surprising that the weighted averages of the CO force constants for each molecule also decrease (17.21, 15.72, 15.48 mdyn/Å) in the same way.

Concluding Remarks. This work, in conjunction with recent work from the Walton group,[4,5] clearly demonstrates the synthetic potential for compounds containing multiple bonds between metal atoms when they are treated with reactants such as CO that can sever the M–M bond. In addition, since CO is also a reducing agent, the oxidation state of the metal may also be changed. Thus, as has now been shown, if the time, CO pressure, and temperature are varied, a wide variety of products is available, and the procedure can, in principle, be optimized on the preferred production of one relative to another. We have not, in this work, actually determined precisely the optimum conditions for each possible product (except perhaps for $ReCl(CO)_5$, where highest CO pressure, longest reaction time, and higher temperatures are clearly desirable), but the basis has been laid for such optimization, should it be desired.

Acknowledgment. The National Science Foundation and the Robert A. Welch Foundation are gratefully acknowledged for their support of this work. We wish also to acknowledge the support of the Materials Technology Center and the Office of Research Development and Administration of SIU-C.

Registry No. **1**, 66841-01-8; **2**, 66841-03-0; **3**, 100815-71-2; **4**, 24551-06-2; $Re_2Cl_6(PEt_3)_2$, 19584-31-7; $Re_2Cl_4(PEt_3)_4$, 55400-06-1; $Re(CO)_4Cl(PEt_3)$, 100897-58-3; $Re(CO)_5Cl$, 14099-01-5.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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Mononuclear Cobalt(II) Complexes Having Alkoxide and Amide Ligands: Synthesis and X-ray Crystal Structures of $[Co(Cl)(OC\text{-}t\text{-}Bu_3)_2{\cdot}Li(THF)_3]$, $[Li(THF)_{4.5}][Co\{N(SiMe_3)_2\}(OC\text{-}t\text{-}Bu_3)_2]$, and $[Li\{Co(N(SiMe_3)_2)(OC\text{-}t\text{-}Bu_3)_2\}]$

Marilyn M. Olmstead, Philip P. Power,* and Gary Sigel

Received August 19, 1985

The syntheses and first structural characterizations of cobalt(II) alkoxide complexes are described. These are the compounds $[Co(Cl)(OC\text{-}t\text{-}Bu_3)_2{\cdot}Li(THF)_3]$ (**1**), $[Li(THF)_{4.5}][Co\{N(SiMe_3)_2\}(OC\text{-}t\text{-}Bu_3)_2]$ (**2**), and $[Li\{Co(N(SiMe_3)_2)(OC\text{-}t\text{-}Bu_3)_2\}]$ (**3**). In all of these complexes Co(II) has the rare distorted trigonal-planar geometry. Other features of interest in these structures involve the inclusion of LiCl as a ligand **1**, the solvated lithium cation in **2** having pseudo-five-coordination rather than four-coordination, and agostic interactions between ligand CH_3's and Co or Li in **1**–**3**. Crystallographic data with Mo Kα (λ = 0.71069 Å) at 140 K: (**1**) a = 12.329 (15) Å, b = 12.614 (11) Å, c = 15.440 (18) Å, α = 78.46 (8)°, β = 68.77 (8)°, γ = 64.86 (7)°, Z = 2, space group $P\bar{1}$; (**2**) a = 11.491 (3) Å, b = 16.143 (6) Å, c = 31.343 (9) Å, β = 99.64 (2)°, Z = 4, space group $P2_1/n$; (**3**) a = 16.150 (10) Å, b = 11.485 (6) Å, c = 20.762 (11) Å, β = 108.90 (4)°, Z = 4, space group Ic. For **1**, R = 0.064, for **2**, R = 0.080, and for **3**, R = 0.055.

Introduction

Over the last few years there has been increasing interest in the synthesis and reactivity of alkoxide and aryloxide complexes of transition metals.[1] For the most part, this work has been confined to early transition elements such as Ti,[2] Zr,[3] Ta,[4] Cr,[5] Mo,[6,7] or W.[8] Very few reports have dealt with the later elements. The sole exceptions to this generalization involve the work of Wilkinson and co-workers, who have described $-OC(H)\text{-}t\text{-}Bu_2$[9] or 1- and 2-adamantoxy[10] derivatives of Cr, Mn, Fe, and Co. However, only one structural characterization (of an iron alkoxide) has been published for elements to the right of the manganese triad.[9] No reports have appeared for either cobalt or nickel derivatives. A number of other structural determinations, however, have dealt with closed-shell Cu(I) complexes.[11] In this laboratory, work has concentrated on the use of large alkoxo and amido groups to achieve low coordination numbers among the elements Cr → Ni.[6,12–15] This work has led to the characterization of interesting species; for example, the first instance of a three-coordinate, d^8, Ni(II)[15] complex and a distorted T-shaped Cr(II)[6] geometry. We now describe further extensions involving the $-OC\text{-}t\text{-}Bu_3$ and $-N(SiMe_3)_2$ ligands that have allowed the isolation and first[16] structural characterization of novel cobalt(II) complexes involving alkoxide ligands. These are $[Co(Cl)(OC\text{-}t\text{-}Bu_3)_2{\cdot}Li(THF)_3]$ (**1**),

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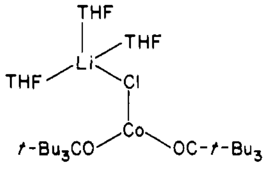
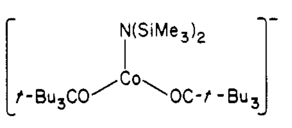
Table I. Crystal Data and Summary of Data Collection and Refinement

	1	2	3
formula	$LiCoClO_5C_{38}H_{78}$	$LiCoO_{6.5}NSi_2C_{50}H_{108}$	$LiCoO_2Si_2NC_{32}H_{72}$
fw	716.37	949.47	624.98
cryst syst	triclinic	monoclinic	monoclinic
space group (conditions)	$P\bar{1}$ (no conditions)	$P2_1/n$ ($0k0$, $k = 2n$; $h0l$, $h + l = 2n$)	Ic ($h + k + l = 2n$; $h0l$, $h(l) = 2n$)
cryst dimens, mm	0.13 × 0.5 × 0.50	0.15 × 0.43 × 0.10	0.30 × 0.275 × 0.125
cryst color and habit	deep aqua blue plates	blue rectangular plates	green plates
a, Å	12.329 (15)	11.491 (3)	16.150 (10)
b, Å	12.614 (11)	16.143 (6)	11.485 (6)
c, Å	15.440 (18)	31.343 (27)	20.762 (11)
α, deg	78.46 (8)	90	90
β, deg	68.77 (8)	99.64 (2)	108.90 (4)
γ, deg	64.86 (7)	90	90
Z	2	4	4
V, Å^3	2023 (3)	5731 (5)	3643.2 (3)
d_{calcd}, g/cm^3	1.18	1.10	1.14
radiation	Mo Kα	Mo Kα	Mo Kα
linear abs coeff, cm^{-1}	5.49	3.80	5.59
temp, K	140	140	140
instrument	$P2_1$	$P2_1$	$P2_1$
scan speed, deg/min	30	15	15
scan width, deg	2.5	1.2	2.3
type of scan	ω	ω	ω
ω offset for bkgds, deg	no bkgd	1.0	1.7
2θ range, deg	0–45	0–45	0–45
range of trans missn factors	1.07–1.27	1.04–1.16	1.06–1.15
octants collcd	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of variables	469	355	257
data/variable ratio	8.1	8.3	7.9
programs	SHELXTL, V.4	SHELXTL, V.4	SHELXTL, V.4
no. of check reflcns	2 (2% decay)	2 (no decay)	2 (no decay)
no. of unique data	5277	7498	2483
no. of data used in refinement	3818 ($I > 3\sigma(I)$)	2955 ($I > 3\sigma(I)$)	2023 ($I > 2\sigma(I)$)
$R(F)$	0.064	0.080	0.055
$R_w(F)$	0.066	0.082	0.053
largest Δ/σ	0.007 for C(22)	0.009 for C(22)	0.012 for C(19)

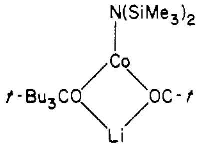
$[Li(THF)_{4.5}][Co\{N(SiMe_3)_2\}(OC\text{-}t\text{-}Bu_3)_2]$ (**2**), and $[Li\{Co(N(SiMe_3)_2)(OC\text{-}t\text{-}Bu_3)_2\}]$ (**3**).



1



anion of **2**
(with [Li(THF)$_{4.5}$]$^+$)



3

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 two times immediately before use. Solutions of the cobalt complexes are exceptionally air-sensitive and immediately darken to a brown color upon exposure to O_2. Anhydrous $CoCl_2$ was purchased from Alfa; *t*-Bu_3COH[17] and $[Co\{N(SiMe_3)_2\}_2]$[18] were synthesized by literature procedures.

$[Co(Cl)(OC\text{-}t\text{-}Bu_3)_2{\cdot}Li(THF)_3]$ (1). A solution of LiOC-*t*-Bu_3, formed by the addition of an *n*-hexane solution of *n*-BuLi (2.4 mL, 1.77 M) to *t*-Bu_3COH (0.8 g, 4 mmol) in THF (15 mL), was added dropwise to a (−78 °C) slurry of $CoCl_2$ (0.26 g, 2 mmol) in Et_2O (15 mL). Stirring was continued while the blue solution was allowed to warm to 25 °C. The volume was reduced by 50% in vacuo, and the solution was then filtered through Celite. Slow cooling to −20 °C afforded the product **1** as blue crystals. Yield: 0.58 g, 40%.

$[Li(THF)_{4.5}][Co\{N(SiMe_3)_2\}(OC\text{-}t\text{-}Bu_3)_2]$ (2). A green solution of $[Co\{N(SiMe_3)_2\}_2]$ (0.61 g, 1.6 mmol) in *n*-hexane (20 mL) was treated with *t*-Bu_3COH (0.64 g, 3.2 mmol) to give a purple solution. After the mixture was stirred for 12 h, 1.6 mmol of $LiN(SiMe_3)_2$ in THF (10 mL) was added. The solution gradually became blue. The volatiles were removed in vacuo and the solids redissolved in a 50/50 mixture of THF/*n*-hexane. Filtration followed by cooling to −20 °C gave the product as blue crystals in low yield. UV (THF): 542 sh, 634, 670 nm.

$[Li\{Co(N(SiMe_3)_2)(OC\text{-}t\text{-}Bu_3)_2\}]$ (3). $[Co\{N(SiMe_3)_2\}_2]$ (1 g, 2.6 mmol) in THF (20 mL) was treated with *t*-Bu_3COH (1.04 g, 5.2 mmol) in THF (20 mL), giving a purple solution. The solution was stirred overnight and then heated for 15 min to 50 °C. Addition of $LiN(SiMe_3)_2$ (2.6 mmol) in THF (20 mL) gave a blue solution. This was stirred for 3 h and the solvent removed completely in vacuo. Extraction with 50/50 *n*-C_6H_{14}/Et_2O (30 mL) gave a blue solution that was filtered and reduced by 50% in volume. Slow cooling to −20 °C gave green crystals of **3** suitable for X-ray studies. Yield: 0.33 g, 20%. UV (THF): 634, 680 nm.

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 device. Calculations were carried out on a Data General Eclipse computer using the SHELXTL program system. The atom form factors, including anomalous scattering, were from ref 19.

Blue single crystals of $[Co(Cl)(OC\text{-}t\text{-}Bu_3)_2{\cdot}Li(THF)_3]$ (**1**) were obtained by slow cooling of THF/Et_2O solutions to −20 °C. These were transferred from the Schlenk tube under N_2 and immediately covered with a layer of hydrocarbon oil to avoid air contamination. A suitable crystal was selected, attached to a glass fiber with silicone grease, and immediately placed in the low-temperature N_2 stream. Lattice constants were determined by a least-squares fit of 24 accurately centered reflections with 20° < 2θ < 35°. Printer plots of several reflections for this and for all crystals examined showed that the crystals had probably cracked upon cooling to our normal data collection temperature of 140 K. However, since they were chemically unstable at room temperature, and since the peaks were broadened but not actually split, the data were collected by scanning the width of the peak but without making a

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background measurement. At the end of the data collection the crystallographic axes were doubled, and background counts were recorded as a function of 2θ by using odd-numbered indices. These data were curve-fitted, and a correction was applied to the intensity data. In our experience this method gives satisfactory results.[20] The data were also corrected for Lorentz, polarization, and absorption effects. The structure was solved by the Patterson technique. In the final cycles of refinement, all non-hydrogen atoms were assigned anisotropic thermal parameters. Most of the hydrogen atoms were included at idealized positions (C–H = 0.96 Å), riding on the bonded carbon, and recalculated with each cycle. Methyl hydrogen atoms were treated as a rigid group that is rotated to achieve optimized positions during refinement. Such a procedure normally gives hydrogen positions well within two esd's of those obtained by free refinement. If the thermal parameters of the methyl hydrogen atoms are tied to those of the bonded carbon, this method requires only three parameters to describe the hydrogens of a methyl group and is therefore attractive when the data/variable ratio is low. Isotropic hydrogen thermal parameters were given the value 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Since two of the methyl groups (on C(11) and C(26)) had hydrogens in close proximity to cobalt, these six hydrogens were allowed to refine with no restrictions. Further details of data collection and refinement are in Table I.

X-ray data on $[Li(THF)_{4.5}][Co\{N(SiMe_3)_2\}(OC\text{-}t\text{-}Bu_3)_2]$ (**2**) were obtained in an identical manner except that a normal background measurement was made. The structure was solved by direct methods. One of the THF molecules occupies a site near a center of inversion. Unreasonable intermolecular contacts between this THF and its symmetry-generated pair ensue if both are present. Furthermore, Fourier peak heights, thermal parameters, and the refinement are in accord with 50% occupancy. This leads to the formulation $Li(THF)_{4.5}$. Hydrogen atoms were included at calculated positions, as for **1**, except those of the disordered THF's, which were not computed. Anisotropic thermal parameters were not employed in this structure. Some of the THF carbons are disordered. Refinement was carried out with fixed thermal parameters and variable occupancies. These are listed in Table II for the C(*N*a) carbons, occupancies K. The C(*N*b) counterparts are at occupancy 1-K. An ad hoc refinement for the THF comprised of O(3) and C(33)–C(36) was used since six possible five-membered rings can be constructed. A pictorial description of the THF disorder has been deposited as supplementary material. Further details are in Table I.

In contrast to **2**, $[Co(OC\text{-}t\text{-}Bu_3)_2\{N(SiMe_3)_2\}Li]$ (**3**) was obtained as green crystals by slowly cooling an ether solution to −20 °C. Lattice constants were determined in the same fashion as for **2** and initially indexed as monoclinic *C* with $\beta = 135.59°$. A transformation to monoclinic *I* reduced β to 108.90°. The structure was solved by the Patterson technique. The intensity distribution statistics strongly indicated an acentric space group; thus, the structure was solved in *Ic* rather than *I*2/*c*. Although the molecular structure has approximate twofold symmetry, it is sufficiently unsymmetrical to rule out *I*2/*c*. For example, the Li–Co–N angle is 156.8 (5)°, Co–N–Si(1) is 117.4 (4)°, and Co–N–Si(2) is 125.5 (5)°. Final refinement was carried out with anisotropic thermal parameters for Co, Si, O, and N. Hydrogen atoms were included by using a riding model as described for **1**. Further details are given in Table I.

Table II lists the atom coordinates for **1**–**3**.

Results and Discussion

The structures of **1**–**3** have a cobalt atom in the rare, approximately trigonal-planar geometry. This low coordination very probably has a basis in the rather large size of the substituents. It is also possible to argue that each cobalt center can be considered as a negatively charged $[CoL_3]^-$ unit and therefore less likely than a neutral species to form bridges leading to higher coordination. Three-coordination is quite rare for cobalt(II) and is limited to a very few complexes, all of which have very bulky substituents. These are the compounds $[\{Co(NR_2)_2\}_2]$ (R = $-SiMe_3$[14] or −Ph[15]) and $[Co\{N(SiMe_3)_2\}_2(PPh_3)]$.[21] Compounds **1**–**3** are the first cobalt alkoxo derivatives to be characterized by X-ray diffraction.

The geometry surrounding cobalt in **1** is illustrated in Figure 1. Selected bond distances and angles are given in Table III. The cobalt is coordinated to two alkoxide oxygens and a chloride ligand. These four atoms are almost coplanar. The large O(1)–Co–O(2) angle, 132.0 (2)°, is presumably due to the steric requirements of the $-OC\text{-}t\text{-}Bu_3$ group. The Co–O distances, ca. 1.84 Å, are consistent with the sum of Shannon–Prewitt radii.[22] These values are also about 0.06 Å shorter than the Co–N distances in similar complexes with amido ligands,[14,15] and this difference corresponds very closely to the atomic radius of oxygen being about 0.05 Å smaller than that of nitrogen. The Co–O–C angles of 138.0 (3) and 139.3 (4)° are significantly larger than the predicted near-tetrahedral value. Such wide angles have been seen in most other alkoxide complexes and are thought to be due to π(p–d) interaction between the oxygen and the metal. In the alkoxide ligands the carbon atoms bound to oxygen and to three *tert*-butyl groups display the usual considerable distortion from tetrahedral values. The enlarged angles and bond distances (average 1.633 Å) about this carbon are due to the strain imposed by three *tert*-butyl substituents. These distortions have been discussed elsewhere.[6,12]

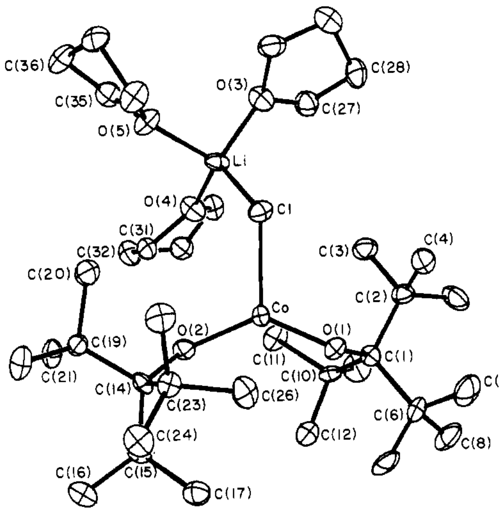
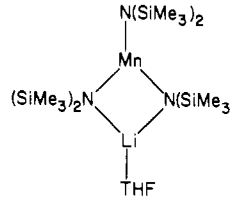


Figure 1. Computer-generated drawing of **1**.

An interesting feature of **1** is the inclusion of LiCl in the coordination sphere of cobalt. A fair number of transition-metal, alkyl, amide, or alkoxide complexes are now known where either lithium halide or lithium ions form an integral part of the coordination sphere. Some of the amides and alkoxides are illustrated in **4**,[14] **5**,[12] **6**,[12] **7**,[6] and **8**.[9] The cobalt complex **1** bears a very



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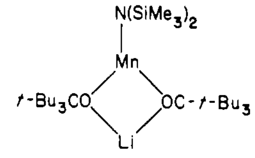

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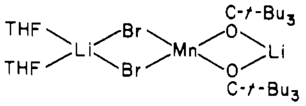

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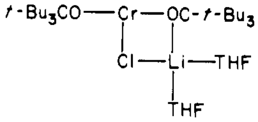

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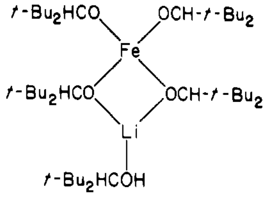

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Table II. Atom Coordinates (×10^4) and Thermal Parameters (×10^3 Å^2)

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
Complex **1**									
Co	3554 (1)	3395 (1)	2175 (1)	20 (1)[a]	C(17)	1859 (6)	6852 (5)	2767 (4)	34 (3)[a]
Cl	4053 (1)	1864 (1)	1293 (1)	28 (1)[a]	C(18)	308 (5)	6030 (5)	3698 (4)	32 (3)[a]
O(1)	4810 (3)	3271 (3)	2612 (2)	24 (2)[a]	C(19)	181 (5)	5421 (4)	1733 (4)	27 (3)[a]
O(2)	1937 (3)	4488 (3)	2338 (2)	24 (2)[a]	C(20)	636 (6)	4229 (5)	1309 (4)	35 (3)[a]
O(3)	3844 (4)	−968 (3)	2117 (2)	33 (2)[a]	C(21)	−879 (5)	5379 (5)	2648 (4)	33 (3)[a]
O(4)	1745 (4)	1112 (3)	3314 (2)	34 (2)[a]	C(22)	−500 (6)	6399 (5)	1087 (4)	36 (3)[a]
O(5)	1838 (4)	854 (3)	1358 (2)	31 (2)[a]	C(23)	2328 (5)	5824 (5)	969 (3)	25 (3)[a]
C(1)	5247 (5)	2771 (4)	3372 (3)	23 (2)[a]	C(24)	1952 (6)	7118 (5)	577 (4)	33 (3)[a]
C(2)	6106 (5)	1378 (5)	3193 (4)	29 (3)[a]	C(25)	2636 (6)	5102 (5)	149 (4)	35 (3)[a]
C(3)	5336 (6)	617 (5)	3367 (4)	35 (3)[a]	C(26)	3652 (5)	5418 (5)	1078 (4)	33 (3)[a]
C(4)	6892 (5)	1180 (5)	2149 (4)	37 (3)[a]	C(27)	4546 (6)	−1637 (5)	2736 (4)	36 (3)[a]
C(5)	7031 (6)	741 (5)	3756 (4)	41 (3)[a]	C(28)	5873 (6)	−2231 (5)	2130 (4)	38 (3)[a]
C(6)	6091 (5)	3485 (5)	3359 (4)	31 (3)[a]	C(29)	5653 (6)	−2552 (5)	1327 (4)	39 (3)[a]
C(7)	7353 (6)	3155 (6)	2556 (5)	47 (4)[a]	C(30)	4495 (6)	−1502 (5)	1221 (4)	40 (3)
C(8)	6415 (7)	3361 (6)	4266 (5)	48 (4)[a]	C(31)	638 (5)	2184 (5)	3497 (4)	33 (3)[a]
C(9)	5430 (6)	4817 (5)	3157 (5)	42 (3)[a]	C(32)	−229 (6)	1945 (5)	4410 (4)	39 (3)[a]
C(10)	4041 (5)	2963 (5)	4307 (4)	28 (3)[a]	C(33)	671 (5)	1142 (5)	4929 (4)	35 (3)[a]
C(11)	2985 (6)	2749 (5)	4139 (4)	33 (3)[a]	C(34)	1774 (5)	426 (5)	4170 (4)	33 (3)[a]
C(12)	3338 (6)	4220 (5)	4615 (4)	34 (3)[a]	C(35)	884 (6)	367 (5)	1674 (4)	35 (3)[a]
C(13)	4316 (7)	2191 (6)	5179 (4)	43 (3)[a]	C(36)	419 (6)	532 (6)	857 (4)	40 (3)[a]
C(14)	1319 (5)	5577 (4)	1925 (3)	23 (2)[a]	C(37)	1583 (6)	478 (5)	28 (4)	34 (3)[a]
C(15)	799 (5)	6545 (4)	2705 (4)	25 (2)[a]	C(38)	2126 (6)	1105 (5)	361 (4)	37 (3)[a]
C(16)	−250 (5)	7723 (5)	2575 (4)	33 (3)[a]	Li	2870 (9)	708 (8)	2078 (6)	29 (4)[a]
Complex **2**									
Co	6488 (1)	2797 (1)	1117 (1)	18 (1)	C(32)	3679 (11)	1029 (9)	561 (4)	51 (4)
O(1)	5682 (7)	3787 (4)	1122 (2)	25 (2)	Li	10242 (25)	7702 (19)	1312 (9)	75 (8)
C(1)	4810 (10)	4332 (7)	1214 (4)	27 (3)	O(3)	10454 (10)	6874 (7)	1831 (4)	75 (3)
C(2)	5400 (10)	5249 (7)	1233 (4)	28 (3)	C(33a)	11264 (27)	6178 (18)	1809 (9)	50
C(3)	4502 (11)	4051 (7)	1688 (4)	30 (3)	C(34b)	11374 (27)	6198 (18)	2522 (10)	50
C(4)	3662 (11)	4214 (7)	825 (4)	33 (3)	C(35)	10260 (19)	6255 (12)	2475 (7)	110 (7)
C(5)	6158 (12)	5355 (8)	868 (4)	40 (4)	C(36a)	9555 (18)	6602 (12)	2074 (6)	50
C(6)	4521 (11)	5986 (7)	1197 (4)	34 (3)	C(33b)	11695 (24)	6709 (17)	2160 (8)	50
C(7)	6301 (12)	5390 (8)	1651 (4)	42 (4)	C(34a)	11514 (23)	5965 (16)	2272 (8)	50
C(8)	5595 (11)	3806 (8)	2017 (4)	43 (4)	C(36b)	10203 (42)	7161 (32)	2165 (15)	50
C(9)	3764 (12)	3229 (8)	1652 (5)	49 (4)	O(4)	8760 (8)	8188 (6)	1389 (3)	55 (3)
C(10)	3796 (12)	4675 (8)	1920 (4)	44 (4)	C(37a)	7652 (21)	7988 (16)	1127 (9)	50
C(11)	3925 (12)	4603 (8)	396 (4)	40 (4)	C(37b)	7628 (32)	7642 (25)	1361 (14)	50
C(12)	2508 (11)	4601 (8)	911 (4)	41 (4)	C(38)	6710 (14)	8205 (9)	1449 (5)	137 (5)
C(12)	3425 (13)	3298 (8)	699 (4)	46 (4)	C(39)	7333 (12)	8929 (8)	1726 (4)	46 (4)
O(2)	7795 (7)	2494 (4)	1515 (2)	24 (2)	C(40)	8553 (17)	8901 (12)	1639 (6)	98 (6)
C(14)	8968 (10)	2475 (6)	1701 (4)	22 (3)	O(5)	9982 (19)	8810 (14)	718 (7)	79 (7)
C(15)	9004 (11)	1925 (7)	2151 (4)	29 (3)	C(41)	10820 (28)	9494 (19)	696 (10)	65 (9)
C(16)	9717 (10)	2003 (7)	1361 (4)	29 (3)	C(42)	10321 (32)	9901 (22)	240 (11)	85 (12)
C(17)	9432 (11)	3413 (7)	1804 (4)	32 (3)	C(43)	9382 (34)	9342 (24)	43 (12)	103 (13)
C(18)	10142 (11)	1994 (8)	2499 (4)	47 (4)	C(44)	8918 (34)	8740 (23)	358 (12)	95 (13)
C(19)	8825 (12)	989 (8)	2058 (4)	43 (4)	O(6)	11654 (9)	8343 (6)	1457 (3)	66 (3)
C(20)	7926 (11)	2144 (9)	2370 (4)	41 (3)	C(45a)	11843 (25)	9098 (17)	1812 (9)	50
C(21)	9871 (13)	2557 (8)	977 (4)	50 (4)	C(45b)	11658 (26)	9230 (18)	1260 (9)	50
C(22)	10970 (12)	1670 (9)	1539 (5)	52 (4)	C(46a)	13000 (25)	9320 (17)	1814 (9)	50
C(23)	8989 (12)	1278 (8)	1130 (4)	45 (4)	C(46b)	12673 (26)	9656 (18)	1519 (9)	50
C(24)	10801 (11)	3541 (9)	1908 (4)	48 (4)	C(47a)	13579 (29)	8858 (20)	1413 (9)	50
C(25)	8936 (12)	4009 (8)	1428 (4)	41 (4)	C(47b)	13559 (30)	8925 (21)	1607 (10)	50
C(26)	8935 (12)	3804 (8)	2187 (4)	43 (4)	C(48a)	12874 (29)	8092 (20)	1361 (9)	50
N	5934 (8)	1990 (5)	649 (3)	23 (2)	C(48b)	12855 (32)	8098 (21)	1544 (10)	50
Si	6157 (3)	2275 (2)	152 (1)	35 (1)	O(7)	10031 (8)	6904 (6)	840 (3)	58 (3)
C(27)	7089 (13)	1520 (9)	−101 (5)	57 (4)	C(49a)	9964 (34)	7144 (24)	380 (11)	50
C(28)	6890 (12)	3304 (7)	156 (4)	35 (3)	C(49b)	10714 (25)	6819 (16)	497 (8)	50
C(29)	4762 (12)	2364 (9)	−265 (4)	51 (4)	C(50)	10027 (17)	6215 (11)	167 (6)	92 (6)
Si(2)	5269 (3)	1116 (2)	793 (1)	31 (1)	C(51)	9341 (15)	5700 (10)	459 (5)	74 (5)
C(30)	5957 (12)	134 (8)	623 (4)	47 (4)	C(52a)	8986 (34)	6314 (22)	709 (12)	50
C(31)	5332 (11)	1047 (8)	1395 (4)	36 (3)	C(52b)	9657 (24)	6028 (16)	912 (8)	50
Complex **3**									
Co	3000	885 (1)	3000	17 (1)[a]	C(14)	3551 (6)	2651 (8)	4250 (4)	20 (2)
Si(1)	4165 (2)	−1283 (2)	3023 (1)	24 (1)[a]	C(15)	4143 (6)	3602 (9)	3990 (5)	26 (2)
Si(2)	2452 (2)	−1554 (3)	3346 (1)	25 (1)[a]	C(16)	2863 (6)	3332 (8)	4562 (4)	23 (2)
O(1)	2332 (4)	1911 (5)	2276 (3)	21 (2)[a]	C(17)	4155 (6)	1726 (9)	4787 (4)	21 (2)
O(2)	3015 (4)	2065 (5)	3662 (3)	20 (2)[a]	C(18)	4530 (7)	3020 (10)	3456 (5)	32 (2)
N	3221 (4)	−742 (6)	3140 (4)	22 (3)[a]	C(19)	3608 (7)	4626 (10)	3581 (5)	36 (3)
Li	2182 (10)	2818 (15)	2963 (8)	29 (4)	C(20)	4921 (7)	4159 (11)	4535 (5)	43 (3)
C(1)	1810 (5)	2030 (8)	1568 (4)	19 (2)	C(21)	2038 (6)	3776 (9)	3977 (5)	29 (2)
C(2)	1863 (6)	3439 (9)	1418 (5)	27 (2)	C(22)	3239 (7)	4368 (9)	5054 (5)	31 (3)
C(3)	2245 (6)	1260 (8)	1124 (4)	19 (2)	C(23)	2429 (7)	2497 (10)	4939 (5)	35 (3)
C(4)	825 (6)	1643 (9)	1521 (4)	25 (2)	C(24)	4573 (7)	2127 (9)	5522 (5)	32 (3)
C(5)	1325 (6)	4214 (10)	1740 (5)	30 (2)	C(25)	3638 (7)	600 (9)	4815 (5)	31 (3)

Table II (Continued)

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
C(6)	1550 (7)	3799 (9)	663 (5)	32 (3)	C(26)	4915 (6)	1241 (9)	4559 (5)	29 (2)
C(7)	2816 (6)	3935 (9)	1731 (5)	30 (2)	C(27)	1890 (7)	−2645 (11)	2677 (5)	44 (3)
C(8)	3125 (6)	1756 (9)	1101 (5)	28 (2)	C(28)	3969 (7)	−2504 (10)	2377 (5)	36 (3)
C(9)	1675 (6)	1093 (9)	367 (4)	25 (2)	C(29)	4744 (7)	−94 (9)	2718 (5)	30 (3)
C(10)	2491 (7)	13 (8)	1411 (5)	30 (2)	C(30)	1571 (6)	−575 (9)	3465 (5)	30 (3)
C(11)	78 (7)	2063 (10)	884 (5)	36 (3)	C(31)	2919 (7)	−2399 (10)	4153 (5)	35 (3)
C(12)	724 (7)	294 (9)	1535 (5)	32 (3)	C(32)	4969 (7)	−1876 (11)	3835 (5)	40 (3)
C(13)	583 (7)	2008 (10)	2157 (5)	34 (3)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (Å) and Angles (deg)

	Complex **1**		
Co–O(1)	1.840 (5)	O(1)–C(1)	1.393 (7)
Co–O(2)	1.838 (3)	O(2)C(14)	1.410 (5)
Co–Cl	2.324 (2)	Li–O (av)	1.922 (10)
Li–Cl	2.354 (11)	C–(*t*-Bu) (av)	1.633 (10)
O(1)–Co–O(2)	132.0 (2)	O–C–(*t*-Bu) (av)	106.4 (5)
O(1)–Co–Cl	115.0 (1)	(*t*-Bu)–C–(*t*-Bu) (av)	112.4 (5)
O(2)–Co–Cl	113.0 (2)	Cl–Li–O (av)	113.2 (5)
Co–Cl–Li	111.5 (3)	O–Li–O (av)	105.3 (5)
Co–O(1)–C(1)	139.3 (4)		
Co–O(2)–C(14)	138.0 (3)		
	Complex **2**		
Co–O(1)	1.849 (7)	Si–C (av)	1.88 (1)
Co–O(2)	1.851 (7)	C–(*t*-Bu) (av)	1.64 (2)
Co–N	1.985 (9)	Li–O(3)	2.09 (3)
O(1)–C(1)	1.40 (1)	Li–O(4)	2.09 (3)
O(2)–C(2)	1.38 (2)	Li–O(5)	2.56 (3)
N–Si(1)	1.69 (1)	Li–O(6)	1.91 (3)
N–Si(2)	1.70 (1)	Li–O(7)	1.94 (3)
O(1)–Co–O(2)	125.0 (3)	O(3)–Li–O(4)	99 (1)
O(1)–Co–N	118.3 (3)	O(3)–Li–O(5)	176 (1)
O(2)–Co–N	116.7 (3)	O(3)–Li–O(6)	100 (1)
Co–O(1)–C(1)	157.3 (7)	O(3)–Li–O(7)	99 (1)
Co–O(2)–C(14)	156.7 (7)	O(4)–Li–O(5)	79 (1)
Co–N–Si(1)	115.2 (5)	O(4)–Li–O(6)	119 (2)
Co–N–Si(2)	116.8 (5)	O(4)–Li–O(7)	111 (1)
Si(1)–N–Si(2)	128.0 (5)	O(5)–Li–O(6)	78 (1)
O–C–(*t*-Bu) (av)	106 (1)	O(5)–Li–O(7)	86 (1)
(*t*-Bu)–C–(*t*-Bu) (av)	112 (1)	O(6)–Li–O(7)	122 (2)
	Complex **3**		
Co–O(1)	1.939 (6)	Si–C (av)	1.883 (10)
Co–O(2)	1.925 (6)	C–(*t*-Bu) (av)	1.633 (15)
Co–N	1.906 (7)	Li–O(1)	1.844 (19)
Co···Li	2.573 (17)	Li–O(2)	1.845 (15)
O(1)–C(1)	1.446 (9)	N–Si(1)	1.735 (8)
O(2)–C(14)	1.417 (10)	N–Si(2)	1.715 (9)
O(1)–Co–O(2)	90.0 (2)	O–C–(*t*-Bu) (av)	107.2 (7)
O(1)–Co–N	138.0 (3)	(*t*-Bu)–C–(*t*-Bu) (av)	112.2 (7)
O(2)–Co–N	128.5 (3)	O(1)–Li–O(2)	95.6 (8)
Co–O(1)–C(1)	147.2 (6)		
Co–O(2)–C(14)	144.4 (6)		
Co–N–Si(1)	117.4 (4)		
Co–N–Si(2)	117.1 (4)		
Si(1)–N–Si(2)	125.5 (5)		

close stoichiometric resemblance to the chromium(II) in complex **7**, which differs only by the absence of a THF molecule. The difference in structure between **1** and **7** seems to be due to the larger size of Cr(II) compared to Co(II). Thus the longer metal–oxygen distance, 1.881 (4) Å (Cr–O)[6] vs. 1.839 (4) Å (Co–O), may permit sufficient steric relief to allow the Li in **6** to coordinate to an alkoxo oxygen with concomitant elimination of one THF molecule. The greater crowding in **1** does not allow coordination of lithium to alkoxide oxygen, and the end-on Li–Cl coordination (Figure 1) is the result. The acute angle at Cl, 111.5 (2)°, is not readily explainable in terms of steric factors and may be a result of ligand packing. The lithium has the common, approximately tetrahedral, coordination with the Li–O distances corresponding closely with those seen in other four-coordinate Li–O species.[23] The Co–Cl distance, 2.324 (2) Å, is close to those seen in other Co(II)[24,25] complexes. The Li–Cl distance, 2.354 (11) Å, is also consistent with the value predicted by extrapolation from the Shannon–Prewitt radii. This is significantly shorter than the crystalline Li–Cl distance, 2.566 Å,[24] which involves six- rather than four-coordinate lithium.

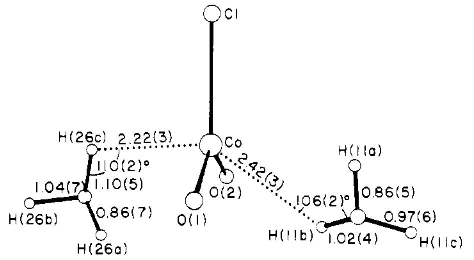

Figure 2. Details of the close Co···H(CH_3) interactions in the structure of **1**. The H(11b)···Co···H(26c) angle is 141 (2)°.

Another interesting aspect of the structure of **1** concerns the agostic[26,27] interactions between some of the methyl hydrogens of the $-OC$-*t*-Bu_3 groups and cobalt. On the basis of refined hydrogen coordinates for the C(11) and C(26) methyl groups, the shortest calculated Co···H distances are 2.23 (3) and 2.42 (3) Å. This is pictured in Figure 2. Even if there were not a large uncertainty in hydrogen positions (due to X-ray data), it would be difficult to determine if the short metal–hydrogen distances represent an attractive or repulsive interaction since a number of factors come into play. The low-valent cobalt coordination sphere can easily accommodate the hydrogen atoms of the two methyl groups. There are no short intermolecular contacts or unusual O–C–C or C–C–C angles that would indicate that the affected hydrogens are being "pulled in" or "pushed out". The C–H distances of the affected hydrogens are longer than the others, but again, the esd's are large. There is one piece of evidence that would argue for a nonpassive interaction, and this is in the partial eclipsing of the C(11) and C(26) methyl groups. Newman projections down these atoms show that the CH_3 groups are not as staggered with respect to the bonded CC_3 group as the other methyl groups in the structure. The smaller of the torsion angles average 37.8° down C(10)–C(11) and 35.4° for C(23)–C(26) vs. 52.2° for C(10)–C(12), 54.1° for C(10)–C(13), 51.0° for C-(23)–C(24), and 51.2° for C(23)–C(25). It is hoped that further chemical studies of these species may eventually reveal if there is activation of the C–H bond. Similar metal–hydrogen interactions have been reported in a number of other transition-metal complexes,[26] but so far as we are aware, this is the first reported example involving cobalt.

The structure of the anion of **2** (Figure 3) shows the cobalt to have a planar three-coordinate arrangement. Selected bond

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(23) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(24) Wells, A. F. "Structural Inorganic Chemistry", 5th ed.; Oxford University Press: New York, 1984; p 444.

(25) The structure of [Co{OC-*t*-Bu(*i*-Bu)$_2$}$_2$$Cl_2Li_2(OEt_2)_2$] has been determined (Co–Cl = 2.315 Å): Sigel, G.; Power, P. P., unpublished results. It has a structure similar to that of **6**.

(26) Andersen, R. A.; Carmona-Guzman, E.; Gibson, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2204. Sigurdson, E. G.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 812.

(27) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

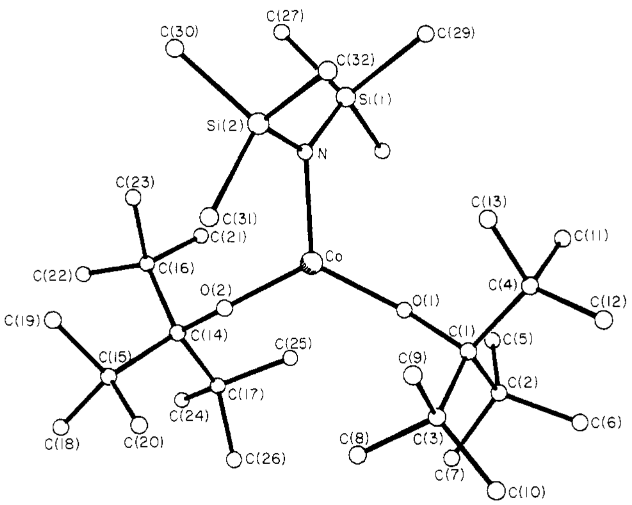

Figure 3. Computer-generated drawing of the anion of **2**.

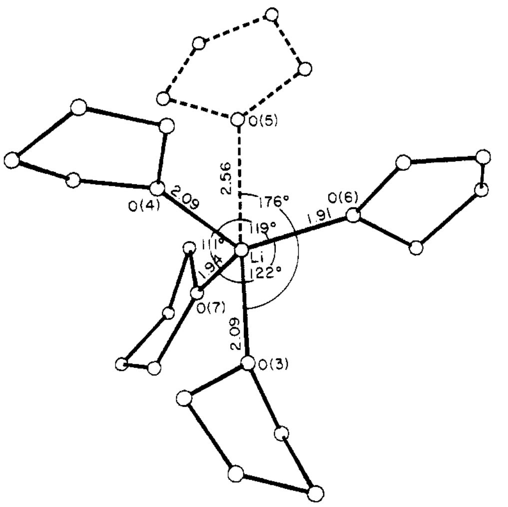

Figure 4. Drawing of the trigonal-bipyramidal geometry of $[Li(THF)_{4.5}]^+$.

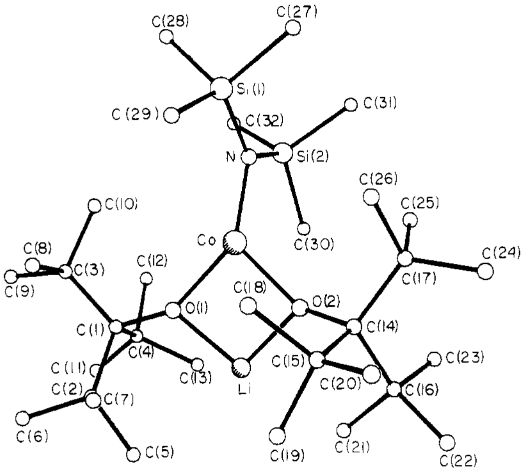

Figure 5. Computer-generated drawing of **3**.

distances and angles are given in Table III. The angles at cobalt are fairly regular, having the values O(1)–Co–N = 118.4 (3)°, O(2)–Co–N = 116.7 (4)°, and O(2)–Co–O(1) = 124.9 (4)°. Interestingly, the widest angle involves the two $-OC\text{-}t\text{-}Bu_3$ groups. This supports the observation[14] that $-OC\text{-}t\text{-}Bu_3$ may be somewhat more sterically demanding than the bulky $-N(SiMe_3)_2$ substituent (compare complexes **4** and **5**). The almost equal Co–O distances are very similar to those found in **1**. The Co–O–C angles of 157.3 (8) and 156.9 (9)° are even wider than the corresponding angles in **1**. This may be because of the greater steric crowding in **2** due to the presence of $-N(SiMe_3)_2$ rather than Cl as a ligand. The Co–N bond distance is 1.984 (9) Å, somewhat longer than the terminal distance seen in $[Co\{N(SiMe_3)_2\}_2]_2$[14] or $[Co\{N(SiMe_3)_2\}_2(PPh_3)]$.[21] It may be that since **2** has an overall negative charge, a slight lengthening in metal–ligand bond distances results. This leads to the prediction that in a neutral $[\{Co(OR)_2\}_2]$ complex the Co–O distances will be even shorter than those seen in either **1** or **2**.[28] Other bond lengths and angles within the $-N(SiMe_3)_2$ or $-OC\text{-}t\text{-}Bu_3$ ligands are unremarkable and are similar to those seen in other metal complexes of this ligand. In contrast to the case of **1**, there are no short Co···H contacts; the shortest are Co···H(8b) = 2.76 (2) Å, Co···H(13b) = 2.79 (2) Å, and Co···H(25c) = 2.73 (2) Å.

An interesting feature of **2** arises from the fact that, in contrast with many other related complexes involving $-OC\text{-}t\text{-}Bu_3$ or $-N(SiMe_3)_2$ ligands such as **1** or **4**–**7**, no lithium or lithium halide species are included in the transition-metal complex. Complex **2** crystallizes as a separate anion and cation. The $[Li(THF)_{4.5}]^+$ countercation is unique since, in the presence of THF, Li^+ usually crystallizes as the tetrahedral $[Li(THF)_4]^+$. The Li–O distance in the latter varies between 1.92 and 1.96 Å. In the present case (see Figure 4), four normal THF's with Li–O distances of 1.90–2.09 Å coordinate to Li^+, but a fifth is occupying a rather large space in the crystal lattice, which also contains a center of symmetry. The THF at this site is statistically disordered about the center of symmetry. It is necessary to postulate the existence of $(Li(THF)_5{}^+\cdots Li(THF)_4{}^+)/(Li(THF)_4{}^+\cdots Li(THF)_5{}^+)$ at this site in order to avoid short C···C and H···H distances that would ensue from $(Li(THF)_5\cdots Li(THF)_5)$. A long Li–O distance of 2.56 (3) Å for the "fifth" THF is the result. The near-trigonal-bipyramidal geometry at Li indicates that this "fifth" group is stereochemically active and occupies an axial position. As might be expected, the Li is pulled out of the trigonal plane by 0.31 (3) Å toward the more tightly bound axial THF. Several five-coordinate Li^+ species are at present known.[23] These generally involve macrocyclic ligands as a part or all of the coordination sites and generally have square-pyramidal geometry. So far as we are aware, the cation of **2** is the first instance of homoleptic Li^+ complex with approximate trigonal-pyramidal geometry.

The structure of **3** is illustrated in Figure 5. Bond distances and angles are given in Table III. The cobalt atom is again three-coordinate, approximately planar, but the angles at Co are severely distorted owing to "pinching" of the O(1)–Co–O(2) angle to 90.02 (2)° as a result of the inclusion of lithium. The corresponding O(1)–Co–O(2) angle in **2** is 124.9 (4)°, a difference of almost 35°. In **3** significant lengthening is seen in both Co–O distances compared to **1**, ca., 1.93 vs. 1.85 Å. This is expected due to the bridging nature of the Co–O bonds in **3**. The Co–N bond in **3**, 1.906 (7) Å, is considerably shorter than in **1**, 1.984 (9) Å. This may be because of the decreased steric crowding around the $-N(SiMe_3)_2$ ligand due to $-OC\text{-}t\text{-}Bu_3$ ligands being pulled away by Li coordination. An alternative explanation may be that the slightly greater electron density on Co in **3** may lead to an increase in the d–p π-interaction between Co and N and a shorter Co–N bond. Support for the latter view also comes from the lengthened Si–N bonds in **3** compared with those in **1**. This is expected since a reduction in the p–d N–Si interaction should lead to a corresponding increase in the N–Co interaction. The Si–N–Si angle in **3**, 125.5 (5)°, is also slightly smaller than the Si–N–Si angle in **1**, consistent with a more covalent Co–N bond in **3**. In this structure, there is a close Li···H(21c) interaction at 2.07 (2) Å and a somewhat long Co···H(10b) contact of 2.45 (2) Å. Similar Li···H interactions have already been noted in the structures of compounds **5** and **6**.

There are also many similarities between **3** and its manganese analogue **4**,[14] and in fact, they are isostructural. The main dif-

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(28) Note added in proof: The recently determined structure of $[(Co\{OC(C_6H_{11})_3\}_2)_2]\cdot THF$, which has an average Co–O(terminal) distance of 1.78 Å, bears out this prediction (Decker, D.; Olmstead, M. M.; Power, P. P.; Sigel, G., unpublished results).

ference is that Mn–N and Mn–O distances are somewhat longer because of Mn's larger radius.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8116355) and the Committee on Research of the University of California for financial support.

Registry No. **1**, 100485-91-4; **2**, 100485-94-7; **3**, 100485-95-8; [Co{N(SiMe$_3$)$_2$}$_2$], 18544-54-2.

Supplementary Material Available: Tables of all bond distances and angles, anisotropic thermal parameters, hydrogen coordinates, and structure factors for **1**–**3** and chart of the disordered THF's in **2** (70 pages). Ordering information is given on any current masthead page.

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Syntheses and Acid Aquation Reactions of Pentakis(methylamine)cobalt(III) Complexes of the Neutral Ligands Urea, Dimethyl Sulfoxide, Dimethylformamide, Trimethyl Phosphate, and Acetonitrile

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Received August 23, 1985

Syntheses of [Co(NH$_2$CH$_3$)$_5$L]$^{3+}$ cations (L = urea, dimethyl sulfoxide, dimethylformamide, trimethyl phosphate, and acetonitrile) based on the [Co(NH$_2$CH$_3$)$_5$(OSO$_2$CF$_3$)](CF$_3$SO$_3$)$_2$ precursor are facile and high-yielding. Acid aquation reactions of these cations occur with rate constants at least 70-fold faster than those reported for the pentaammine analogues at 25 °C, this general rate enhancement being apparently steric in origin. While activation enthalpies for the pentakis(methylamine) and pentaammine complexes are similar, both activation entropies and activation volumes are more positive, yet not particularly sensitive to the size of the neutral leaving group. A dissociative I$_d$ type mechanism operates. The more positive $\Delta S^\ddagger$ and $\Delta V^\ddagger$ values for Co(NH$_2$CH$_3$)$_5$L^{3+} compared with Co(NH$_3$)$_5$L^{3+} imply a diminished role for an incoming water molecule in the dissociated transition state, which accords with the steric crowding known in pentakis(methylamine) complexes. These results parallel earlier observations of $\Delta S^\ddagger$ and $\Delta V^\ddagger$ variation in the chloro analogues, although overall electrostrictive effects present with the charged leaving group are markedly diminished in this case where neutral leaving groups are employed.

Introduction

In recent attempts to gain a more intimate understanding of each of the apparently disparate mechanisms for spontaneous aquation reactions of cobalt(III) and chromium(III) amine complexes, we have been investigating various simple pentaamine systems.[3-5] Two systematic approaches have been adopted: first, study of complexes with neutral leaving groups;[3,4] second, study of the effect of varying the amine non leaving groups.[5] Both temperature and pressure dependence of aquation reactions have been probed to obtain a more extensive data base for analysis.

Where charged leaving groups are involved, solvent electrostriction changes in forming the transition state contribute significantly to both activation entropy ($\Delta S^\ddagger$) and activation volume ($\Delta V^\ddagger$).[6,7] When neutral leaving groups are employed, changes in electrostriction in the activation process are minimized;[3,8] $\Delta V^\ddagger$ and $\Delta S^\ddagger$ then define much more closely the intrinsic volume and entropy changes in attaining the transition state, and this is the basis for our first approach. The effect of the cation size and related steric effects had not been probed systematically until recently, when the system M(NH$_2$R)$_5$Cl^{2+} (M = Co, Cr; R = H, CH$_3$) was studied.[5] The M(NH$_2$R)$_5$Y^{n+} system is the current focus for our second approach, since it represents the simplest example of increased cation size with constant charge and leaving group, and since only unidentate ligands are involved, motions and rearrangements of chelate rings are not operating. In this work, we pursue these approaches in tandem, with a study of the Co(NH$_2$CH$_3$)$_5$L^{3+} (L = unidentate neutral ligand) system and comparison with Co(NH$_3$)$_5$L^{3+} analogues.

Aquation reactions of cobalt(III) and chromium(III) halo amines have been extensively studied in recent decades, leading to evidence of mechanistic disparity.[9-11] Reactions of cobalt(III) are generally accepted to be dominated by bond-breaking (dissociative) processes, while those of chromium(III) are apparently bond-making (associative) in character. This difference was defined in comparative studies of pentaammine and pentakis(methylamine) complexes since an increase in the rate of aquation in Co(NH$_2$CH$_3$)$_5$X^{2+} compared with Co(NH$_3$)$_5$X^{2+} (X = Cl$^-$, CF$_3$SO$_3$$^-$) is consistent with steric relief in a dissociated activated state, whereas the chromium(III) system exhibits retardation, appropriate for steric congestion of an associated transition state.[12,13] While a recent study has implied a significant change in the importance of bond-making and bond-breaking processes from the pentaammine- to the pentakis(methylamine)chlorochromium(III) complexes,[5] this did not lead to an assertion of mechanistic uniformity for cobalt(III) and chromium(III) overall; rather, the observation was based on a bond-making mechanism operating in the sterically uncrowded Cr(NH$_3$)$_5$Cl^{2+}. Yet it is with neutral leaving groups that mechanistic differentiation is most obvious. Solvent exchange on Co(NH$_3$)$_5$(OH$_2$)$^{3+}$ exhibits $\Delta V^\ddagger$ = +1.2 cm^3 mol^{-1},[14] while on Cr(NH$_3$)$_5$(OH$_2$)$^{3+}$, $\Delta V^\ddagger$ = −5.8 cm^3 mol^{-1},[15] for example. Dissociative interchange (I$_d$) and associative interchange (I$_a$) mechanisms operate respectively. Study of a range of Cr(NH$_3$)$_5$L^{3+} complexes to complement the available data for Co(NH$_3$)$_5$L^{3+} is under way[4] and will allow extension of this at present strictly limited comparison with neutral leaving groups.

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