CO)_5^-$ was realized. Longer photolysis periods resulted in decomposition of the product whether pyrex or unfiltered radiation was used. Thus, production of $(Ph_3Sn)_2V(CO)_5^-$ from $Na_3V(CO)_5$ [7,8] appears to be the best route presently known.

Structure of $[Et_4N][(Ph_3Sn)_2V(CO)_5]$

Because of vanadium's demonstrated reluctance to become seven-coordinate [23,26], and since the spectroscopic properties of $(Ph_3Sn)_2V(CO)_5^-$ did not rule out the possibility of an unprecedented tin—carbonyl oxygen interaction (e.g., $Ph_3SnV(CO)_4(COSnPh_3)^-$) we felt that a structural study of this compound was in order.

The crystal structure of $[TEA][(Ph_3Sn)_2V(CO)_5]$ consists of discrete tetraethylammonium cations and bis(triphenyltin)pentacarbonylvanadate anions. An investigation of the interionic distances reveals no abnormal interactions. A view of the anion, phenyl hydrogens not included, is shown in Fig. 1. The vanadium atom is heptacoordinated to the five carbonyl and two triphenyltin ligands. Idealized seven-coordinate geometries have been discussed by Muetterties [28]: pentagonal bipyramid (D_{5h}), monocapped octahedron (C_{3v}), monocapped trigonal prism (C_{2v}), and the trigonal base-tetragonal base (C_s). Muetterties notes that these geometries are all very closely related and that slight distortions will interchange one geometry for another. Few seven-coordinate struc-

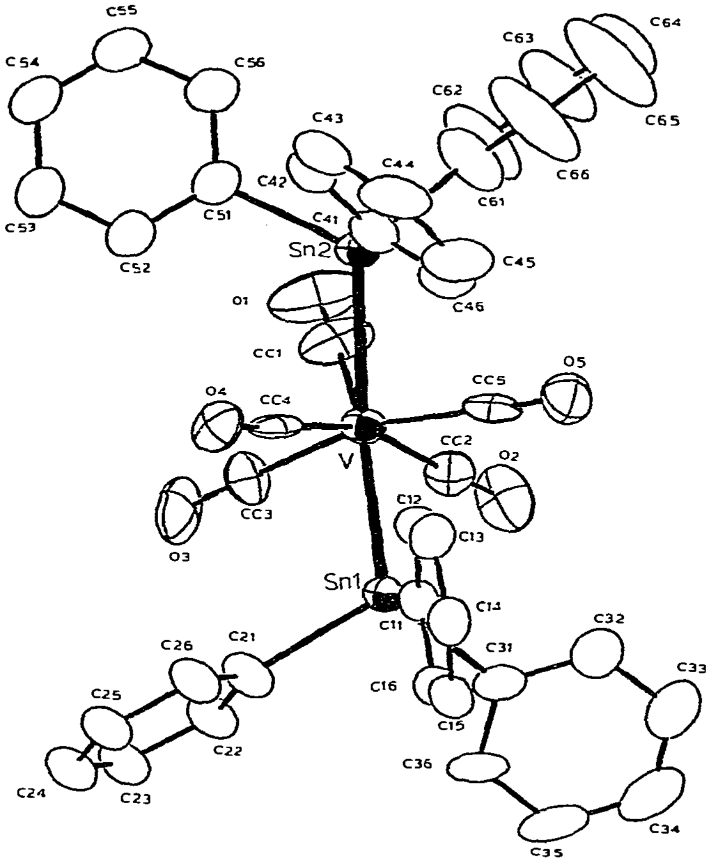


Fig. 1. View of $(Ph_3Sn)_2V(CO)_5^-$ showing the atom labelling scheme (phenyl hydrogens not shown).

tures have been published, and most of those either contain multidentate ligands [29—31] or are polymeric in nature [32]. Of the known $ML_{7-n}X_n$ complexes where L and X are simple monodentate ligands, the pentagonal bipyramid is the dominant structure [33—35], although examples of the monocapped trigonal prism (NbF_7^{2-}) [36] and of the monocapped octahedron ($NbOF_6^{3-}$) [37] have been reported. Drew has recently published a particularly useful review on seven-coordination chemistry [38].

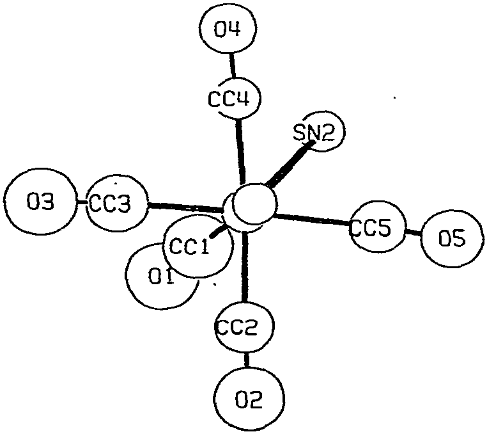
The nature of the coordination geometry of the vanadium in this structure is such that, upon examination, only the pentagonal bipyramidal structure may be unambiguously ruled out. Interestingly, the pentagonal bipyramid is the favored structure on the basis of ligand—ligand repulsions [28]. Depending upon which axis is viewed, one can see the coordination geometry as any of the other three idealized structures, although some imagination is needed due to the distortions caused by the bulkiness of the triphenyltin ligands.

The geometry can be described as a monocapped trigonal prism when viewed down the Sn(1)—V bond (Fig. 2). If the Sn(2) atom is considered to be geometrically equivalent to the CC(1)—O(1) carbonyl ligand, then this view has the approximate C_{2v} symmetry of a monocapped trigonal prism. The opposing triangular faces are bounded by Sn(2)—CC(4)—CC(5) and CC(1)—CC(2)—CC(3). Sn(1) then caps the rectangular face defined by CC(2)—CC(3)—CC(4)—CC(5).

Alternatively, the geometry can be described as a trigonal base-tetragonal base when viewed along the plane defined by Sn(1), Sn(2) and V (Fig. 3). This view shows the trigonal base composed of CC(1)—CC(2)—CC(3) and the tetragonal base composed of Sn(1)—CC(4)—Sn(2)—CC(5). This view, which has approximate C_s symmetry with the mirror plane containing atoms Sn(1), Sn(2), V, CC(1), and O(1), corresponds to the trigonal base-tetragonal base model which has a vertex of the trigonal base positioned over a vertex of the tetragonal base [28].

Finally, the geometry can be described as a monocapped octahedron when viewed down the Sn(2)—V bond (Fig. 4). If the Sn(1) atom is considered geometrically equivalent to carbonyls 2 and 3, then this view has the approximate C_{3v} symmetry of the monocapped octahedron. The octahedron is defined by Sn(1)—CC(1) axial and CC(2), CC(3), CC(4), CC(5) equatorial. The Sn(2) atom then caps the trigonal face defined by CC(1)—CC(4)—CC(5). The extent of distortion of the octahedron from a regular configuration is indicated by the Sn(1)—V—CC(1) angle of 155.0° and the mean Sn(1)—V—equatorial carbonyl angle of 80.7°, which differ significantly from 180 and 90°, respectively. However, when compared to other seven-coordinate structures described as monocapped octahedra, the L—M—L angles are fairly consistent. Table 5 lists some important angles for various monocapped octahedral complexes.

As indicated previously, $(Ph_3Sn)_2V(CO)_5^-$ can be prepared by the addition of one equivalent of Ph_3SnCl to a solution of $Ph_3SnV(CO)_5^{2-}$, which is likely to be isostructural with the isoelectronic $Ph_3SnMn(CO)_5$ of known C_{4v} coordination geometry [39]. This reaction may be viewed as a capping of one of the four equivalent faces of the octahedron by the incoming triphenyltin group approximately *trans* to the original tin group. Due to the bulkiness of the two tri-



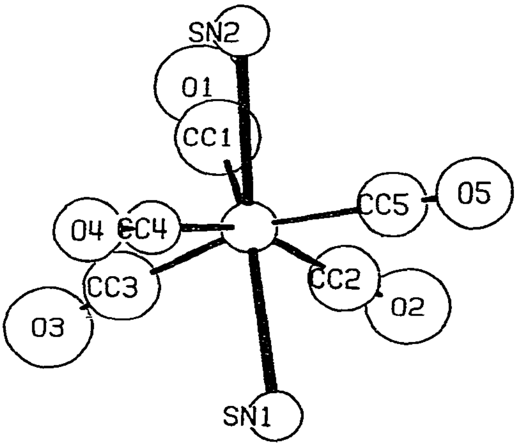


Fig. 2. View of the vanadium coordination sphere looking down the Sn(1)—V bond showing the C_{2v} symmetry of a monocapped trigonal prism.

Fig. 3. View of the vanadium coordination sphere along the plane defined by Sn(1), V, and Sn(2), showing the tetragonal base-trigonal base geometry.

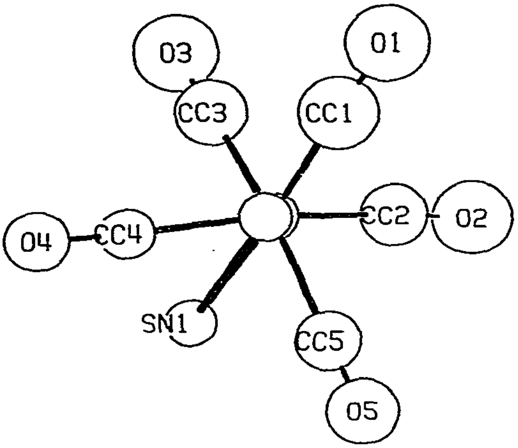


Fig. 4. View of the vanadium coordination sphere looking down the Sn(2)—V bond, showing the C_{3v} pseudosymmetry of a monocapped octahedron.

phenyltin groups, however, the choice of a coordination environment about the vanadium is at best a difficult one.

The tetraethylammonium cation shows no unusual features. The mean N—C and C—C distances are 1.54 and 1.59 Å, respectively, being in good agreement with the expected average C—C and N—C single bond lengths of 1.54 Å. The angular parameters are more ambiguous with mean C—N—C and N—C—C angles of 110 and 112° being approximately tetrahedral, although the large range of values precludes a definite assignment. However, since the tetraethylammonium cation possesses an almost spherical Van der Waals shape, it can pack with various orientations of its atoms and yet maintain essentially the same interatomic contacts [40—44].

The phenyl rings were required to be planar with C—C distances of 1.39 Å and C—H distances of 1.0 Å. An examination of the librational parameters of the six phenyl groups shows that only one ring, phenyl 3, has no libration in any direction. Through an allowance of the phenyl rings to librate about their Sn—C bonds and the assignment of anisotropic thermal factors to each atom in

TABLE 5

SELECTED ANGULAR DATA ON MONOCAPPED OCTAHEDRAL COMPLEXES (AVERAGED VALUES) [a]

Complex	Ref.	CL—M—A_c	CL—M—A_u	A_u—M—A_u	A_c—M—A_c
$V(CO)_5(SnPh_3)_2^-$	—	71.9	128.2	85.8	110.3
$Mo(CO)_3Br_2(dppe)$	55	73.6	125.5	89.7	112.3
$Mo(CO)_2Br_2(Ph_2AsCH_2AsPh_2)_2$ [b]	56	73	128	86	112
$W(CO)_3Br_2(Ph_2AsCH_2AsPh_2)$	57	72	128	[c]	[c]
$Ho(PhCOCHCOPh)_3 \cdot H_2O$	58	74	131	82.1	112.4

[a] Notation: CL = capping ligand; M = central metal; A_c = ligand on capped face of octahedron; A_u = ligand on uncapped face of octahedron *trans* to the capped face. [b] One of the $Ph_2AsCH_2AsPh_2$ ligands is monodentate. [c] Paper is a short communication; these parameters were not reported.

the group, the carbons were able to assume their thermal banana shape which corresponds to a large coefficient in one direction and small coefficients in the other two directions. The restriction in ORFLS for only isotropic temperature factors for atoms in a rigid group led to a physically unrealistic model. Interestingly, Bryan [39] has also observed such an anomaly in a phenyl ring of a triphenyltin ligand, but resolves the problem via the use of a disordered model.

The mean V—Sn distance of 2.771 Å, the mean Sn—C distance of 2.19 Å, the mean V—Sn—C angle of 115.7°, and the mean C—Sn—C angle of 102.6° are all average with respect to other M—$SnPh_3$ (M = Fe, Mn, Cr) structures [39,45, 46]. The carbonyls are all basically linear with carbonyl 1 being bent more than the others due to steric interaction with the triphenyltin ligand. The mean V—C distance and C—O distance of 1.94 and 1.16 Å, respectively, agree well with the analogous values reported for other vanadium carbonyl systems [47—54].

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