This is small compared to those of the synthetic complexes we have studied but still within the range observed for copper phenolate complexes.[15,16] Among the binuclear complexes, the phenolate-bridged pyridine complex exhibits a significantly larger extinction coefficient than does the phenolate-bridged pyrazole complex. Both complexes exhibit well-enhanced phenolate vibrations in their Raman spectra, so resonance Raman experiments on the binuclear copper proteins should yield valuable insights.

Resonance Raman studies have provided evidence for dioxygen binding in oxyhemocyanin[47,48] and oxytyrosinase[49] and for azide binding in corresponding azide complexes.[2] However, current efforts to probe the 400-nm region of the proteins appear to be hampered by fluorescence problems.[2] Should these difficulties be alleviated, our studies suggest that the observation of a phenolate ν_{C-O} at ca. 1300 cm^{-1} or higher in resonance Raman experiments on these proteins would support the proposal for an endogenous phenolate bridge in the met and oxy forms of hemocyanin and tyrosinase.

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Registry No. A, 86593-50-2; B, 79846-28-9; C, 93531-98-7; D, 93531-99-8; E, 93532-00-4; F, 82281-85-4; G, 93532-01-5; H, 93532-02-6; M″, 93532-03-7; 3-methylsalicylaldehyde, 824-42-0; 1,2-diaminoethane, 107-15-3; ^{18}O, 14797-71-8; tyrosinase, 9002-10-2.

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Three-Coordinate Metal Amides of Manganese(II) and Cobalt(II): Synthesis and X-ray Structure of the First Tris(silylamide) of Manganese and the X-ray Crystal Structures of $[M_2(N(SiMe_3)_2)_4]$ (M = Mn, Co)

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Three low-coordinate metal amides containing the bis(trimethylsilyl)amido group have been characterized by X-ray diffraction and elemental analysis. The molecular structures of $[Mn(N(SiMe_3)_2)_3Li(THF)]$ (**1**), $[Mn_2(N(SiMe_3)_2)_4]$ (**2**), and $[Co_2(N(SiMe_3)_2)_4]$ (**3**) have the amido group acting as both a bridging and a terminal ligand. The crystal data [Mo Kα (λ = 0.71069 Å)] at 140 K are as follows: (**1**) a = 11.678 (2) Å, b = 19.362 (2) Å, c = 17.020 (3) Å, β = 108.77 (1)°, Z = 4, space group $P2_1/n$; (**2**) a = 17.997 (2) Å, b = 14.942 (1) Å, c = 18.636 (2) Å, β = 121.24 (1)°, Z = 4 (dimers), space group $C2/c$; (**3**) a = 17.907 (3) Å, b = 14.644 (2) Å, c = 18.633 (3) Å, β = 120.47 (2)°, Z = 4 (dimers), space group $C2/c$. For **1**–**3** R = 0.031, 0.031, and 0.037, respectively. Complex **1** is the first homoleptic tris(silylamide) of manganese. Both **2** and **3** are dimeric in the solid state. All three complexes exhibit the coordination number 3 at the metal centers.

Introduction

The bis(trimethylsilyl)amido group has been used extensively to stabilize low coordination numbers and oxidation states throughout the periodic table.[1] The ligand was initially employed for this purpose with the first-row transition elements by Wannagat and Bradley.[2-8] This work resulted in the synthesis of the trivalent complexes $[M(N(SiMe_3)_2)_3]$[5], where M = Sc, Ti, V, Cr, and Fe, along with the bivalent compounds $[M(N(SiMe_3)_2)_2]$,[6-8] where M = Mn, Fe,[9] Co, and Ni.

X-ray structural reports have been published for the tris((trimethylsilyl)amides) of Ti, V, Cr, Fe, and many f-block elements.[4,5,10-12] Spectroscopic data for the remaining trivalent derivatives point to similar trigonal-planar structures although some trigonal-pyramidal structures have been found for Nd, Sc, Yb, and Eu.[13,14]

The X-ray crystal structure of $[Mn_2(N(SiMe_3)_2)_4]$ is the only reported structural example of a homoleptic[15] bivalent bis(silyl)amide complex.[6] However, structures of a few heteroleptic bis(silylamido) derivatives have been described. Three examples of these are the complexes [Cr(N-

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Table I. Crystallographic Data and Summary of Intensity Data Collection and Structure Refinement for **1-3**

formula	$C_{22}H_{62}N_3OLiMnSi_6$	$C_{24}H_{72}N_4Mn_2Si_8$	$C_{24}H_{72}N_4Co_2Si_8$
fw	615.15	751.43	759.42
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$C2/c$
T, K	140	140	140
a, Å	11.678 (2)	17.997 (2)	17.907 (3)
b, Å	19.362 (2)	14.942 (1)	14.644 (2)
c, Å	17.020 (3)	18.636 (2)	18.633 (3)
β, deg	108.77 (1)	121.24 (1)	120.47 (2)
V, Å^3	3643.7	4284.8	4211.3
Z	4	4 (dimers)	4 (dimers)
d_{calcd}, g cm^{-3}	1.12	1.17	1.20
cryst size, mm	0.25 × 0.35 × 0.48	0.81 × 0.69 × 0.60	0.51 × 0.26 × 0.27
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)		
μ, cm^{-1}	5.9	8.6	10.6
scan type	ω	ω	ω
scan speed, deg min^{-1}	30	60	30
scan range, deg	1.1	1.0	1.5
ω bkgd offsets, deg	±1.1	±1.0	±1.5
2θ limits, deg; *hkl* measd	0–45; $h,k,\pm l$	0–50; $h,k,\pm l$	0–45; $h,k,\pm l$
no. of unique data	4757	3638	2702
std reflcns (no decay obsd)	(0,0,6) (2,3,–2)	(8,2,–12) (0,10,2)	(3,5,–1) (0,2,5)
no. of reflcns used in LS ($F > 6\sigma(F)$)	3628	2672	1969
no. of parameters	555	318	318
R	0.031	0.031	0.037
R_w ($w = 1/\sigma^2(\lvert F \rvert)$)	0.032	0.032	0.038
GOF	1.17	1.07	1.19
G[a]	0.000 35	0.000 38	0.000 69

[a] The function minimized is $\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$ with $w = (\sigma^2(F_o) + GF_o^2)^{-1}$.

$(SiMe_3)_2)_2(THF)_2]$,[16] $[Co(N(SiMe_3)_2)_2(PPh_3)]$,[17] and $[Yb(N(SiMe_3)_2)_2(Me_2PCH_2CH_2PMe_2)]$.[18]

We are interested in the synthesis and characterization of late-transition-metal amides (and metal alkoxides)[19,20] for a number of reasons. First of all, only a few examples are known and the scarcity of such complexes has not been adequately explained. The only other structurally characterized homoleptic late-transition-metal amides are the compounds $[Co_2(NPh_2)_4]$,[21] $[(CuNEt_2)_4]$,[22] and $[(CuN(SiMe_3)_2)_4]$.[8,10,23] Second, there appears to be considerable doubt about the structures of some of the known compounds. For example, $[Co_2(N(SiMe_3)_2)_4]$ was reported to exist as a monomer in dilute hexane solution and the crystalline state.[24,25] We will show that the complex exists as a dimer in the solid phase. In addition, the reported structure of $[Co_2(NPh_2)_4]$ is also incorrect.[21]

We are also interested in the extension of the range of oxidation states and the stabilization of monomeric homoleptic complexes for the late-transition-metal amides. As part of our initial studies in this area we now report the low-temperature X-ray crystal structures of the complexes $[M_2(N(SiMe_3)_2)_4]$, where M = Mn and Co, and the first tris(silylamido)manganese complex $[Mn(N(SiMe_3)_2)_3Li(THF)]$ (**1**).

Experimental Section

General Procedures. All reactions were performed by using either modified Schlenk techniques (under N_2) or a Vacuum Atmospheres HE43-2 drybox (under argon). Solvents were freshly distilled from drying agents and degassed three times immediately before use. Solutions of these manganese and cobalt complexes are exceptionally air sensitive and immediately darken to violet or brown solutions if small controlled amounts of O_2 are added. When excess oxygen is present, these solutions turn black/brown rapidly and deposit solids that are only soluble in concentrated mineral acids. Anhydrous $MnBr_2$ and $CoCl_2$ (Aldrich) were used as purcashed. $[Co_2(N(SiMe_3)_2)_4]$,[7] $[Co_2(NPh_2)_4]$,[21] $[Mn_2(N(SiMe_3)_2)_4]$,[6,8] $[Mn(N(SiMe_3)_2)_2(THF)]$,[19,25] and lithium bis(trimethylsilyl)amide[5] were prepared by previously described procedures. Melting points were determined in capillaries sealed under argon. Elemental microanalyses were performed at the University of California, Berkeley, and at the University of California, Davis.

$[Mn(N(SiMe_3)_2)_3Li(THF)]$ (1). Anhydrous $MnBr_2$ (3.90 g) and lithium bis(trimethylsilyl)amide (10.00 g) were added to chilled (–30 °C) THF (65 mL). The mixture was then heated to reflux for 5 h and then allowed to cool to 20 °C. The solvent was removed in vacuo, and the residue was distilled as a pink oil, bp 88–100 °C (4×10^{-3} torr). The product slowly crystallized upon cooling to 20 °C. The pink solid is contaminated with a small amount of $[Mn(N(SiMe_3)_2)_2(THF)]$[26] but can be recrystallized from a concentrated hexane solution cooled to –30 °C in 64% yield. Complex **1** can also be prepared by treating $[Mn(N(SiMe_3)_2)_2(THF)]$ with 1 equiv of $[Li(N(SiMe_3)_2)]$ in THF;[19] mp 125 °C. Anal. Calcd for $C_{22}H_{62}N_3OLiMnSi_6$: C, 42.96; H, 10.16; N, 6.83. Found: C, 42.7; H, 10.1; N, 6.9.

X-ray Crystallographic Studies. All X-ray data were collected with a syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device, using a procedure described earlier.[27] Further details are in Table I.

All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors, including anomalous scattering, were from ref 28. The three structures were solved by direct methods, phasing difference electron density maps in consecutive steps.

Large, well-shaped, pale pink single crystals of $[Mn(N(SiMe_3)_2)_3Li(THF)]$ (**1**) were obtained by cooling a concentrated hexane solution to –30 °C. After the crystals were removed from

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Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for **1**

atom	*x*	*y*	*z*	U^a
Mn	9538 (1)	2149 (1)	6313 (1)	15 (1)*
Si(1)	7945 (1)	1827 (1)	7700 (1)	20 (1)*
Si(2)	7098 (1)	1313 (1)	5971 (1)	19 (1)*
Si(3)	10466 (1)	3660 (1)	6980 (1)	20 (1)*
Si(4)	8533 (1)	3688 (1)	5348 (1)	21 (1)*
Si(5)	11544 (1)	963 (1)	6667 (1)	18 (1)*
Si(6)	11198 (1)	1817 (1)	5150 (1)	19 (1)*
O(1)	6378 (2)	3482 (1)	6590 (1)	26 (1)*
N(1)	8032 (2)	1865 (1)	6705 (1)	17 (1)*
N(2)	9283 (2)	3246 (1)	6248 (1)	16 (1)*
N(3)	10796 (2)	1597 (1)	5999 (1)	17 (1)*
C(1)	8580 (3)	1054 (2)	8357 (2)	37 (1)*
C(2)	8783 (3)	2573 (2)	8314 (2)	31 (1)*
C(3)	6349 (3)	1883 (2)	7704 (2)	31 (1)*
C(4)	7651 (3)	1219 (2)	5064 (2)	28 (1)*
C(5)	7030 (3)	415 (2)	6361 (2)	36 (1)*
C(6)	5502 (3)	1624 (2)	5540 (2)	30 (1)*
C(7)	11376 (3)	4250 (2)	6540 (2)	28 (1)*
C(8)	9964 (3)	4225 (2)	7701 (2)	33 (1)*
C(9)	11553 (3)	3001 (2)	7610 (2)	29 (1)*
C(10)	7197 (3)	3167 (2)	4742 (2)	28 (1)*
C(11)	9400 (3)	3874 (2)	4622 (2)	32 (1)*
C(12)	7955 (3)	4548 (2)	5561 (2)	33 (1)*
C(13)	13219 (3)	1097 (2)	7069 (2)	35 (1)*
C(14)	11020 (4)	952 (2)	7594 (2)	30 (1)*
C(15)	11218 (3)	79 (2)	6211 (2)	34 (1)*
C(16)	12217 (3)	2585 (2)	5370 (2)	30 (1)*
C(17)	9844 (3)	2005 (2)	4236 (2)	28 (1)*
C(18)	12022 (3)	1123 (2)	4777 (2)	28 (1)*
C(19)	5269 (3)	3624 (2)	4917 (2)	43 (1)*
C(20)	4608 (3)	4167 (2)	6225 (2)	51 (2)*
C(21)	4998 (4)	4017 (2)	7135 (3)	68 (2)*
C(22)	6296 (4)	3816 (2)	7329 (2)	49 (2)*
Li(1)	7756 (4)	2937 (3)	6557 (3)	24 (2)*

[a] In this and the following tables asterisks indicate equivalent isotropic *U* defined, as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for **2**

atom	*x*	*y*	*z*	*U*
Mn(1)	0	1495 (1)	2500	15 (1)*
Mn(2)	0	3376 (1)	2500	15 (1)*
Si(1)	1976 (1)	1985 (1)	2903 (1)	18 (1)*
Si(2)	623 (1)	2881 (1)	1294 (1)	18 (1)*
Si(3)	413 (1)	−409 (1)	3434 (1)	21 (1)*
Si(4)	876 (1)	5282 (1)	3288 (1)	23 (1)*
N(1)	747 (1)	2438 (1)	2234 (1)	15 (1)*
N(2)	0	158 (2)	2500	18 (1)*
N(3)	0	4714 (2)	2500	18 (2)*
C(1)	2720 (2)	2686 (2)	3044 (2)	25 (1)*
C(2)	1951 (2)	1828 (2)	3966 (2)	26 (1)*
C(3)	1940 (2)	861 (2)	2554 (2)	24 (1)*
C(4)	1092 (2)	2185 (2)	788 (2)	28 (2)*
C(5)	−552 (2)	3033 (2)	494 (2)	27 (1)*
C(6)	1144 (2)	4007 (2)	1467 (2)	24 (1)*
C(7)	423 (2)	321 (2)	4257 (2)	33 (2)*
C(8)	−258 (2)	−1407 (2)	3348 (2)	45 (2)*
C(9)	1553 (2)	−820 (2)	3871 (2)	34 (2)*
C(10)	1871 (2)	4572 (2)	3781 (2)	33 (2)*
C(11)	702 (2)	5659 (2)	4149 (2)	40 (2)*
C(12)	1185 (2)	6300 (2)	2914 (2)	37 (2)*

a Schlenk tube inside the drybox, they were protected from air contamination by a layer of epoxy resin. A large crystal was cut to a suitable size, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream (140 K). Final lattice parameters were determined by a least-squares refinement of 20 accurately centered reflections with 25° < 2θ < 35°. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

The space group was uniquely determined as $P2_1/n$ from the systematic absences for $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$). Although the precise stoichiometry was unknown initially, the correct structure was found and subsequently refined by least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms. All of the 62 H atoms were detected in a difference electron density map; their sites compared well with coordinates calculated according to carbon hybridization. The H atoms were included in the refinement and allowed to refine isotropically. The refinement converged with $R = 0.031$ for the 3628 reflections used. Table II contains the final atomic coordinates for **1**.

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for **3**

atom	*x*	*y*	*z*	*U*
Co(1)	0	1568 (1)	2500	13 (1)*
Co(2)	0	3332 (1)	2500	13 (1)*
Si(1)	1777 (1)	1994 (1)	2892 (1)	16 (1)*
Si(2)	587 (1)	2901 (1)	1277 (1)	16 (1)*
Si(3)	434 (1)	−345 (1)	3431 (1)	19 (1)*
Si(4)	867 (1)	5242 (1)	3288 (1)	20 (1)*
N(1)	720 (2)	2450 (2)	2228 (2)	13 (1)*
N(2)	0	256 (3)	2500	16 (2)*
N(3)	0	4636 (3)	2500	17 (2)*
C(1)	2705 (3)	2707 (3)	3019 (3)	24 (2)*
C(2)	1942 (3)	1840 (3)	3956 (3)	22 (2)*
C(3)	1913 (3)	858 (3)	2520 (3)	20 (2)*
C(4)	1074 (3)	2195 (3)	782 (3)	26 (2)*
C(5)	−588 (3)	3049 (3)	474 (3)	24 (2)*
C(6)	1129 (3)	4040 (3)	1462 (3)	23 (2)*
C(7)	449 (4)	357 (4)	4281 (3)	29 (2)*
C(8)	−239 (4)	−1362 (4)	3350 (4)	35 (3)*
C(9)	1572 (3)	−773 (4)	3833 (3)	29 (2)*
C(10)	1885 (3)	4546 (3)	3795 (3)	27 (2)*
C(11)	673 (3)	5642 (3)	4133 (3)	34 (3)*
C(12)	1163 (3)	6277 (3)	2895 (3)	31 (3)*

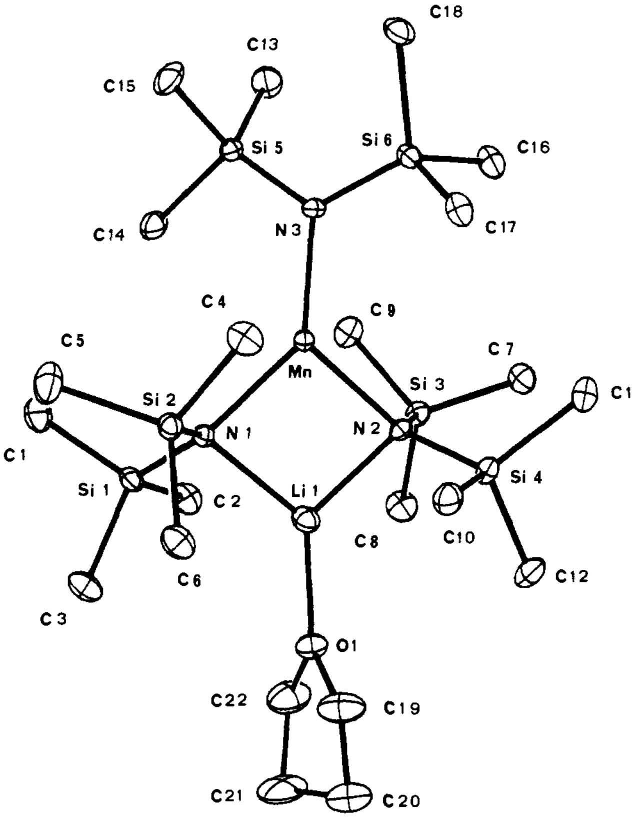

Figure 1. Computer-generated perspective diagram of **1**. The hydrogen atoms have been omitted for clarity.

Pink crystals of $[Mn_2(N(SiMe_3)_2)_4]$ (**2**) and green crystals of $[Co_2(N(SiMe_3)_2)_4]$ (**3**) were obtained by cooling concentrated hexane solutions to −30 °C. The crystals were handled by the procedure described earlier for **1**. The systematic absences were consistent with the space groups *C*2/*c* or *Cc*. The space group *C*2/*c* was assumed and confirmed by the successful refinement of the structures. The non-hydrogen atoms were refined with anisotropic thermal parameters. All 72 hydrogen atoms were located in a difference electron density

Table V. Some Selected Bond Distances (Å) and Angles (deg) for **1**

(a) Bond Distances			
Mn-N(1)	2.143 (3)	Mn-N(2)	2.143 (2)
Mn-N(3)	2.023 (3)	Mn-Li(1)	2.718 (6)
Si(1)-N(1)	1.731 (3)	Si(1)-C(1)	1.872 (3)
Si(2)-N(1)	1.737 (2)	Li(1)···C(2)	2.93 (1)
Si(3)-N(2)	1.730 (2)	Li(1)···C(10)	2.98 (1)
Si(4)-N(2)	1.728 (2)	Li(1)···H(2c)	2.46 (3)
Si(5)-N(3)	1.709 (2)	Li(1)···H(10b)	2.47 (3)
Si(6)-N(3)	1.711 (3)	Li(1)···Si(1)	2.860 (6)
O(1)-C(19)	1.453 (3)	O(1)-C(22)	1.445 (5)
O(1)-Li(1)	1.939 (6)	N(1)-Li(1)	2.104 (6)
N(2)-Li(1)	2.101 (6)	C(19)-C(20)	1.495 (6)
C(20)-C(21)	1.495 (6)	C(21)-C(22)	1.496 (6)
(b) Bond Angles			
N(1)-Mn-N(2)	99.0 (1)	N(1)-Mn-N(3)	133.2 (1)
N(2)-Mn-N(3)	127.7 (1)	N(1)-Mn-Li(1)	49.6 (1)
N(2)-Mn-Li(1)	49.5 (1)	N(3)-Mn-Li(1)	173.6 (1)
N(1)-Si(1)-C(1)	118.8 (1)	N(1)-Si(1)-C(2)	109.3 (1)
C(1)-Si(1)-C(2)	104.4 (1)	N(1)-Si(1)-C(3)	111.9 (1)
C(1)-Si(1)-C(3)	104.3 (2)	C(2)-Si(1)-C(3)	107.3 (2)
N(1)-Si(2)-C(4)	110.5 (1)	N(1)-Si(2)-C(5)	113.9 (1)
N(2)-Si(3)-C(7)	114.8 (1)	N(1)-Si(2)-C(6)	113.5 (1)
N(2)-Si(4)-C(10)	108.5 (1)	N(2)-Si(3)-C(8)	113.3 (1)
N(3)-Si(5)-C(13)	113.3 (1)	N(2)-Si(3)-C(9)	109.5 (1)
N(3)-Si(6)-C(16)	111.1 (1)	N(2)-Si(4)-C(11)	117.0 (1)
C(16)-Si(6)-C(17)	109.1 (1)	N(2)-Si(4)-C(12)	112.3 (1)
C(16)-Si(6)-C(18)	106.0 (2)	N(3)-Si(5)-C(14)	109.5 (1)
C(19)-O(1)-C(22)	108.0 (3)	N(3)-Si(5)-C(15)	112.9 (1)
C(22)-O(1)-Li(1)	123.8 (2)	N(3)-Si(6)-C(17)	111.3 (1)
Mn-N(1)-Si(2)	108.8 (1)	N(3)-Si(6)-C(18)	114.6 (1)
Mn-N(1)-Li(1)	79.6 (2)	C(17)-Si(6)-C(18)	104.3 (1)
Si(2)-N(1)-Li(1)	119.0 (2)	C(19)-O(1)-Li(1)	128.2 (3)
Mn-N(2)-Si(4)	124.0 (1)	Mn-N(1)-Si(1)	128.8 (1)
Mn-N(2)-Li(1)	79.6 (2)	Si(1)-N(1)-Si(2)	117.2 (1)
Si(4)-N(2)-Li(1)	97.7 (2)	Si(1)-N(1)-Li(1)	96.0 (2)
Mn-N(3)-Si(6)	120.8 (1)	Mn-N(2)-Si(3)	110.9 (1)
O(1)-C(19)-C(20)	106.7 (3)	Si(3)-N(2)-Si(4)	118.0 (1)
Mn-Li(1)-O(1)	173.1 (2)	Si(3)-N(2)-Li(4)	119.8 (2)
O(1)-Li(1)-N(1)	129.0 (3)	Mn-N(3)-Si(5)	117.5 (1)
O(1)-Li(1)-N(2)	129.1 (3)	Si(5)-N(3)-Si(6)	121.4 (2)
C(19)-C(20)-C(21)	102.0 (3)	N(1)-Li(1)-N(2)	101.6 (2)
O(1)-C(22)-C(21)	105.7 (3)	Mn-Li(1)-N(2)	50.9 (1)
Mn-Li(1)-N(1)	50.9 (1)		

map. The H atoms were included in the refinement and allowed to refine isotropically. For **2**, the refinement converged with $R = 0.031$ for the 2672 reflections used. For **3**, the refinement converged with $R = 0.037$ for the 1969 reflection used. The final difference maps showed no residues of significance (maximum peak 0.46 e Å^{-3}). Tables III and IV contain the final atomic coordinates for **2** and **3**.

Discussion

[Mn(N(SiMe$_3$)$_2$)$_3$Li(THF)] (1). This structure (Figure 1) is of interest since it is the first monomeric homoleptic three-coordinate manganese amide. Table V contains some selected bond distances and angles for **1**. The geometry at manganese is distorted trigonal planar. The atoms N(1), N(2), N(3), Mn, Li(1), and O(1) are essentially coplanar. The dihedral angle between the Mn, N(1), N(2), N(3) plane and the Mn, N(3), Si(5), Si(6) plane is 44.3°. This is slightly less than the characteristic angle of ca. 51° in other tris(silylamides).[3,4] This angle is believed to be a compromise of steric factors that favor an angle of 90° and electronic factors (ligand-to-metal π bonding) that favor a zero dihedral angle. The dihedral angle in [Li(Mn(N(SiMe$_3$)$_2$)(*t*-Bu$_3$CO)$_2$)] (**4**) is 88.1°.[19] Packing effects in the crystal structure probably influence the dihedral angle a great deal. The average bridging Mn–N and N–Si bond distances are slightly shorter than those found in **2**. The Mn–N(3) distance is just slightly longer than the Mn–N distance of 2.001 (3) Å in **4**. The average terminal N–Si distance is less than the average N–Si distance for the bridging amides. The geometry at N(3) is different from that at N(1) or N(2). The Si(5)–N(3)–Si(6) angle of 121.4 (2)° is wider than the average Si–N–Si angle for the bridging amides.

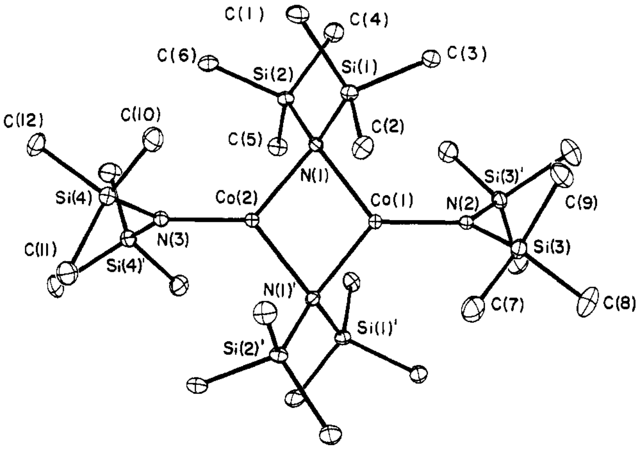

Figure 2. Computer-generated perspective diagram of **3**. The complex **2** is isostructural. The hydrogen atoms have been omitted for clarity.

The Mn···Li(1) distance of 2.718 (6) Å is larger than the Mn···Li(1) distance of 2.640 (7) Å in **4** or 2.650 (19) Å in [Li$_2$(MnBr$_2$(OCt-Bu$_3$)$_2$)(THF)$_2$][19] (**5**). These distances are similar to other structures that have been discribed as strongly associated ion pairs where the Li atom acts as an electron-rich partner due to electron donation from a nearby donor molecule.[29-31] The excess charge on lithium aids in the formation of a Coulombic interaction between the metal and also permits electron transfer to the π acceptor orbitals on the bridging ligands. Molecule **1** can also be viewed as an acid–base complex. The lone pairs on the amido nitrogens can donate electron density to either the manganese or the lithium atoms. The N–Si distances in the bridging amido groups support a compromise between these two views.

Complexes **1** and **4** are very soluble in hydrocarbon solvents due to the ability of the N(SiMe$_3$)$_2^-$ and *t*-Bu$_3$CO$^-$ groups in providing a hydrocarbon-like exterior. The main difference between the N(SiMe$_3$)$_2^-$ group and the *t*-Bu$_3$CO$^-$ group that the latter is able to intercalate ions such as Li$^+$ without permitting the Li$^+$ ion to associate with a donor molecule such as THF. Since the steric bulk of the *t*-Bu$_3$CO$^-$ group is greatest about three bonds distant from the metal, it forces the electron-deficient Li$^+$ ion to interact (Li···H = 2.1–2.2 (1), Li···C = 2.46–2.52 (2) Å) with the closest methyls in the *t*-Bu$_3$CO$^-$ group.[19,20,32] The Li$^+$ ion in **1** associates with a THF molecule and has weaker Li···C and Li···H interactions than **4** and **5**. The N(1)–Si(1)–C(2) and N(2–)Si(4)–C(10) angles are 109.3 (1) and 108.5 (1)° while the other N–Si–C angles average 115 (1)°. The shortest Li···Si distances is similar to the shortest Li···C distances. Similar interactions have been reported for [Eu(N(SiMe$_3$)$_2$)$_3$Na] and [Yb(N(SiMe$_3$)$_2$)$_3$Na].[12,18]

The THF molecule in **1** is not disordered as is often the case in room-temperature determinations.

[M$_2$(N(SiMe$_3$)$_2$)$_4$] (M = Mn (2) or Co (3)). In order to compare our low-temperature results for **1** with those of complex [Mn$_2$(N(SiMe$_3$)$_2$)$_4$] (**2**), we have redetermined the structure of this complex at 140 K and its corresponding cobalt analogue **3** (see Figure 2).

The low-temperature X-ray structure of **2** is similar to the previously reported room-temperature structure.[6] Upon cooling to 140 K, the dimer contracts along the C_2 axis that

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Table VI. Some Selected Bond Distances (Å) and Angles (deg) for **2** and **3**

(a) Bond Distances for **2**			
Mn(1)-Mn(2)	2.811 (1)	Mn(1)-N(1)	2.174 (3)
Mn(1)-N(1′)	2.174 (3)	Mn(1)-N(2)	1.997 (3)
Mn(2)-N(3)	1.999 (3)	Mn(2)-N(1)	2.170 (3)
Si(1)-N(1)	1.771 (2)	Mn(2)-N(1′)	2.170 (3)
Si(2)-N(1)	1.775 (3)	Si(2)-C(6)	1.870 (3)
Si(3)-N(2)	1.720 (2)	N(3)-Si(4′)	1.721 (2)
Si(4)-N(3)	1.721 (2)	N(2)-Si(3′)	1.720 (2)
(b) Bond Angles for **2**			
N(1)-Mn(1)-N(2)	130.4 (1)	N(1)-Mn(1)-N(1′)	99.2 (1)
N(1)-Si(1)-C(1)	115.6 (1)	N(1)-Si(1)-C(2)	108.2 (2)
C(1)-Si(1)-C(2)	106.8 (1)	N(1)-Si(1)-C(3)	112.9 (1)
C(1)-Si(1)-C(3)	106.3 (2)	C(2)-Si(1)-C(3)	106.5 (2)
N(1)-Si(2)-C(4)	115.5 (1)	N(1)-Si(2)-C(5)	110.1 (2)
C(5)-Si(2)-C(6)	106.7 (1)	N(1)-Si(2)-C(6)	111.8 (1)
N(2)-Si(3)-C(7)	111.0 (1)	N(2)-Si(3)-C(8)	112.6 (1)
N(3)-Si(4)-C(10)	111.1 (1)	N(2)-Si(3)-C(9)	113.7 (1)
Mn(1)-N(1)-Mn(2)	80.6 (1)	N(3)-Si(4)-C(11)	113.1 (1)
Mn(2)-N(1)-Si(1)	130.3 (1)	N(3)-Si(4)-C(12)	113.6 (1)
Mn(2)-N(1)-Si(2)	102.0 (1)	Mn(1)-N(1)-Si(1)	98.8 (1)
Mn(1)-N(2)-Si(3)	119.5 (1)	Mn(1)-N(1)-Si(2)	133.7 (1)
Si(3)-N(2)-Si(3′)	121.0 (2)	Si(1)-N(1)-Si(2)	112.2 (2)
Mn(2)-N(3)-Si(4′)	119.6 (1)	Si(4)-N(3)-Si(4′)	120.8 (2)
(c) Bond Distances for **3**			
Co(1)-Co(2)	2.583 (1)	Co(1)-N(1)	2.062 (4)
Co(1)-N(2)	1.922 (5)	Co(1)-N(1′)	2.062 (4)
Co(2)-N(1)	2.062 (4)	Co(2)-N(3)	1.910 (5)
Co(2)-N(1′)	2.062 (4)	Si(1)-N(1)	1.785 (3)
Si(2)-C(6)	1.872 (5)	Si(2)-N(1)	1.790 (4)
N(2)-Si(3′)	1.739 (3)	Si(3)-N(2)	1.739 (3)
N(3)-Si(4′)	1.744 (3)	Si(4)-N(3)	1.744 (3)
(d) Bond Angles for **3**			
Co(2)-Co(1)-N(1)	51.2 (1)	Co(2)-Co(1)-N(2)	180.0
N(1)-Co(1)-N(2)	128.8 (1)	Co(1)-Co(2)-N(3)	180.0
N(1)-Co(1)-N(1′)	102.4 (2)	N(1)-Si(1)-C(2)	108.8 (2)
N(1)-Co(2)-N(3)	128.8 (1)	N(1)-Si(1)-C(3)	111.6 (2)
N(1)-Si(1)-C(1)	116.1 (2)	N(1)-Si(2)-C(5)	111.4 (2)
C(1)-Si(1)-C(2)	106.4 (2)	N(1)-Si(2)-C(6)	110.5 (2)
C(1)-Si(1)-C(3)	105.7 (2)	N(2)-Si(3)-C(8)	112.2 (2)
N(1)-Si(2)-C(4)	115.0 (2)	N(2)-Si(3)-C(9)	114.2 (2)
N(2)-Si(3)-C(7)	111.9 (2)	N(3)-Si(4)-C(11)	113.7 (2)
N(3)-Si(4)-C(10)	111.8 (2)	N(3)-Si(4)-C(12)	113.0 (2)
Co(1)-N(1)-Co(2)	77.6 (2)	Co(1)-N(1)-Si(1)	99.8 (2)
Co(2)-N(1)-Si(1)	129.8 (2)	Co(1)-N(1)-Si(2)	133.5 (2)
Co(2)-N(1)-Si(2)	103.1 (2)	Si(1)-N(1)-Si(2)	112.7 (2)
Co(1)-N(2)-Si(3)	120.4 (1)	Co(2)-N(3)-Si(4)	120.6 (1)
Si(3)-N(2)-Si(3′)	119.2 (3)	Si(4)-N(3)-Si(4′)	118.9 (3)

connects the atoms Mn(1), Mn(2), N(2), and N(3). The Mn(1)–Mn(2) distance is shortened from 2.841 (1) to 2.811 (1) Å. In **2** and **3**, both metal atoms, N(1), N(1)′, N(2), and N(3) are coplanar. The geometry at each of the three-coordinate metal centers is distorted trigonal planar, with each metal being bound to one terminal amido group and two bridging groups. Selected bond distances and angles for **2** and **3** are given in Table VI.

As expected, the angles at the terminal nitrogen atoms differ radically from those of the bridging nitrogen atoms. The geometry at N(2) and N(3) is nearly trigonal planar, with the Si(3)–N(2)–Si(3)′ angle being 120.9 (2)° for **2** and 119.2 (3)° for **3**, while the Si(1)–N(1)–Si(2) angle is 112.2 (2)° for **2** and 112.7 (2)° for **3**. The bond distances and angles in **1**–**3** support the view that greater covalent binding exists between the metal and the ligands in **2** and **3**.

The dimers **2** and **3** are thus roughly isostructural, and the only significant differences involve the metal–metal and metal–nitrogen distances. The Co(1)–Co(2) distance is 2.583 (1) a (ca. 0.23 Å shorter than the Mn–Mn distance), and the terminal and bridging nitrogen–cobalt distances are about 0.1 Å shorter than in the manganese analogue. These differences can be explained on the basis of the smaller size of Co(II) compared to Mn(II).

The large differences between the structure of $[Co_2(NPh_2)_4]$ and **3** prompted us to reinvestigate its structure. Our findings are in sharp contrast to the reported non-amido-bridged structure of $[Co_2(NPh_2)_4]$. Our X-ray data show it to have a very similar structure to **3**.[21,33] The metal–metal distances in **2** and **3** suggest that while a metal–metal interaction may occur, the degree of magnetic coupling cannot be accounted for solely in terms of metal–metal distance. Support for this view comes from magnetic susceptibility data. The magnetic moments of **2** and **3** are 3.34 and 4.83 μ_B at 296 K while the magnetic moment of $[Co_2(NPh_2)_4]$ is 1.72 μ_B even though it has a similar Co–Co distance of 2.566 (3) Å.[6,21,24,33]

The nickel complex $[Ni_2(NPh_2)_4]$ is isostructural with the cobalt analogue.[34] The only major difference involves the metal–metal distance. The Ni–Ni distance of 2.327 (1) Å is the shortest Ni–Ni distance reported for Ni(II).

Our results suggest that the groups $N(SiMe_3)_2^-$ and NPh_2^- can act as effective bridging or terminal ligands with many late-row transition metals. Many of the complexes formed are thermally stable but are exceedingly reactive to O_2 and NO. We are currently investigating the properties of the NPh_2^- ligand with some other early and late-first-row transition metals and will present our results in a future paper.

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Registry No. **1**, 93280-43-4; **2**, 67806-74-0; **3**, 93280-44-5.

Supplementary Material Available: Full tables of bond distances and angles, anisotropic thermal parameters, hydrogen coordinates, and observed and calculated structure factors (65 pages). Ordering information is given on any current masthead page.

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