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*-$C_6H_4(SbMe_2)_2$ over $Me_2Sb(CH_2)_3SbMe_2$, 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*-$C_6H_4(PPh_2)(SeMe)$, and Dr. M. B. Hursthouse for the X-ray data collection on the Queen Mary College, London/SERC diffractometer.

Registry No. *trans*-$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2Br_2]Br$, 108347-45-1; *trans*-$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2Cl_2][CoCl_4]$, 108347-47-3; *trans*-$[Co\{Me_2Sb(CH_2)_3SbMe_2\}_2Br_2]Br$, 108347-48-4; *trans*-$[Co\{Me_2Sb(CH_2)_3SbMe_2\}_2I_2]I$, 108365-72-6; *trans*-$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2I_2]I$, 108347-49-5; *trans*-$[Co\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Cl_2]BF_4$, 108347-51-9; *trans*-$[Co\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br_2]BF_4$, 108347-53-1; *trans*-$[Co\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}I_2]I$, 108347-54-2; $[Co\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2Cl]BF_4$, 108347-56-4; $[Co\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2Br]BF_4$, 108393-22-2; $[Co\{o\text{-}C_6H_4(PPh_2)(SeMe)\}_2Cl]BF_4$, 108347-58-6; $[Co\{o\text{-}C_6H_4(PPh_2)(SeMe)\}_2Br]BF_4$, 108393-24-4; *trans*-$[Co\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2Br_2]BF_4$, 108347-60-0; *trans*-$[Co\{o\text{-}C_6H_4(PPh_2)(SeMe)\}_2Cl_2]BF_4$, 108347-62-2; *trans*-$[Co\{o\text{-}C_6H_4(PPh_2)(SeMe)\}_2Br_2]BF_4$, 108347-64-4; *fac*-$[Co\{o\text{-}C_6H_4(PPh_2)(SMe)\}_3](BF_4)_3$, 108347-66-6; *fac*-$[Co\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_3](BF_4)_3$, 108347-68-8; *trans*-$[Co\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2Cl_2]BF_4$, 108347-70-2; *trans*-$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2Cl_2]Cl$, 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 $[CoCl_4]^{2-}$ 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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(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 $Zn[Si(SiMe_3)_3]_2$

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The thermally stable silyl complexes $M[Si(SiMe_3)_3]_2$ (M = Zn, **1a**; M = Cd, **1b**; M = Hg, **1c**) are prepared by reaction of the appropriate metal halides with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ in diethyl ether. 2,2'-Bipyridine (bpy) reacts with **1a** and **1b** to form the 1:1 adducts $M[Si(SiMe_3)_3]_2(bpy)$ (M = Zn, **2a**; M = Cd, **2b**). The above silyl complexes are characterized by elemental analyses and NMR spectroscopy (^{1}H, ^{13}C, and ^{29}Si). Compound **1a** is the first zinc silyl to be structurally characterized. Crystals of $C_{18}H_{54}Si_8Zn$ (**1a**) are triclinic, $P\bar{1}$, with a = 9.483 (3) Å, b = 9.762 (3) Å, c = 12.765 (5) Å, α = 67.76 (3)°, β = 70.87 (3)°, γ = 60.95 (3)°, V = 940.3 (5) Å^3, 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 $M(SiMe_3)_2$ (M = Zn, Cd, Hg).[2] Apart from $Hg(SiMe_3)_2$, 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 chemistry[5] have prompted us to search for new silylating agents. In particular, we have sought new methods for introducing the sterically hindered $-Si(SiMe_3)_3$ ligand into the coordination sphere of high-valent, coordinatively unsaturated metal complexes. The lithium silyl $(THF)_3LiSi(SiMe_3)_3$[6] can be used to silylate some metal halides,[5g,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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Table I. NMR Data for New Compounds[a]

compd	phys properties	^1H NMR, δ	^{13}C NMR, δ	^{29}Si NMR, δ	λ_{max}, nm [ϵ, L mol^{-1} cm^{-1}]
1a	colorless cryst mp 194–195 °C burns in air	0.35 (s, $SiMe_3$)	4.54	−123.9 ($Si(SiMe_3)_3$) −7.18 ($SiMe_3$)	352.0 [800]
1b	pale green cryst mp 154–160 °C fumes in air	0.33 (s, $SiMe_3$)	4.74	−109.2 ($Si(SiMe_3)_3$) −6.28 ($SiMe_3$)	358.4 [1500]
1c	pale yellow cryst mp 199–200 °C slow dec in air	0.34 (s, $SiMe_3$)	4.71	−54.5 ($Si(SiMe_3)_3$) −2.84 ($SiMe_3$)	387.2 [700] 340.0 [2000]
2a	purple cryst mp 180–183 °C air sensitive	0.27 (s, 54 H, $SiMe_3$) 6.54, 6.90, 7.10, 8.84 (all m, 2 H, bpy)	5.11 ($SiMe_3$) 121.6, 124.7, 138.4, 149.4, 150.1 (bpy)	−150.8 ($Si(SiMe_3)_3$) −6.60 ($SiMe_3$)	258.0 [5000]
2b	red cryst mp 147–148 °C air sensitive	0.29 (s, 54 H, $SiMe_3$) 6.59, 6.97, 7.25, 8.70 (all m, 2 H, bpy)	4.94 ($SiMe_3$) 122.0, 124.6, 138.1, 149.6, 152.2 (bpy)	−139.1 ($Si(SiMe_3)_3$) −5.89 ($SiMe_3$)	276.7 [8500]

[a] All spectra recorded in benzene-d_6 at 300 MHz (^1H), 75.5 MHz (^{13}C), and 59.6 MHz (^{29}Si) and at 23 °C.

the use of milder reagents for the preparation of new transition-metal silyls.

This paper describes the synthesis and characterization of the new series of thermally stable, binary group 12 silyl derivatives $M[Si(SiMe_3)_3]_2$ (M = Zn, Cd, Hg) and the bipyridine adducts $M[Si(SiMe_3)_3]_2(bpy)$ (M = Zn, Cd). NMR and UV data are presented, along with an X-ray crystallographic study of $Zn[Si(SiMe_3)_3]_2$, the first zinc silyl to be structurally characterized.

Results and Discussion

Treatment of ethereal solutions of the appropriate metal halide with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ produces the new metal silyls $M[Si(SiMe_3)_3]_2$ (**1a–c**, eq 1). Compounds **1a–c** were obtained

$$MX_2 + 2(THF)_3LiSi(SiMe_3)_3 \xrightarrow{OEt_2} M[Si(SiMe_3)_3]_2 + 2LiX \qquad (1)$$

$$\begin{aligned} &\textbf{1a}\text{: M = Zn, X = Cl}\\ &\textbf{1b}\text{: M = Cd, X = Cl}\\ &\textbf{1c}\text{: M = Hg, X = Br}\end{aligned}$$

in 56–81% yield after crystallization from concentrated pentane solutions. Physical and spectral properties are collected in Table I.

Unlike their trimethylsilyl analogues,[2] these $-Si(SiMe_3)_3$ derivatives are thermally stable for prolonged periods in the absence of air. After several weeks under nitrogen, **1b** begins to show signs of decomposition, crumbling to a gray powder. Compound **1b** is much less stable in benzene-d_6 solution, decomposing entirely within 3 days at 22 °C. In contrast, **1a** and **1c** are stable indefinitely in the solid state under nitrogen and are stable in benzene-d_6 solution for at least 3 days.

1a reacts rapidly and cleanly with dry HCl(g) (benzene-d_6) to yield $HSi(SiMe_3)_3$ and $ZnCl_2$. Hydrolysis of **1a** takes place much more slowly (5 equiv of H_2O, benzene-d_6, $t_{1/2} \approx$ hours at 22 °C), again producing $HSi(SiMe_3)_3$ as the only $SiMe_3$-containing species as shown by ^1H NMR. This reactivity contrasts with that of the analogous alkyl derivatives $M[C(SiMe_3)_3]_2$,[9] which exhibit unusually high thermal and chemical stabilities. For example, these compounds are air-stable and are resistant to hydrolysis, even in refluxing tetrahydrofuran–water. The zinc derivative $Zn[C(SiMe_3)_3]_2$ is unreactive toward boiling concentrated hydrochloric acid, and toward bromine in carbon tetrachloride.[9]

Initial attempts to use compounds **1a** and **1c** as silylating reagents have failed. **1a** is unreactive toward the following metal halides in diethyl ether or benzene solvents at 22 °C: $TaCl_5$, $TiCl_4$, $ZrCl_4$, and $VCl_3(THF)_3$. There was no reaction after 8 h between **1a** and $ZrCl_4$ (or $TaCl_5$) in refluxing benzene. Refluxing benzene solutions of Cp^*TaCl_4 and **1a** or **1c** (1:1) gave dark brown solutions from which oily paramagnetic mixtures were isolated. These reactions were not pursued further.

Complexes **1a** and **1b** readily coordinate bipyridine to form the 1:1 adducts **2a** and **2b** (eq 2). These highly colored (see Table I) crystalline materials exhibit thermal stabilities comparable to those of their silyl precursors but are much less air sensitive. The cadmium derivative **2b** is again the least stable in solution. In common with alkyl and aryl complexes of mercury,[10] the silyl **1c** shows no tendency toward adduct formation with bipyridine (1 equiv, 2 days, 20 °C, benzene-d_6). These observations reflect the decreasing Lewis acid character of the metal as one proceeds down group 12 from Zn to Hg. Dialkylzinc–bipyridine complexes are also highly colored due to a metal-to-ligand charge-transfer transition.[10]

$$M[Si(SiMe_3)_3]_2 + bpy \xrightarrow{pentane} M[Si(SiMe_3)_3]_2(bpy) \qquad (2)$$

$$\begin{aligned} &\textbf{2a}\text{: M = Zn}\\ &\textbf{2b}\text{: M = Cd}\end{aligned}$$

NMR Studies. NMR data for all new compounds are given in Table I. The ^1H and ^{13}C NMR parameters are only shifted slightly on changing the central metal atom and/or its coordination environment. In contrast, changes in the ^{29}Si NMR parameters are much more pronounced. Factors contributing to shielding of ^{29}Si nuclei have been extensively reviewed;[11] it is generally accepted that the paramagnetic shielding term dominates and that substituent electronegativities play an important role.[11] As seen in Table I, for compounds **1a–c** the ^{29}Si NMR shifts move to lower field on descending the group from zinc to mercury. Both types of silicon atoms in these molecules follow this trend; although, as expected, the effect is much greater for the silicon directly bonded to the metal. Similar trends have been observed in the dialkyls $M(CH_2SiMe_3)_2$[12] (M = Zn, Cd, Hg), where the ^{13}C resonance of the methylene carbons shifts to lower field in going from zinc to mercury. The ^{29}Si NMR spectra of **2a** and **2b** show that the $-Si(SiMe_3)_3$ resonance experiences a large upfield shift (ca. 30 ppm) on coordination of bipyridine to the metal. The effect on the $-Si(SiMe_3)_3$ chemical shift is much smaller (ca. 0.5 ppm) and is in the opposite direction.

Description of the Structure of 1a. Clear, colorless crystals of **1a** were grown from concentrated pentane solution at −45 °C. Crystal and data collection parameters are summarized in Table II. Relevant geometrical parameters are given in Tables III and IV.

As seen in Figure 1, **1a** adopts a D_{3d} structure in the solid state, with the central zinc atom lying at an inversion center. The two

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Table II. Crystal, Data Collection, and Refinement Parameters for **1a**

(a) Crystal Parameters			
formula	$C_{18}H_{54}Si_8Zn$	γ, deg	60.95 (3)
cryst syst	triclinic	V, Å^3	940.3 (5)
space group	$P\bar{1}$	Z	1
a, Å	9.483 (3)	D(calcd), g cm^{-3}	1.00
b, Å	9.762 (3)		
c, Å	12.765 (5)	temp, °C	23
α, deg	67.76 (3)	μ, cm^{-1}	9.3
β, deg	70.87 (3)	cryst dimens, mm	0.26 × 0.32 × 0.32
(b) Data Collection			
diffractometer	Nicolet R3m/μ	reflecns collected	2123
radiation	Mo Kα (λ = 0.71073 Å)	unique data	2010
monochromator	graphite	R(int), %	2.52
scan technique	$\theta/2\theta$	unique data, $5\sigma(F_0)$	1039
2θ scan range, deg	$4° \le 2\theta \le 42°$	std reflecns	3 std/197 reflecns
data collected	$\pm h, \pm k, \pm l$	decay	≤1%
scan speed, deg/min	variable, 5–20		
(c) Refinement			
R_F, %	7.58	GOF	1.423
R_{wF}, %	7.79	data/parameter	8.38
$\Delta(\rho)$, e Å^{-3}	0.63		
mean shift/esd max	0.033	g^a	0.002

[a] $w^{-1} = \sigma^2(F_0) + gF_0^2$.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å$^2 \times 10^3$)

	x	y	z	U^a
Zn	5000	5000	5000	61 (2)
Si(1)	3733 (5)	4264 (5)	6921 (4)	62 (2)
Si(2)	5580 (6)	3372 (6)	8115 (5)	91 (3)
Si(3)	1448 (5)	6645 (5)	7213 (4)	84 (3)
Si(4)	3015 (6)	2210 (5)	7063 (4)	85 (3)
C(1)	4746 (27)	2774 (25)	9625 (15)	169 (20)
C(2)	7467 (23)	1584 (26)	7754 (20)	198 (21)
C(3)	6215 (26)	5008 (27)	7887 (20)	172 (22)
C(4)	407 (46)	6579 (31)	8525 (22)	538 (39)
C(5)	1916 (30)	8291 (27)	6767 (36)	405 (41)
C(6)	7 (39)	7268 (39)	6409 (36)	459 (48)
C(7)	1828 (25)	1648 (23)	8497 (16)	155 (19)
C(8)	4881 (23)	334 (19)	6860 (20)	180 (19)
C(9)	1808 (27)	2894 (24)	5927 (18)	165 (20)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Zn[Si(SiMe_3)_3]_2$ (**1a**)

Zn–Si(1)	2.342 (4)	Zn–Si(1a)	2.342 (4)
Si(1)–Si(2)	2.317 (8)	Si(1)–Si(3)	2.339 (5)
Si(1)–Si(4)	2.343 (9)	Si(2)–C(1)	1.80 (2)
Si(2)–C(2)	1.87 (2)	Si(2)–C(3)	1.86 (3)
Si(3)–C(4)	1.63 (3)	Si(3)–C(5)	1.71 (3)
Si(3)–C(6)	1.71 (5)	Si(4)–C(7)	1.84 (2)
Si(4)–C(8)	1.86 (2)	Si(4)–C(9)	1.86 (3)
Si(1)–Zn–Si(1a)	180.0 (1)	Zn–Si(1)–Si(2)	108.2 (2)
Zn–Si(1)–Si(3)	104.8 (2)	Si(2)–Si(1)–Si(3)	111.9 (3)
Zn–Si(1)–Si(4)	106.9 (2)	Si(2)–Si(1)–Si(4)	112.0 (2)
Si(3)–Si(1)–Si(4)	112.6 (3)	Si(1)–Si(2)–C(1)	112.5 (9)
Si(1)–Si(2)–C(2)	110.2 (10)	C(1)–Si(2)–C(2)	107.8 (9)
Si(1)–Si(2)–C(3)	110.0 (7)	C(1)–Si(2)–C(3)	108.7 (13)
C(2)–Si(2)–C(3)	107.5 (11)	Si(1)–Si(3)–C(4)	116.7 (9)
Si(1)–Si(3)–C(5)	112.9 (8)	C(4)–Si(3)–C(5)	107.0 (20)
Si(1)–Si(3)–C(6)	113.0 (13)	C(4)–Si(3)–C(6)	103.4 (19)
C(5)–Si(3)–C(6)	102.5 (18)	Si(1)–Si(4)–C(7)	111.6 (9)
Si(1)–Si(4)–C(8)	110.6 (8)	C(7)–Si(4)–C(8)	106.7 (8)
Si(1)–Si(4)–C(9)	109.7 (8)	C(7)–Si(4)–C(9)	109.7 (11)
C(8)–Si(4)–C(9)	108.4 (11)		

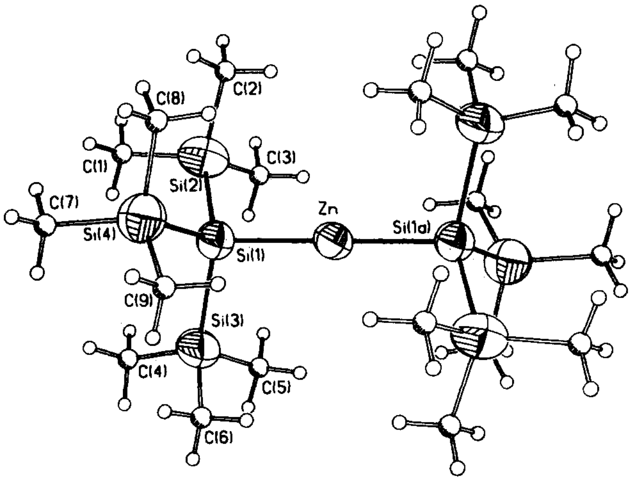

Figure 1. Molecular structure and labeling scheme for $Zn[Si(SiMe_3)_3]_2$ (**1a**). High thermal activity in the methyl groups required depiction of the C and H atoms as arbitrarily sized spheres.

–$Si(SiMe_3)_3$ ligands are bonded in a linear fashion to the metal (Si(1)–Zn–Si(1a) = 180.0 (1)°) and are staggered with respect to each other. The Zn–Si bond distance, 2.342 (4) Å, is close to that expected on the basis of covalent radii (2.35 Å, from covalent radii for Zn (1.18 Å[13]) and for Si (1.17 Å[14])). There is a small but significant deviation from tetrahedral environments about Si(1) and Si(1a). The average Si–Si–Si angle is 112.2 (3)°, and the average Zn–Si–Si angle is 106.6 (2)°. The mean Si–Si distance, 2.333 (7) Å, is slightly shorter than the corresponding distance in $Si(SiMe_3)_4$,[15] 2.361 (3) Å. For comparison, in the silyls $(CO)_5MSi(SiMe_3)_3$ (M = Mn,[16] Re[17]), the mean Si–Si–Si angles are 106.1 (3) and 105.8 (6)°, respectively. The mean M–Si–Si angles for these complexes are 112.7 (3) and 113.0 (5)°, and the mean Si–Si distances are 2.374 (8) and 2.37 (1) Å, respectively. In the last two compounds, distortions in the –$Si(SiMe_3)_3$ ligands were ascribed to steric repulsions between the silyl ligand and the $M(CO)_4$ equatorial planes. Undoubtedly steric factors are important in the observed distortions in **1a**, although here the effect is in the opposite direction; the $SiMe_3$ groups are bent toward, rather than away from, the metal atom.

Experimental Section

All manipulations were conducted under an atmosphere of nitrogen or argon by using Schlenk techniques and/or a Vacuum Atmospheres glovebox unless stated otherwise. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Galbraith or Schwarzkopf Laboratory; UV–vis spectra were recorded on an IBM 9420 instrument using 0.3–4 mM pentane solutions in a 1.00-cm quartz cell equipped with a Teflon needle valve and a ground-glass joint. Infrared spectra were recorded on a Perkin-Elmer 1330 instrument. NMR spectra were recorded on a GE QE-300 instrument at 300 MHz (^{1}H), 75.5 MHz (^{13}C), and 59.6 MHz (^{29}Si). An INEPT sequence[18] was employed to enhance signals in the ^{29}Si spectra. In this way, acceptable spectra could be obtained in less than 20 min with ca. 50 mg of compound in 0.4 mL of benzene-d_6. Zinc dichloride and cadmium dichloride were dried by refluxing with thionyl chloride. Mercuric bromide was recrystallized from hot ethanol and dried under vacuum. The lithium silyl $(THF)_3LiSi(SiMe_3)_3$ was prepared by the literature procedure.[6] Bipyridine was recrystallized from hot ethanol and dried under vacuum.

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Zn[Si(SiMe$_3$)$_3$]$_2$ (1a). A solution of $ZnCl_2$ (0.57 g, 4.2 mmol) and (THF)$_3$LiSi(SiMe$_3$)$_3$ (4.00 g, 8.40 mmol) in diethyl ether (30 mL) was stirred at room temperature for 10 h. After removal of volatiles under dynamic vacuum, the colorless residue was extracted into pentane (50 mL). Concentrating (to ca. 5 mL) and cooling to −45 °C for 12 h gave the product as colorless hexagonal plates (1.91 g, 81%), mp 194–195 °C. Anal. Calcd for $C_{18}H_{54}Si_8Zn$: C, 38.6; H, 9.71. Found: C, 38.6; H, 9.63. Mass spectrum (*m/e*): calcd for $C_{18}H_{54}Si_8Zn$, 560; found, 560 (most abundant peak with correct isotope envelope). IR (Nujol, CsI; cm^{-1}): 1385 m, 1298 w, 1250 s, 1223 s, 1085 br w, 1035 w, 825 br s, 737 m, 680 s, 618 s, 445 m, 407 m, 306 w.

Cd[Si(SiMe$_3$)$_3$]$_2$ (1b). The above procedure was repeated with $CdCl_2$ (0.19 g, 1.0 mmol) and (THF)$_3$LiSi(SiMe$_3$)$_3$ (1.00 g, 2.13 mmol) in diethyl ether (20 mL). The solution was stirred for 18 h and then worked up as above to give 0.45 g (74%) of pale green crystals, mp 154–160°C dec. Anal. Calcd for $C_{18}H_{54}CdSi_8$: C, 35.6; H, 8.96. Found: C, 35.6; H, 8.99. IR (Nujol, CsI; cm^{-1}): 1384 m, 1298 w, 1250 s, 1235 s, 1090 br w, 1037 m, 830 br s, 738 m, 678 s, 616 s, 450 m, 390 m, 295 w.

Hg[Si(SiMe$_3$)$_3$]$_2$ (1c). A solution of $HgBr_2$ (0.38 g, 1.1 mmol) and (THF)$_3$LiSi(SiMe$_3$)$_3$ (1.00 g, 2.1 mmol) in diethyl ether was stirred for 45 min. Workup as above yielded 0.41 g (56%) of pale yellow crystals, mp 199–200 °C. Anal. Calcd for $C_{18}H_{54}HgSi_8$: C, 31.1; H, 7.82. Found: C, 30.8; H, 7.80. IR (Nujol, CsI; cm^{-1}): 1382 m, 1297 w, 1248 s, 1233 s, 828 br s, 735 m, 678 s, 614 s, 451 m, 382 m, 290 w.

Zn[Si(SiMe$_3$)$_3$]$_2$(bpy) (2a). Pentane (30 mL) was added to a mixture of Zn[Si(SiMe$_3$)$_3$]$_2$ (0.20 g, 0.36 mmol) and bipyridine (0.056 g, 0.36 mmol). After the mixture was stirred for 10 min, the purple solution was filtered and concentrated to ca. 5 mL in vacuo. Cooling to −45 °C gave purple crystals (mp 180–183 °C) of the product in 77% yield (0.20 g). Anal. Calcd for $C_{28}H_{62}N_2Si_8Zn$: C, 46.9; H, 8.72. Found: C, 46.7; H, 8.79. IR (Nujol, CsI; cm^{-1}): 1589 m, 1432 s, 1302 m, 1230 br s, 1146 m, 1006 m, 830 br s, 751 s, 730 s, 672 s, 608 s, 431 m, 407 m.

Cd[Si(SiMe$_3$)$_3$]$_2$(bpy) (2b). The above method was followed with Cd[Si(SiMe$_3$)$_3$]$_2$ (0.20 g, 0.33 mmol) and bipyridine (0.051 g, 0.33 mmol). Bright red crystals (mp 147–148 °C) were isolated in 60% yield (0.15 g). Anal. Calcd for $C_{28}H_{62}CdN_2Si_8$: C, 44.0; H, 8.18. Found: C, 43.8; H, 8.21. IR (Nujol, CsI; cm^{-1}): 1585 m, 1545 w, 1430 s, 1201 m, 1228 s, 1145 m, 999 m, 830 br s, 750 s, 730 s, 672 s, 617 s, 438 m, 400 m.

Reaction of 1a with HCl. A 5-mm septum-capped NMR tube was charged with **1a** (0.020 g, 0.035 mmol) and benzene-d_6 (0.4 mL). Dry HCl gas (5 cm^3, excess) was then added to the NMR tube with a gastight syringe. Reaction occurred immediately to produce a white precipitate (presumably $ZnCl_2$) and HSi(SiMe$_3$)$_3$ as the only product detected by ^1H NMR.

Reaction of 1a with H_2O. To a 5-mm septum-capped NMR tube containing **1a** (0.020 g, 0.035 mmol) and benzene-d_6 (0.4 mL) was added H_2O (3 μL, 0.17 mmol). Over the course of a few hours, the reaction proceeded to give an insoluble white material and HSi(SiMe$_3$)$_3$ (by ^1H NMR).

Collection of Diffraction Data. Crystal data and the parameters used during the collection of diffraction data are collected in Table II. A colorless crystal of **1a** was sealed in a glass capillary. **1a** was found to crystallize in the triclinic space group $P\bar{1}$. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $14° < 2\theta < 21°$. No absorption correction was needed (regular crystal shape, $\mu = 9.3\ cm^{-1}$). The structure displayed an unusually high thermal activity in the methyl groups, and the absence of diffraction data beyond $2\theta = 42°$ and the very low density ($D = 1.00\ cm^{-3}$) are in keeping with a very loose lattice packing. The particularly high thermal parameters for the methyl groups of Si(3) may additionally contain unresolved rotational disorder.

Solution and Refinement of the Structure. The structure was solved intuitively, with Zn placed at ($^1/_2$, $^1/_2$, $^1/_2$). The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and were refined anisotropically. Hydrogen atom positions were calculated and fixed in idealized positions (d(C–H) = 0.96 Å; thermal parameters equal 1.2 times the isotropic equivalent for the carbon to which it was attached). The final difference Fourier synthesis showed only a diffuse background (maximum 0.63 e/Å^3). An inspection of F_o vs. F_c values and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic error. All computer programs used in the data collection and refinement are contained in the Nicolet (Madison, WI) program package SHELXTL (version 5.1).

Atomic coordinates are provided in Table III and bond distances and angles in Table IV. Additional data are available as supplementary material.

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Registry No. 1a, 108168-22-5; **1b**, 108168-23-6; **1c**, 61576-80-5; **2a**, 108150-76-1; **2b**, 108150-77-2; (THF)$_3$LiSi(SiMe$_3$)$_3$, 81859-95-2.

Supplementary Material Available: Table 2S, listing anisotropic thermal parameters, and Table 3S, listing hydrogen atom coordinates and their isotropic thermal parameters (2 pages); Table 1S, listing calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Cesium Molybdenum Alum, $Cs[Mo(H_2O)_6](SO_4)_2 \cdot 6H_2O$, at 110 K

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The X-ray crystal structure of cesium molybdenum alum provides the first structural characterization of the hexaaquamolybdenum(III) ion: Mo–O is 2.089 (1) Å. The alum belongs to the β class and has the cubic cell dimension $a = 12.442$ (1) Å at 110 K. Refinement of the structure (space group $Pa\bar{3}$) was made on the basis of 2791 reflections to $R = 0.0214$. A general discussion of the conformations of transition-metal hexaaqua ions is given. The occurrence of pyramidally ligating water molecules in certain α-alums is ascribed to a partial avoidance of π overlap with low-spin d^6 metal ions. The angular overlap model has been used to calculate the electronic stabilization energies of different conformations of d^n hexaaqua ions containing planarly ligating water molecules. In the alums, however, the conformation taken by the hexaaqua ions is that which fits the hydrogen-bonding pattern of the structure.

The hexaaquamolybdenum(III) ion has recently[1,2] been isolated in the solid state by preparation of cesium molybdenum alum, $Cs[Mo(H_2O)_6](SO_4)_2 \cdot 6H_2O$, whose low-temperature X-ray crystal structure is reported here. The structure gives a characterization of the $[Mo(H_2O)_6]^{3+}$ ion and extends the large series of cesium alum structure determinations already made.[3,4] These alum structures are important in the study of hexaaqua ions because the alums for many trivalent metal ions are the only compounds in which the hexaaqua ions may be isolated. It has thus been

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(2) Since the publication of ref 1 the magnetic susceptibility of the alum has been measured from 5 K to room temperature. The observed susceptibility is $\chi = 5.67 \times 10^{-3}$ cgsu mol^{-1} at 298 K, which corresponds to the magnetic moment of $[Mo(H_2O)_6]^{3+}$ being $\mu_{eff} = 3.77\ \mu_B$ when correction for diamagnetism has been made.

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