

Coordination Chemistry of Higher Oxidation States. 25.¹ Synthesis and Properties (Including ⁵⁹Co NMR Spectra) of Cobalt(III) Complexes of Ligands Containing Two Tertiary Stibine Groups. Crystal Structure of *trans*-[Co(*o*-C₆H₄(SbMe₂)₂)₂Cl₂]₂[CoCl₄]

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Cobalt(III) complexes of two ligands containing two tertiary stibine groups, [Co(*o*-C₆H₄(SbMe₂)₂X₂)X (X = Cl, Br, I) and [Co(Me₂Sb(CH₂)₃SbMe₂)₂X₂]X (X = Br, I), have been prepared and shown to have *trans* pseudooctahedral cations. The synthesis of *trans*-[Co(*o*-C₆H₄(SbMe₂)₂(PMe₂)₂X₂)Y (X = Cl, Br, I; Y = X, BF₄), *trans*-[Co(*o*-C₆H₄(PPh₂)(SMe)₂X₂)BF₄], *trans*-[Co(*o*-C₆H₄(PPh₂)(SeMe)₂X₂)BF₄ (X = Cl, Br), and *fac*-[Co(*o*-C₆H₄(PPh₂)(SMe)₃)(BF₄)₃] are described. The complexes have been characterized by UV-visible spectroscopy and multinuclear (¹H, ³¹P{¹H}, ⁷⁷Se{¹H}) NMR as appropriate. ⁵⁹Co NMR spectra are reported for these complexes, and the characteristic ranges of the ⁵⁹Co chemical shifts for Co(III) complexes containing neutral heavy groups VB and VIB (groups 15 and 16) donor ligands are established. The X-ray structure of [Co(*o*-C₆H₄(SbMe₂)₂)₂Cl₂]₂[CoCl₄] has been determined. Crystals belong to the tetragonal system, space group *I*4₁/*a* (No. 88), with *a* = 25.264 (6) Å, *c* = 9.720 (9) Å, and *Z* = 4. The structure was refined to an *R* of 0.058 from 1237 observed reflections (*F* > 3σ(*F*)). The cobalt of the cation is located on a center of symmetry (Co-Sb = 2.505 (1), 2.478 (1) Å; Co-Cl = 2.263 (4) Å), and the anion has 4 symmetry (Co-Cl = 2.287 (6) Å).

Introduction

Very few examples of complexes containing ligands with two tertiary stibine groups (ditertiary stibine complexes) are known, particularly with high or medium oxidation state metal centers,²⁻⁵ which is mainly a reflection of the poor donor properties of the large soft antimony, although the difficult syntheses of the distibine ligands² have no doubt further limited studies. Here we report the synthesis and properties of cobalt(III) complexes of two distibines, and of a phosphine-stibine, which allowed the extension of our previous study⁶ of ⁵⁹Co NMR spectra of heavy group VB (groups 15)³⁴ donor complexes to antimony ligands. Similar data on phosphine-thioether and phosphine-selenoether complexes are included.

Experimental Section

Physical measurements were made as described in previous parts⁴⁻⁶ of the series. ⁵⁹Co NMR spectra were recorded as before,⁶ with chemical shifts reported with the high frequency positive convention relative to external aqueous K₃[Co(CN)₆] (δ = 0).

The ligands were made by literature methods—*o*-C₆H₄(SbMe₂)₂,⁷ *o*-C₆H₄(PMe₂)(SbMe₂),⁷ Me₂Sb(CH₂)₃SbMe₂,⁸ *o*-C₆H₄(PPh₂)(SMe),⁹ and *o*-C₆H₄(PPh₂)(SeMe).⁹

Dibromobis(*o*-phenylenebis(dimethylstibine)cobalt(III) Bromide. The ligand (0.15 g, 0.4 mmol) was added to a dinitrogen-purged solution of [Co(H₂O)₆]Br₂ (0.053 g, 0.19 mmol) in propan-2-ol containing a few drops of 48% HBr, and the solution was stirred for 15 min. The blue solution was then exposed to air for 2 h, when it rapidly turned brown. The brown precipitate was filtered off, rinsed with propan-2-ol (5 cm³) and diethyl ether (5 cm³) and dried in vacuo. Anal. Calcd for C₂₀H₃₂Br₃CoSb₄: C, 22.7; H, 3.1. Found: C, 22.5; H, 3.0.

The following compounds were made similarly:

[Co(*o*-C₆H₄(SbMe₂)₂)₂Cl₂]Cl. Anal. Calcd for C₂₀H₃₂Cl₃CoSb₄: C, 26.0; H, 3.5. Found: C, 26.1; H, 3.5.

[Co(Me₂Sb(CH₂)₃SbMe₂)₂Br₂]Br. Anal. Calcd for C₁₄H₃₆Br₃CoSb₄: C, 17.0; H, 3.7. Found: C, 16.8; H, 3.4.

[Co(Me₂Sb(CH₂)₃SbMe₂)₂I₂]I. Anal. Calcd for C₁₄H₃₆CoI₃Sb₄: C,

14.9; H, 3.2. Found: C, 14.4; H, 3.3.

Diiodobis(*o*-phenylenebis(dimethylstibine)cobalt(III) Iodide. [Co(*o*-C₆H₄(SbMe₂)₂)₂Br₂]Br (0.04 g, 0.038 mmol) in ethanol (5 cm³) was refluxed with NaI (0.08 g) for 20 min. The dark red solution was evaporated to dryness, the residue extracted with CH₂Cl₂ (3 × 15 cm³), filtered, and the solvent removed in vacuo. Anal. Calcd for C₂₀H₃₂CoI₃Sb₄: C, 20.0; H, 2.7. Found: C, 20.4; H, 2.9.

Dichlorobis(*o*-(dimethylphosphino)phenyl)dimethylstibine)cobalt(III) Tetrafluoroborate. The ligand (0.35 g, 1.2 mmol) was added to a dinitrogen-purged solution of [Co(H₂O)₆]Cl₂ (0.06 g, 0.25 mmol) and [Co(H₂O)₆](BF₄)₂ (0.085 g, 0.25 mmol) in ethanol (15 cm³). After being stirred for 10 min, the solution was exposed to air and stirred for several hours. Concentration in vacuo produced a greenish precipitate, which was filtered off, rinsed with ethanol and diethylether, and dried in vacuo. Anal. Calcd for C₂₀H₃₂BCl₂CoF₄P₂Sb₂: C, 30.3; H, 4.0. Found: C, 30.5; H, 4.1.

[Co(*o*-C₆H₄(PMe₂)(SbMe₂)₂)₂Br₂]BF₄ was made similarly. Anal. Calcd for C₂₀H₃₂BBR₂CoF₄P₂Sb₂: C, 27.2; H, 3.7. Found: C, 26.5; H, 3.7.

[Co(*o*-C₆H₄(PMe₂)(SbMe₂)₂)₂I₂]I was made similarly, except that a [Co(H₂O)₆]I₂: ligand ratio of 1:2 was used, and a few drops of 45% HI were added to provide the extra anion. Anal. Calcd for C₂₀H₃₂CoI₃P₂Sb₂: C, 23.6; H, 3.2. Found: C, 23.4; H, 3.2.

[Co(*o*-C₆H₄(PPh₂)(EMe)₂X]BF₄ (E = S, Se; X = Cl, Br) compounds were made by the method of Dyer and Meek,⁹ and had satisfactory analyses.

[Co(*o*-C₆H₄(PPh₂)(EMe)₂X₂]BF₄ (E = S, Se; X = Cl, Br). The corresponding [Co(*o*-C₆H₄(PPh₂)(EMe)₂X]BF₄ was dissolved in CH₂Cl₂, and the calculated amount of X₂ added dropwise [Co:X₂ 1:0.5 mol ratio] as a solution in CCl₄. The solution was filtered and then concentrated in vacuo until the product separated.

E = S; X = Cl. Anal. Calcd for C₃₈H₃₄BCl₂CoF₄P₂S₂: C, 54.8; H, 4.4. Found: C, 55.0; H, 4.5.

E = S; X = Br. Anal. Calcd for C₃₈H₃₄BBR₂CoF₄P₂S₂: C, 49.5; H, 4.0. Found: C, 49.0; H, 4.3.

E = Se; X = Cl. Anal. Calcd for C₃₈H₃₄BCl₂CoF₄P₂Se₂: C, 49.2; H, 3.7. Found: C, 48.8; H, 3.8.

E = Se; X = Br. Anal. Calcd for C₃₈H₃₄BBR₂CoF₄P₂Se₂: C, 44.9; H, 3.4. Found: C, 45.2; H, 3.4.

Tris(*o*-(methylthio)phenyl)diphenylphosphine)cobalt(III) Tetrafluoroborate. [Co(*o*-C₆H₄(PPh₂)(SMe)₂Cl₂]BF₄ (0.06 g, 0.07 mmol) in CH₂Cl₂ (10 cm³) was stirred overnight with *o*-C₆H₄(PPh₂)(SMe) (0.025 g, 0.08 mmol) and AgBF₄ (0.03 g, 0.15 mmol). The white precipitate was removed by filtration, and the green filtrate was concentrated in vacuo until the green product was deposited. Anal. Calcd for C₅₇H₅₁B₃CoF₁₂P₃S₃: C, 55.0; H, 4.1. Found: C, 55.6; H, 4.3.

Tris(*o*-(dimethylphosphino)phenyl)dimethylstibine)cobalt(III) tetrafluoroborate was prepared in fashion similar to the corresponding *o*-phenylenebis(dimethylarsine)⁹ complex except that the product was isolated by triturating the oil obtained with diethyl ether and filtering off a slightly sticky solid. Treatment of this solid with CH₂Cl₂ removed some oxidized ligand and the light brown product was filtered off and dried in vacuo. Anal. Calcd for C₃₀H₄₈B₃CoF₁₂P₃Sb₃: C, 30.4; H, 4.1. Found: C, 30.2; H, 4.0.

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Table I. Atomic Coordinates for $[\text{Co}\{\text{o-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2\text{Cl}_2][\text{CoCl}_4]$

	x	y	z	$U_i^a \text{ \AA}^2$
Co(1)	0.0000	0.0000	0.0000	33.6 (19)
Co(2)	0.0000	0.7500	0.3750	49.0 (25)
Sb(1)	0.02411 (5)	-0.05231 (5)	0.2098 (1)	36.6 (7)
Sb(2)	0.06568 (5)	0.06737 (5)	0.0720 (1)	38.5 (7)
Cl(1)	0.0644 (2)	-0.0418 (2)	-0.1200 (5)	50.1 (30)
Cl(2)	0.0390 (2)	0.8112 (2)	0.5157 (7)	70.2 (38)
C(1)	-0.0300 (8)	-0.0641 (8)	0.3738 (20)	55.3 (131)
C(2)	0.0587 (8)	-0.1283 (7)	0.1836 (22)	56.2 (135)
C(3)	0.0887 (7)	-0.0104 (6)	0.3081 (20)	37.7 (110)
C(4)	0.1123 (8)	-0.0313 (7)	0.4221 (21)	51.4 (129)
C(5)	0.1568 (8)	-0.0057 (8)	0.4778 (23)	55.8 (138)
C(6)	0.1751 (8)	0.0394 (7)	0.4124 (25)	59.9 (144)
C(7)	0.1508 (7)	0.0600 (7)	0.2997 (21)	44.7 (117)
C(8)	0.1067 (7)	0.0349 (7)	0.2441 (20)	39.9 (111)
C(9)	0.1274 (9)	0.0868 (10)	-0.0614 (27)	80.5 (175)
C(10)	0.0404 (9)	0.1421 (8)	0.1370 (29)	80.0 (169)

^aEquivalent isotropic temperature factor from anisotropic atom ($\times 10^3$).

X-ray Data and Structure Solution. Brown air-stable needle crystals were obtained from $[\text{Co}\{\text{o-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2\text{Cl}_2]\text{Cl}$ in ethanol by vapor diffusion of diethyl ether over several days. Subsequent structural analysis established that the crystals examined were $[\text{Co}\{\text{o-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2\text{Cl}_2][\text{CoCl}_4]$ (see Discussion). Photographic examination established the crystal system, the Laue group ($4/m$), and the approximate cell dimensions. Accurate cell dimensions were obtained from 25 accurately centered reflections on an Enraf-Nonius CAD-4 diffractometer equipped with Mo $K\alpha$ radiation.

The crystals are tetragonal, $a = 25.264$ (6) \AA , $c = 9.720$ (9) \AA , $V = 6204.0 \text{ \AA}^3$, and mol wt 1979.3 for $\text{C}_{40}\text{H}_{64}\text{Cl}_8\text{Co}_2\text{Sb}_8$, with $D_{\text{calc}} = 2.118$, $D_{\text{meas}} = 2.13(2) \text{ g cm}^{-3}$, and $Z = 4$ for space group $I4_1/a$ (No. 88) (systematic absences: hkl , $h + k + l \neq 2n$; $hk0$, $h(k) \neq 2n$; $00l$, $l \neq 4n$), $F(000) = 3716$, and $\mu(\text{Mo } K\alpha) = 45.61 \text{ cm}^{-1}$.

Data were collected from a room-temperature crystal ($0.50 \times 0.05 \times 0.05 \text{ mm}$) mounted in a thin-wall glass capillary with Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) and graphite monochromator. A total of 2164 reflections were recorded ($1.5 < \theta < 22^\circ$) for hkl (h (0–26), k (0–26), l (0–10)). The three check reflections showed no significant change during the experiment and a ψ -scan empirical absorption correction was applied to the data (transmission: max, 99.8%; min, 72.3%) together with the usual Lp factor. After removal of systematically absent reflections and averaging ($R_{\text{int}} = 0.089$), there remained 1911 unique reflections. Omitting observations with $F < 3\sigma(F)$ (674) left 1237 reflections used in the analysis.

The E statistics supported the centrosymmetric space group, and the structure was solved by using the direct-methods strategy available in SHELX.¹⁰ This located the heavy atoms, and subsequent structure factor and electron density syntheses found the remaining Cl and C atoms. A difference electron density synthesis at a later stage of refinement indicated the position of several H atoms and these were introduced into the model with calculated positions ($d(\text{C-H}) = 0.95 \text{ \AA}$). Methyl hydrogens were positioned by assuming an initial staggered conformation. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ converged to $R = 0.058$ ($R_w = 0.060$) ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$), 136 parameters, anisotropic (Sb, Co, Cl, C) and isotropic (H) thermal parameters, $w = 1/(\sigma^2(F) + 0.001F^2)$, max shift/error = 0.1, reflections/parameters = 9.1). The final difference electron density synthesis showed all features in the range 0.91 to -1.68 e \AA^{-3} . Scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref 11 (Sb, Co) and SHELX¹⁰ and all calculations were performed with the computer programs SHELX,¹⁰ ORTEP,¹² and XANADU¹³ on an ICL2976 computer.

The non-hydrogen atomic positions are given in Table I, referred to the coordinate origin on $\bar{1}$, and the calculated hydrogen positions, thermal parameters, and structure factors are available as supplementary material.

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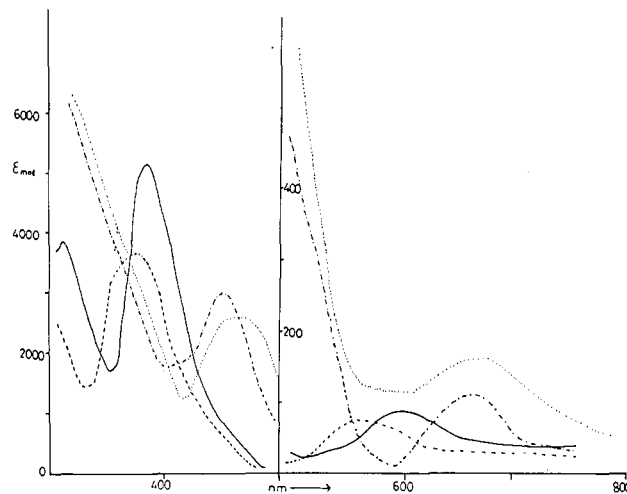


Figure 1. UV-visible spectra: (a) $\text{trans-}[\text{Co}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]\text{BF}_4$ (---); (b) $\text{trans-}[\text{Co}\{\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2\text{Cl}_2]\text{ClO}_4$ (—); (c) $\text{trans-}[\text{Co}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2\}_2\text{Cl}_2]\text{BF}_4$ (- · - · -); (d) $\text{trans-}[\text{Co}\{\text{o-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2\text{Cl}_2]\text{Cl}$ (···). Spectra a and b were recorded for the compounds in Me_2SO solution while spectra c and d were run in ethanol solution.

Results

Stibine Complexes. $[\text{Co}\{\text{o-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2\text{X}_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $[\text{Co}\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}_2\text{X}_2]\text{X}$ ($\text{X} = \text{Br}, \text{I}$) were readily obtained by reaction of the ligands with alcoholic solutions of $[\text{Co}(\text{H}_2\text{O})_6]\text{X}_2$ containing some added HX , followed by air oxidation. No cobalt(II) intermediates were isolated in these reactions, although no specific attempts were made to obtain them under rigorously oxygen-free conditions. A previous attempt to prepare Co(II) complexes of $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$ was unsuccessful.⁸ The phosphine-stibine analogues $[\text{Co}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2\}_2\text{X}_2]\text{Y}$ ($\text{X} = \text{Cl}, \text{Br}; \text{Y} = \text{BF}_4; \text{X} = \text{Y} = \text{I}$) were obtained in an essentially similar manner, the use of BF_4 as counterion in the two cases prevents contamination with $[\text{CoX}_4]^{2-}$ salts. Several attempts to prepare $[\text{Co}\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}_2\text{Cl}_2]\text{Cl}$ gave gray-green materials, which contained oxidized ligand, some unchanged cobalt(II) chloride, and a species soluble in CH_2Cl_2 that gave a ^{59}Co NMR resonance at ca. +4200 ppm. This value is reasonable for a $\text{CoSb}_2\text{Cl}_2^+$ unit (see below) and suggests that the desired complex is produced, but is too unstable to be isolated in a pure state.

The ditertiary stibine complexes are air-stable solids, and appear stable for several hours in acetone or ethanol solution, but decompose slowly in CH_2Cl_2 and more rapidly in MeCN or dimethyl sulfoxide (Me_2SO) producing $[\text{CoX}_4]^{2-}$ as one of the decomposition products readily identified by its electronic spectrum. The phosphine-stibine complexes are as expected more stable but still decompose on standing in Me_2SO solution. All the complexes are diamagnetic, consistent with t_{2g}^6 Co(III). The electronic spectra (Table II, Figure 1) contain a weak band at 14000–16000 cm^{-1} , which is consistent with a trans disposition of the halides and is assigned as $^1A_{1g} \rightarrow ^1E_g$ in D_{4h} symmetry.¹⁴ The further absorptions at ca. 18000–22000 cm^{-1} have $\epsilon_{\text{mol}} > 10^3 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$, which would normally lead to a $L \rightarrow M$ charge-transfer assignment. However anomalously high ϵ_{mol} values for d-d transitions have been observed in related systems^{14–16} containing soft donor ligands and for some platinum-metal complexes of stibine ligands,¹⁷ and an alternative assignment in terms of the metal-centered $^1A_{1g} \rightarrow ^1A_{2g}$ transition is possible. Figure 1 compares the spectra of $[\text{Co}\{\text{o-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2\text{Cl}_2]\text{Cl}$ and $[\text{Co}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2\}_2\text{Cl}_2]\text{BF}_4$ with those of the diphosphine

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Table II. Selected Spectroscopic Data

complex	color	$\delta(^1\text{H})^a$	$\delta(^{31}\text{P}\{^1\text{H}\})^b$	$\delta(^{59}\text{Co})^c$	$E_{\text{max}}/10^3 \text{ cm}^{-1}$ ($\epsilon_{\text{mol}}/\text{dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$)
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2\text{Cl}_2\}_2\text{BF}_4]$	yellow-green	1.4 (m) ^d	61.7	+4330 ^e	15.3 (114), 22.2 (2900), 29.4 (13490) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2\text{Br}_2\}_2\text{BF}_4]$	red-brown	1.5 (m) ^d	60.0	+4280 ^e	15.35 (175), 20.75 (2140), 28.9 (10135) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2\text{I}_2\}_2\text{I}]$	red-black	1.85 (m) ^d	47.0	+5480	14.4 (89), 16.9 (497), 19.75 (2250), 28.1 (18640) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_3\}_2(\text{BF}_4)_3]$	orange-brown		60.5, 64.5	+390 ^e	21.8 (160), 31.95 (2450) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{Cl}_2\}_2\text{Cl}]$	yellow-green	1.3 (s)		+4575	14.9 (152), 21.65 (2450), 29.2 (11610) ^g
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{Br}_2\}_2\text{Br}]$	red-brown	1.5 (s)		+4710	14.9 (163), 20.0 (1313), 28.4 (8080) ^g
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{I}_2\}_2\text{I}]$	red-purple	1.8 (s)		+6560	14.5 (175), 16.95 (615), 19.8 (1910), 27.3 (5110) ^g
$[\text{Co}\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}_2\text{Br}_2\text{Br}]$	red-brown	1.3 (s)		+4450	15.2 (50), 18.9 (1260), 20.5 (1765), 26.3 (2805) ^g
$[\text{Co}\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}_2\text{I}_2\text{I}]$	brown	1.35 (s)		+6565	13.6 (sh), 16.7 (825), 19.0 (2475), 25.6 (5540) ^g
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_2\text{Cl}_2\}_2\text{BF}_4]$	green		44.7	+3475	15.1 (222), 17.0 (190), 26.3 (1790) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_2\text{Br}_2\}_2\text{BF}_4]$	yellow-brown		44.2	+3430	14.6 (132), 16.6 (98), 25.6 (5570) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SeMe})_2\text{Cl}_2\}_2\text{BF}_4]$	yellow-brown		61.0 ^h	+4445	15.7 (200), 17.6 (184), 26.5 (9190) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SeMe})_2\text{Br}_2\}_2\text{BF}_4]$	yellow-brown		59.0 ⁱ	+4400	16.8 (241), 25.8 (9850), 28.6 (8750) ^f
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_3\}_2(\text{BF}_4)_3]$	yellow-green		56.8	+2620	17.5 (66), 26.0 (2310) ^f

^a Me resonance only in CDCl₃ relative to Me₄Si. ^b Relative to external 85% H₃PO₄, CH₂Cl₂ solutions. $\delta(^{31}\text{P}\{^1\text{H}\})$ for the free ligands: *o*-C₆H₄(PMe₂)(SbMe₂), -55.0; *o*-C₆H₄(PPh₂)(SMe), -13.5; *o*-C₆H₄(PPh₂)(SeMe), -10.7. ^c ± 50 ppm relative to K₃Co(CN)₆ in water, spectra obtained in CH₂Cl₂ solution unless indicated otherwise. ^d Complex overlapping resonances. ^e Me₂SO solution. ^f CH₂Cl₂ solution. ^g EtOH solution. ^h $\delta(^{77}\text{Se}) = +395$ (t); $^2J(^{77}\text{Se}-^{31}\text{P}) = 30$ Hz. ⁱ $\delta(^{77}\text{Se}) = +428$ (t); $^2J(^{77}\text{Se}-^{31}\text{P}) = 30$ Hz. Free ligand $\delta(^{77}\text{Se}) = +189$ ppm relative to neat Me₂Se.

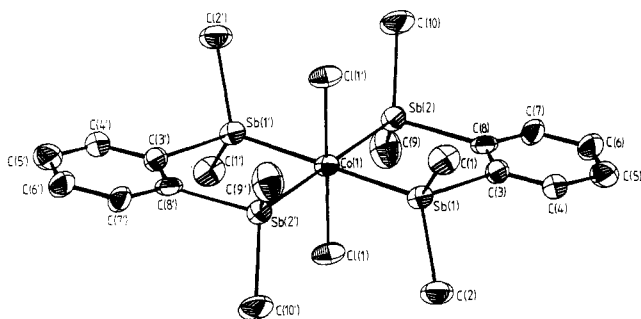


Figure 2. View of the cation of $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{Cl}_2\}_2][\text{CoCl}_4]$ showing the atom-numbering scheme. Thermal ellipsoids were drawn with 40% probability boundary surfaces and with hydrogen atoms omitted for clarity.

and diarsine analogues, clearly demonstrates that the complexes are isostructural, and shows the systematic changes with donor set. Confirmation of the *trans*-[Co(bidentate)₂X₂]⁺ geometry comes from the ¹H NMR spectra, which show single $\delta(\text{Me})$ resonances for the distibine complexes (cis isomers should have four resonances of equal intensity¹⁸), and from the X-ray study of $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{Cl}_2\}_2][\text{CoCl}_4]$ (below). The ¹H NMR spectra of the complexes of *o*-C₆H₄(PMe₂)(SbMe₂) are less clear due to overlap of the $\delta(\text{Me}-\text{Sb})$ and $\delta(\text{Me}-\text{P})$ resonances, but the ³¹P{¹H} spectra contain a single resonance for each complex and hence a single isomer with equivalent phosphorus atoms is present.

The synthesis of $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_3\}_2(\text{BF}_4)_3]$ was attempted via the route used⁶ to obtain other [Co(L-L)₃]³⁺: reaction of Co(OAc)₂ with excess L-L in ethanol followed by air oxidation and precipitation with HBF₄. The spectroscopic properties (Table II), particularly the $\delta(^{59}\text{Co}) +390$ value, are persuasive evidence for the CoP₃Sb₃ unit—compare CoP₆ at $\delta -2500$, CoAs₆ at $\delta -320$, and CoP₃As₃ at $\delta -910$.⁶

Structure of $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{Cl}_2\}_2][\text{CoCl}_4]$. This compound is the first ditertiary stibine complex of any metal to be structurally characterized. Inspection of the crystallographic literature¹⁹ found some 19 examples of stibine complexes, all of monodentates (R₃Sb) and most with metal carbonyls. The structure showed that the crystals isolated were $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{Cl}_2\}_2][\text{CoCl}_4]$ even though the starting compound was the corresponding chloride. Slow solvolysis of the cations to produce $[\text{CoCl}_4]^{2-}$ has been observed in a number of solvents (see above). The present cation contains a Co atom located on a center of symmetry with bond angles at the Co very close to 90°. A view of the cation is shown in Figure 2, and bond distances and angles are given in Table III.

Table III. Bond Distances (Å) and Angles (deg) for $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\text{Cl}_2\}_2][\text{CoCl}_4]$ ^a

Co(1)—Cl(1)	2.263 (4)	Sb(1)—C(1)	2.12 (2)
Co(1)—Sb(1)	2.505 (1)	Sb(1)—C(2)	2.12 (2)
Co(1)—Sb(2)	2.478 (1)	Sb(1)—C(3)	2.17 (2)
		Sb(2)—C(8)	2.13 (2)
Co(2)—Cl(2)	2.287 (6)	Sb(2)—C(9)	2.09 (2)
C—H (fixed)	0.95	Sb(2)—C(10)	2.09 (2)
C(3)—C(4)	1.36 (2)	Sb(1)⋯Sb(2)	3.470 (2)
C(4)—C(5)	1.41 (3)	Sb(1)⋯Sb(2')	3.577 (2)
C(5)—C(6)	1.38 (3)	Sb(1)⋯Cl(1)	3.374 (5)
C(6)—C(7)	1.36 (3)	Sb(2)⋯Cl(1)	3.331 (5)
C(7)—C(8)	1.39 (2)	Sb(1)⋯Cl(1')	3.379 (5)
C(8)—C(3)	1.38 (2)	Sb(2)⋯Cl(1')	3.381 (5)
Cl(1)—Co(1)—Sb(1)	89.9 (1)	Co(1)—Sb(1)—C(1)	121.9 (5)
Cl(1)—Co(1)—Sb(2)	89.1 (1)	Co(1)—Sb(1)—C(2)	118.6 (6)
Cl(1)—Co(1)—Sb(1')	90.1 (1)	Co(1)—Sb(1)—C(3)	106.5 (5)
Cl(1)—Co(1)—Sb(2')	90.9 (1)	Co(1)—Sb(2)—C(8)	106.4 (5)
Sb(1)—Co(1)—Sb(2)	88.3 (1)	Co(1)—Sb(2)—C(9)	119.1 (7)
Sb(1)—Co(1)—Sb(2')	91.8 (1)	Co(1)—Sb(2)—C(10)	120.1 (6)
C(1)—Sb(1)—C(2)	103.2 (8)	C(8)—Sb(2)—C(9)	102.4 (8)
C(1)—Sb(1)—C(3)	102.8 (8)	C(8)—Sb(2)—C(10)	105.0 (8)
C(2)—Sb(1)—C(3)	100.6 (7)	C(9)—Sb(2)—C(10)	101.7 (10)
Sb(1)—C(3)—C(4)	120 (1)	C(3)—C(4)—C(5)	119 (2)
Sb(1)—C(3)—C(8)	117 (1)	C(4)—C(5)—C(6)	118 (2)
Sb(2)—C(8)—C(3)	121 (1)	C(5)—C(6)—C(7)	122 (2)
Sb(2)—C(8)—C(7)	121 (1)	C(6)—C(7)—C(8)	120 (2)
Cl(2)—Co(2)—Cl(2 ⁱⁱ)	106.6 (4)	C(7)—C(8)—C(3)	118 (2)
Cl(2)—Co(2)—Cl(2 ⁱⁱⁱ)	111.0 (4)	C(8)—C(3)—C(4)	123 (2)

^a Symmetry operations: (i) $-x, -y, -z$; (ii) $-x, 3/2 - y, z$; (iii) $3/4 - y, 3/4 + x, 3/4 - z$.

The Co—Cl distance (2.263 (4) Å) may be compared with Co—Cl in $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\text{Cl}_2\}_2]^+$ (2.256 (3) Å)²⁰ and in $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\text{Cl}_2\}_2]^+$ (2.253 (av) Å),²¹ and the Co—Sb distances (2.505 (1), 2.478 (1) Å) are similar to that found for Co—Sb(Ph₃) (2.540 Å) in the glyoximate complex $[\text{Co}(\text{SbPh}_3)(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Cl}]$.²² The antimony ligand is the analogue of the well-known *o*-phenylenebis(dimethylarsine) and the Co—Sb distances may be compared with Co—As found in $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\text{Cl}_2\}_2]^+$ (2.334 (2) Å). The increased "bite" of the ligand (3.470 (2) Å) over the arsenic analogue²³ (~3.20 Å) reflects the longer Sb—C rather than changes in the ligand angles. The C₆ ring is planar (maximum deviation 0.01 (1) Å), but as noted before

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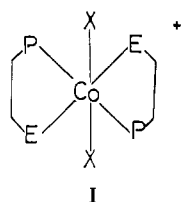
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for the arsenic analogue,²³ there is a dihedral angle of 8.7° between the C₆ ring and the CoSb₂ plane. The geometry about the Sb atom is similar to the phosphorus²¹ and arsenic²⁰ analogues with Me-Sb-Me ~ 102° and Co-Sb-Me ~ 120°. The Sb-C and C-C distances appear unexceptional.

The [CoCl₄]²⁻ anion is well documented, and in the present example the Co is on a special position (4b) and has 4 (S₄) point group symmetry. It has a Co-Cl distance of 2.287 (6) Å and a maximum deviation of 2.9 (4)° from the idealized tetrahedral value. The anion is thus very close to a regular tetrahedron whereas many other examples are appreciably more distorted.²⁴

***o*-C₆H₄(PPh₂)(SMe) and *o*-C₆H₄(PPh₂)(SeMe).** The cobalt(II) complexes of dithio- and diselenoethers are decomposed on treatment with halogens, although cobalt(III) complexes have been obtained with tetra-¹⁵ and hexathiamacrocycles.²⁵ Cobalt(II) complexes of the phosphine-thioether and phosphine-selenoether ligands, [Co(L-L)₂Br]ClO₄ (L-L = *o*-C₆H₄(PPh₂)(SMe), *o*-C₆H₄(PPh₂)(SeMe)), were reported⁹ by Dyer and Meek, and we have prepared [Co(L-L)₂X]BF₄ (X = Cl, Br) by a similar route. These red-brown Co(II) complexes can be oxidized to [Co(L-L)₂X₂]BF₄ by careful treatment with the appropriate halogen in a chlorocarbon solvent. Excess halogen causes decomposition and oxidation of the neutral ligands, easily detected by ³¹P NMR spectroscopy. The [Co(L-L)₂X₂]BF₄ are decomposed by strong donor solvents, and even in chlorocarbons slow decomposition occurs on standing, evident by the appearance of new resonances in the ³¹P NMR spectra and of bands characteristic of [CoX₄]²⁻ in the visible spectra.¹⁴ The presence of weak absorptions at 14000–17000 cm⁻¹ in the visible spectra of [Co(L-L)₂X₂]⁺ (Table II) shows the expected *trans*-CoX₂ unit is present, while the single ³¹P NMR resonance points to the presence of a single isomer. For [Co(*o*-C₆H₄(PPh₂)(SeMe)₂)₂]BF₄ it was also possible to record ⁷⁷Se NMR spectra (⁷⁷Se, *I* = 1/2, 7%) (Table II), each complex producing a single broad resonance that under high resolution appeared as a partially resolved triplet. The latter would indicate two equivalent phosphorus atoms and hence the “all-*trans*” isomer (I).



Addition of *o*-C₆H₄(PPh₂)(SMe), δ(³¹P) = -13.5, to a dichloromethane solution of [Co(*o*-C₆H₄(PPh₂)(SMe)₂Cl₂]⁺, δ(³¹P) = +44.7, caused a decrease in the intensity of the latter resonance, and a new resonance appeared at +56.8 ppm. When the [Co(*o*-C₆H₄(PPh₂)(SMe)₂Cl₂]⁺/ligand ratio was 1:1, only the latter species was present. The complex formed, [Co(*o*-C₆H₄(PPh₂)(SMe)₃](BF₄)₃, was isolated by reaction of the chloro complex, ligand, and AgBF₄ in a 1:1:2 mol ratio in CH₂Cl₂ and is assigned a *fac* structure on the basis of the single ³¹P NMR resonance. If pyramidal inversion at the group VIB atom is slow on the NMR time scale, two further isomers of I would be expected with the -E-Me (E = S, Se) groups on the same or opposite sides of the P₂E₂ plane. Inversion rates in coordinated thio- and selenoethers are very dependent upon the metal, metal oxidation state, and trans ligand,²⁶ and little is known about Co(III) complexes.²⁷ The single ³¹P (and ⁷⁷Se) resonance in each complex suggest only a single species and hence rapid inversion, although it should be noted that the resonances are broad (due to scalar broadening by the

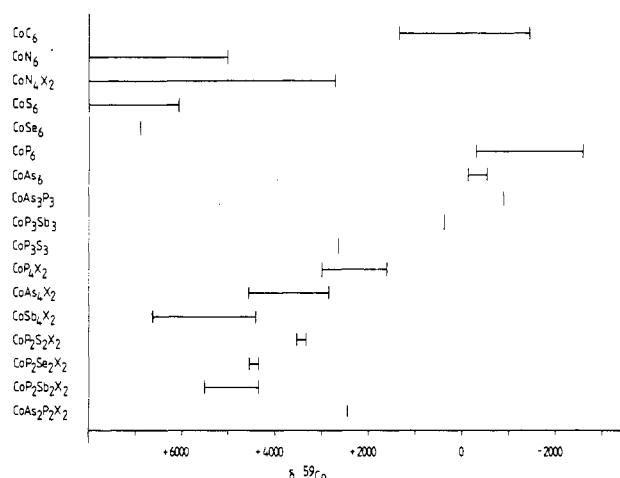


Figure 3. Characteristic cobalt chemical shift [$\delta(^{59}\text{Co})$] ranges for various donor sets upon Co(III). Data on CoC₆, CoN₆, CoN₄X₂, CoS₆, CoSe₆ were taken from ref 29; the remainder are from ref 6 and this work.

quadrupolar ⁵⁹Co)^{6,28} and closely spaced resonances might not be resolved. Unfortunately a variable-temperature NMR study that might clarify this point is precluded by the poor solubility and stability of these complexes in solution.

⁵⁹Co NMR Data. We have reported elsewhere the characteristic chemical shifts observed for cobalt(III) phosphine and arsine complexes,⁶ and a major aim of the present study was to extend this work to include other donor atoms—Sb, S, and Se. The complexes gave single broad resonances (*W*_{1/2} ca. 14 000–20 000 Hz), with no resolved coupling to the donor atoms. For homoleptic complexes CoL₆³⁺, δ(⁵⁹Co) exhibits an inverse dependence upon the ¹A_{1g} → ¹T_{1g} electronic spectral transition energy,²⁹ with different linear regressions observed for C, N, and O and for heavier donor atom complexes, while a single regression for all donors can be achieved³⁰ by incorporating the nephelauxetic parameter β₃₅. For lower symmetry complexes the lifting of the degeneracy results in splitting of the ¹A_{1g} → ¹T_{1g} transition, and in these cases a linear dependence of δ(⁵⁹Co) upon the weighted mean of the energies of the bands originating from the splitting of the ¹A_{1g} → ¹T_{1g} is observed.²⁹ For heavier (soft) donors, it is common for low-lying charge-transfer transitions to obscure some of the d-d bands, and this prevents both the calculation of the “weighted mean” transition energy and β₃₅. These problems were found in the present case but it is clear that the ⁵⁹Co chemical shift dependence upon the lower d-d transition energies generally holds. As observed previously for the diphosphine and diarsine analogues,⁶ the δ(⁵⁹Co) are very similar for corresponding chloro and bromo complexes, with the iodides having significantly higher frequency resonances. In complexes of *o*-C₆H₄(PMe₂)(SbMe₂), the antimony exerts the dominant effect upon the chemical shifts, which are much closer to those of the distibine analogues than to the diphosphines. No data for CoS₄X₂ or CoSe₄X₂ sets are available, but for the hybrid ligands a consistent trend is present: [Co(*o*-C₆H₄(PPh₂)₂)₂Cl₂]⁺ (δ = 2200⁶) < [Co(*o*-C₆H₄(PPh₂)(SMe)₂Cl₂]⁺ (δ = 3475) < [Co(*o*-C₆H₄(PPh₂)(SeMe)₂Cl₂]⁺ (δ = 4445).

Figure 3 summarizes the data currently available (ref 6 and 29 and this work) upon δ(⁵⁹Co) as a function of donor set (minimal dependence upon stereochemistry is observed). In some cases data on only one or two examples are available, and this accounts for the very narrow ranges, which will no doubt increase when more examples are studied. Despite the very large line widths it is

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evident that ^{59}Co NMR chemical shifts provide very useful information about the constitution of cobalt(III) complexes.

Discussion

As indicated in the Introduction, ligands with large soft antimony donor atoms might be expected to have little affinity for hard small high oxidation state metal centers. The successful synthesis of relatively stable Co(III) complexes shows that this is an oversimplification. Several factors will contribute to the stability of these complexes: (i) the t_{2g}^6 configuration is very stable, offering maximum ligand field stabilization energy in six-coordinate environments, and the electronic spectra show that the distibines exert a strong ligand field although considerably weaker than diphosphines or diarsines; (ii) cobalt(III) is inert to ligand substitution reactions, which is important since the free ligands are readily oxidized (conversely the lability of d^7 Co(II) is probably a major factor in the failure to isolate Co(II) complexes);³³ (iii) the greater stability of $o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$ over $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$, for example in the successful isolation of the chloride complex of the former, can be ascribed both to the more favorable ring size formed upon chelation (five vs. six) and to the "o-phenylene backbone effect" observed in other systems.^{5,21,31}

Acknowledgment. We thank Southampton University (H.C.J.) and the SERC (M.D.S.) for support, Dr. E. G. Hope for recording some of the cobalt NMR spectra, T. Kemmitt for the sample of $o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SeMe})$, and Dr. M. B. Hursthouse for the X-ray data collection on the Queen Mary College, London/SERC diffractometer.

Registry No. *trans*-[Co($o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$)₂Br]₂Br, 108347-45-1; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$)₂Cl]₂[CoCl₄], 108347-47-3; *trans*-[Co{Me₂Sb(CH₂)₃SbMe₂}₂Br]₂Br, 108347-48-4; *trans*-[Co{Me₂Sb(CH₂)₃SbMe₂}₂I]₂I, 108365-72-6; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$)₂I]₂I, 108347-49-5; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2$)₂Cl]₂BF₄, 108347-51-9; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2$)₂Br]₂BF₄, 108347-53-1; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2$)₂I]₂I, 108347-54-2; [Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_2$)₂Cl]BF₄, 108347-56-4; [Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_2$)₂Br]BF₄, 108393-22-2; [Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SeMe})_2$)₂Cl]BF₄, 108347-58-6; [Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SeMe})_2$)₂Br]BF₄, 108393-24-4; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_2$)₂Br]₂BF₄, 108347-60-0; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SeMe})_2$)₂Cl]₂BF₄, 108347-62-2; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SeMe})_2$)₂Br]₂BF₄, 108347-64-4; *fac*-[Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_3$)](BF₄)₃, 108347-66-6; *fac*-[Co($o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_3$)](BF₄)₃, 108347-68-8; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})_2$)₂Cl]₂BF₄, 108347-70-2; *trans*-[Co($o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$)₂Cl]₂Cl, 108347-71-3.

Supplementary Material Available: Tables of thermal parameters for non-hydrogen atoms (Table S-IV) and calculated atomic coordinates for H atoms (Table S-V) and a figure depicting the [CoCl₄]²⁻ anion (3 pages); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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 (33) Attempts to isolate the d^7 Ni(III) complexes [Ni($o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$)₂X]₂X (X = Cl, Br) failed, although transient ESR spectra, $g = 2.04$ (isotropic) characteristic of Ni(III), were obtained from [Ni($o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$)₂Br]₂ + Br₂ in chlorocarbon solvents at low temperature.³²

- (34) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Contribution from the Chemistry Departments, D-006, University of California, San Diego, La Jolla, California 92093, and University of Delaware, Newark, Delaware 19716

Preparation and Characterization of Tris(trimethylsilyl)silyl Derivatives of Zinc, Cadmium, and Mercury. X-ray Crystal Structure of Zn[Si(SiMe₃)₃]₂

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The thermally stable silyl complexes M[Si(SiMe₃)₃]₂ (M = Zn, **1a**; M = Cd, **1b**; M = Hg, **1c**) are prepared by reaction of the appropriate metal halides with 2 equiv of (THF)₃LiSi(SiMe₃)₃ in diethyl ether. 2,2'-Bipyridine (bpy) reacts with **1a** and **1b** to form the 1:1 adducts M[Si(SiMe₃)₃]₂(bpy) (M = Zn, **2a**; M = Cd, **2b**). The above silyl complexes are characterized by elemental analyses and NMR spectroscopy (¹H, ¹³C, and ²⁹Si). Compound **1a** is the first zinc silyl to be structurally characterized. Crystals of C₁₈H₅₄Si₈Zn (1a) are triclinic, $P\bar{1}$, with $a = 9.483$ (3) Å, $b = 9.762$ (3) Å, $c = 12.765$ (5) Å, $\alpha = 67.76$ (3)°, $\beta = 70.87$ (3)°, $\gamma = 60.95$ (3)°, $V = 940.3$ (5) Å³, and $Z = 1$. The molecule is located on an inversion center with Zn at the origin.

Introduction

Complexes containing bonds between silicon and a group 12 metal have been known for many years.¹ Recently, the isolation of thermally unstable zinc and cadmium derivatives completed the family of binary silyls M(SiMe₃)₂ (M = Zn, Cd, Hg).² Apart from Hg(SiMe₃)₂, which has been shown to be a useful silylating reagent,^{3,4} the reactivity of zinc, cadmium, and mercury silyl derivatives has not been extensively investigated.

Our studies of transition-metal-silicon chemistry⁵ have prompted us to search for new silylating agents. In particular, we have sought new methods for introducing the sterically hindered -Si(SiMe₃)₃ ligand into the coordination sphere of high-valent, coordinatively unsaturated metal complexes. The lithium silyl (THF)₃LiSi(SiMe₃)₃⁶ can be used to silylate some metal hal-

ides,^{5b,h,7} but in many cases decomposition resulting from reduction of the metal center is observed.⁸ We have therefore investigated

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