

Low-Valent Chemistry of Cobalt Amide. Synthesis and Structural Characterization of Cobalt(II) Amido, Aryloxy, and Thiolate Compounds

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The binuclear cobalt(II) amide complex $[(\text{CoL}_2)_2 \cdot (\text{TMEDA})]$ (**1**) [$\text{L} = \text{N}(\text{Si}^t\text{BuMe}_2)(2\text{-C}_5\text{H}_3\text{N-6-Me})$; $\text{TMEDA} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$] has been synthesized by the reaction of anhydrous CoCl_2 with 2 equiv of $[\text{Li}(\text{L})(\text{TMEDA})]$. X-ray crystallography revealed that complex **1** consists of two $\{\text{CoL}_2\}$ units linked by one TMEDA ligand molecule, which binds in an unusual N,N' -bridging mode. Protolysis of **1** with the bulky phenol $\text{Ar}^{\text{Me}}\text{OH}$ ($\text{Ar}^{\text{Me}} = 2,6\text{-}^t\text{Bu}_2\text{-4-MeC}_6\text{H}_2$) and thiophenol ArSH ($\text{Ar} = 2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$) gives the neutral monomeric cobalt(II) bis(aryloxy) $[\text{Co}(\text{OAr}^{\text{Me}})_2(\text{TMEDA})]$ (**2**) and dithiolate $[\text{Co}(\text{SAr})_2(\text{TMEDA})]$ (**3**), respectively. Complexes **1–3** have been characterized by mass spectrometry, microanalysis, magnetic moment, and melting-point measurements, in addition to X-ray crystallography.

Introduction

The chemistry of transition metal amides has attracted much interest over the past decade because of their important roles in various industrial^{1–3} and biological processes.^{2,4} Although the chemistry of amido complexes of the early transition metals has been developed in detail, that of the low-valent late transition metals remains relatively unexplored.^{5,6} One of the factors that hinders the development of the chemistry of the latter complexes may be ascribed to an unfavorable combination between the “hard” anionic amido ligand and the “soft” low-valent late transition metal center.^{5,6} Moreover, the “reluctance” of the low-valent late transition metal center to function as a π -acceptor

for the lone-pair electron density of the amido moiety through ($d \leftarrow p$) π -bonding interaction may also impose an unfavorable effect on the stability of the M–N bond.^{5,7}

Strategies for the synthesis of amido complexes of the low-valent late transition metals usually involve the incorporation of “soft” phosphine donors as supporting ligands^{3,6} or the utilization of sterically hindering aryl- and alkylamido ligands.^{8–11} In recent years, the chemistry of the N -functionalized amido ligands $[\text{N}(\text{R})(2\text{-C}_5\text{H}_4\text{N})]^-$ ($\text{R} = \text{Ph}$,^{12,13} $2\text{-C}_5\text{H}_4\text{N}$,^{14,15} SiMe_3 ,¹⁶ 1-adamantyl^{17}), $[\text{N}(\text{R})(2\text{-C}_5\text{H}_3\text{N-6-Me})]^-$ ($\text{R} = \text{SiMe}_3$,¹⁸ 1-adamantyl^{17}), $[\text{N}(\text{SiMe}_3)(2\text{-C}_5\text{H}_3\text{N-4-Me})]^-$,¹⁹ and $[\text{N}(\text{SiMe}_3)(8\text{-C}_9\text{H}_6\text{N})]^-$ ²⁰ has attracted much interest, and a number of main-group and transition metal amido complexes with unusual coordination geometry have been isolated. However, reports of late transition metal amides derived from these ligands remain scarce.^{15a,c,e–g,19a} One of the current issues in our laboratory focuses on the syntheses, structures, and reactivities of amido metal complexes derived from sterically demanding aryl- and

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alkylamido ligands. We reasoned that bulkiness of substituents on the amido nitrogen does impose an important influence on the structure of the corresponding amido metal complexes. Accordingly, two sterically more encumbered *N*-functionalized amido ligands $[\text{N}(\text{R})(2\text{-C}_5\text{H}_3\text{N-6-Me})]^-$ ($\text{R} = \text{Si}^i\text{BuMe}_2$, Si^iBuPh_2) have been developed in our laboratory.^{21,22a} With these sterically more demanding ligands, a number of main-group and transition metal amido complexes with quite different structures have been prepared and structurally characterized.^{21,22} Herein we report the synthesis and crystal structure of a novel binuclear cobalt(II) amide $[(\text{CoL}_2)_2(\text{TMEDA})]$ (**1**) [$\text{L} = \text{N}(\text{Si}^i\text{BuMe}_2)(2\text{-C}_5\text{H}_3\text{N-6-Me})$; $\text{TMEDA} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$] in which the TMEDA ligand binds two cobalt ions in an unusual *N,N'*-bridging coordination mode. Subsequent reactions of **1** with the bulky phenol $\text{Ar}^{\text{Me}}\text{OH}$ ($\text{Ar}^{\text{Me}} = 2,6\text{-}^i\text{Bu}_2\text{-4-MeC}_6\text{H}_2$) and thiophenol ArSH ($\text{Ar} = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$) gave the neutral mononuclear cobalt(II) bis(aryloxide) $[\text{Co}(\text{OAr}^{\text{Me}})_2(\text{TMEDA})]$ (**2**) and dithiolate $[\text{Co}(\text{SAr})_2(\text{TMEDA})]$ (**3**), respectively.

Experimental Section

General Procedures. All experiments were performed under a purified nitrogen atmosphere using modified Schlenk techniques or in a Braun MB 150-M drybox. Solvents were dried over and distilled from calcium hydride (hexane) or sodium benzophenone (ether, THF, and toluene) and degassed twice before use. Anhydrous CoCl_2 was purchased from Fluka and was used as received. 2-(*tert*-Butyldimethylsilyl)amino-6-picoline was prepared as described.²¹ 2,6-ⁱBu₂-4-MeC₆H₂-OH ($\text{Ar}^{\text{Me}}\text{OH}$) was purchased from Aldrich and was recrystallized from hexane before use. 2,4,6-ⁱBu₃C₆H₂SH (ArSH) was prepared according to literature procedures.²³

Physical Measurements. Melting points were recorded on an Electrothermal melting point apparatus and were uncorrected. EI mass

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spectra were obtained on a Hewlett-Packard 5989B Mass Engine spectrometer. Magnetic moments were measured in benzene solutions at 300 K by the Evans method.²⁴ Elemental analyses were performed by MEDAC Ltd., Brunel University, U.K.

Syntheses. $[(\text{CoL}_2)_2(\text{TMEDA})]$ (1**).** A solution of 2-(*tert*-butyldimethylsilyl)amino-6-picoline (2.68 g, 12 mmol) and TMEDA (1.82 mL, 12 mmol) in ether (10 mL) at 0 °C was slowly treated with a solution of ⁿBuLi in hexane (1.6 M, 9.0 mL, 14.4 mmol). The reaction mixture was stirred for 15 min at room temperature, and all volatiles in the resulting solution were removed in vacuo. The solid residue was washed twice with hexane and dried under vacuum. It was redissolved in ether (20 mL) and added to a suspension of CoCl_2 (0.78 g, 6.0 mmol) in the same solvent (10 mL) at 0 °C. The reaction mixture was stirred for 24 h at room temperature and was filtered. The filtrate was concentrated under reduced pressure to give complex **1** as a green crystalline solid. Yield: 2.3 g (68%). Mp: 66–69 °C. EI-MS (70 eV): m/z 502 (11) $[\text{CoL}_2]^+$, 445 (35) $[\text{CoL}_2 - ^i\text{Bu}]^+$, 222 (3) $[\text{L}]^+$. $\mu_{\text{eff}} = 3.06 \mu_{\text{B}}$ per Co atom. Anal. Found: C, 57.23; H, 8.33; N, 12.70. Calcd for $\text{C}_{54}\text{H}_{100}\text{N}_{10}\text{Co}_2\text{Si}_4$: C, 57.93; H, 9.00; N, 12.51.

$[\text{Co}(\text{OAr}^{\text{Me}})_2(\text{TMEDA})]$ (2**).** To a solution of $\text{Ar}^{\text{Me}}\text{OH}$ (0.85 g, 3.86 mmol) in hexane (10 mL) was slowly added a solution of **1** (1.08 g, 0.97 mmol) in the same solvent (30 mL) at 0 °C. The resultant solution was stirred at room temperature for a further 24 h. All volatiles were then removed in vacuo to give a green residue, which was washed twice with hexane and dried under vacuum. Toluene was added to redissolve the residue, and the solution was filtered through Celite. The filtrate was concentrated under reduced pressure. Crystals of complex **2** was obtained after 1 day. Yield: 0.57 g (48%). Mp: 227–230 °C (dec). EI-MS (70 eV): m/z 498 (12) $[\text{Co}(\text{OAr}^{\text{Me}})_2]^+$, 220 (34) $[\text{Ar}^{\text{Me}}\text{O}]^+$, 205 (100) $[\text{Ar}^{\text{Me}}\text{O} - \text{Me}]^+$. $\mu_{\text{eff}} = 3.64 \mu_{\text{B}}$. Anal. Found: C, 70.55; H, 10.06; N, 4.68. Calcd for $\text{C}_{36}\text{H}_{62}\text{N}_2\text{CoO}_2$ (613.81): C, 70.33; H, 10.33; N, 4.55.

$[\text{Co}(\text{SAr})_2(\text{TMEDA})]$ (3**).** A solution of **1** (1.32 g, 1.18 mmol) in hexane (30 mL) was added to a solution of ArSH (1.32 g, 4.74 mmol) in hexane (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 h and filtered, and the filtrate was concentrated under reduced pressure. Crystallization at –30 °C afforded complex **2** as reddish-brown needles. Yield: 0.76 g (44%). Mp: 142–146 °C (dec). EI-MS (70 eV): m/z 278 (26) $[\text{ArS}]^+$, 263 (34) $[\text{ArS} - \text{Me}]^+$, 221 (6) $[\text{ArS} - ^i\text{Bu}]^+$. $\mu_{\text{eff}} = 3.78 \mu_{\text{B}}$. Anal. Found: C, 68.56; H, 10.10; N, 3.77. Calcd for $\text{C}_{42}\text{H}_{74}\text{N}_2\text{CoS}_2$: C, 69.09; H, 10.22; N, 3.84.

X-ray Structure Analysis. Single-crystals of **1–3** suitable for crystallographic studies were mounted in glass capillaries and sealed under nitrogen. Details of crystal parameters, data collection, and structural refinement are summarized in Table 1. Data were collected on a Rigaku RAXIS-IIC diffractometer at 294 K using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) by taking oscillation photos. The structures were solved by direct phase determination using the computer program SHELX-97 on a PC 486 computer and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms.²⁵ Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factors.²⁶

Results and Discussion

Synthesis of $[(\text{CoL}_2)_2(\text{TMEDA})]$ (1**).** The lithium reagent $[\text{Li}(\text{L})(\text{TMEDA})]^{21}$ was readily prepared by lithiation of 2-(*tert*-butyldimethylsilyl)amino-6-picoline (HL), in the presence of TMEDA, with a solution of ⁿBuLi in hexane at 0 °C. Complex **1** was synthesized by treating a suspension of CoCl_2 in diethyl ether with 2 equiv of $[\text{Li}(\text{L})(\text{TMEDA})]$ at ambient temperature. The resultant solution was filtered and concentrated to afford **1** as a green crystalline solid in a satisfactory yield (68%) (Scheme 1).

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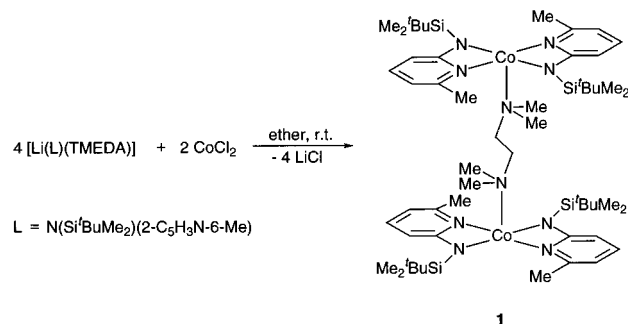
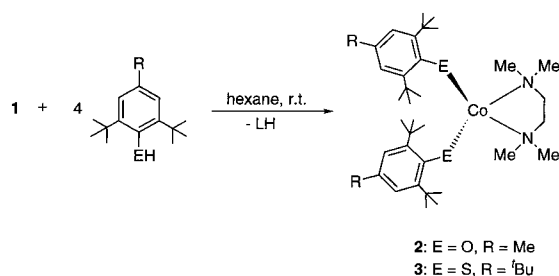
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Table 1. Crystal Data for Complexes 1–3

	1	2	3
mol formula	C ₅₄ H ₁₀₀ Co ₂ N ₁₀ Si ₄	C ₃₆ H ₆₂ CoN ₂ O ₂	C ₄₂ H ₇₄ CoN ₂ S ₂
mol wt	1119.66	613.81	730.08
cryst size, mm ³	0.40 × 0.40 × 0.30	0.30 × 0.25 × 0.22	0.40 × 0.25 × 0.20
cryst syst	triclinic	monoclinic	orthorhombic
space group	<i>P</i> 1	<i>P</i> 21/ <i>c</i>	<i>P</i> na2(1)
<i>a</i> , Å	12.046(2)	18.196(4)	23.177(5)
<i>b</i> , Å	12.286(3)	14.902(3)	11.056(2)
<i>c</i> , Å	12.291(3)	13.428(3)	17.263(4)
β , deg	72.65(3)	90.00(3)	90
<i>Z</i>	1	4	4
<i>V</i> , Å ³	1660.8(6)	3641.1(13)	4423.6(15)
density, g cm ⁻³	1.119	1.120	1.096
abs coeff, mm ⁻¹	0.610	0.502	0.510
no. of reflns collected	4809	8169	10495
unique data measd	4809	5129	3857
obsd data with $I \geq 2\sigma(I)$	4242	3838	3222
no. of variable	317	371	401
final <i>R</i> indices [$I \geq 2\sigma(I)$] ^a	R1 = 0.0643 wR2 = 0.1779	R1 = 0.0784 wR2 = 0.1683	R1 = 0.0876 wR2 = 0.2217
<i>R</i> indices (all data) ^a	R1 = 0.0733 wR2 = 0.1875	R1 = 0.1202 wR2 = 0.1892	R1 = 0.1077 wR2 = 0.2372

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2}.$$

Scheme 1**Scheme 2**

Protolysis of 1. Reactions of **1** toward protic reagents such as the phenol Ar^{Mc}OH and thiophenol ArSH, which bear bulky *ortho* substituents, have been studied. Complex **1** reacted smoothly with 4 equiv of Ar^{Mc}OH or ArSH in hexane to give the corresponding neutral monomeric cobalt(II) bis(aryloxide) [Co(OAr^{Mc})₂(TMEDA)] (**2**) and dithiolate [Co(SAr)₂(TMEDA)] (**3**), respectively (Scheme 2).

Complexes **1–3** are very sensitive to oxygen and moisture. They are very soluble in common organic solvents, such as diethyl ether, THF, hexanes, and toluene. They were characterized by mass spectrometry, microanalysis, magnetic moment, and melting-point measurements, as well as single-crystal X-ray diffraction studies. The mass spectrum of complex **1** showed only signals due to the mononuclear species [CoL₂]⁺ ($m/z = 502$, 11%), indicating loss of the TMEDA ligand in the vapor phase. Molecular ion peaks were not observed in the mass spectra of complexes **2** and **3**. For **2**, fragmentation peaks such as [Co(OAr^{Mc})₂]⁺ ($m/z = 498$, 12%) and [Ar^{Mc}O]⁺ ($m/z = 220$,

34%) were observed. The mass spectrum of **3** showed only peaks due to [ArS]⁺ ($m/z = 278$, 26%) and its fragments.

The protolysis of transition metal amides by bulky phenols and thiols has proven to be a versatile route to the corresponding aryloxide and thiolate complexes. It is well-documented that transition metal aryloxides and thiolates usually have a high tendency to associate and form insoluble polymers.²⁷ This renders their characterization difficult to carry out. However, the degree of association can be reduced by introduction of bulky aryl or alkyl substituents on the aryloxide or thiolate ligands. Accordingly, a number of homoleptic and heteroleptic cobalt(II) alkoxide and thiolate complexes with low degrees of association have been isolated by utilizing sterically demanding alkoxy and thiolato ligands. On the other hand, neutral monomeric transition metal aryloxide and thiolate complexes with a N₂O₂ and N₂S₂ coordination environment remain elusive. Complexes **2** and **3** represent rare examples of complexes with these types of coordination environment.

X-ray Structural Studies. The molecular structure of complex **1** with the atom numbering scheme is depicted in Figure 1. Selected bond distances and angles are shown in Table 2. The X-ray structure of **1** features an unusual binuclear complex which consists of two bis(amido)cobalt(II) {CoL₂} units bridged by one TMEDA molecule. Each amido ligand L binds to the cobalt(II) center in a *N,N'*-chelating fashion, forming a {CoN₄} moiety. Coordination from one dimethylamino unit of the TMEDA ligand completes a distorted trigonal bipyramidal coordination geometry around each cobalt center. The two amido nitrogens N(1) and N(3) and the amino nitrogen N(5) from TMEDA define the trigonal plane (sum of bond angles = 359.8°). The remaining two axial sites are occupied by the pyridyl nitrogens N(2) and N(4): N(2)–Co–N(4) = 172.6(1)°. Deformation of the N(2)–Co–N(4) angle away from linearity may be a consequence of the highly strained four-membered metallacycle rings, the N_{amido}–Co–N_{pyridyl} bite angles being 62.7(1)–63.8(1)°. A noteworthy feature of complex **1** is the unusual *N,N'*-bridging coordination mode of the TMEDA

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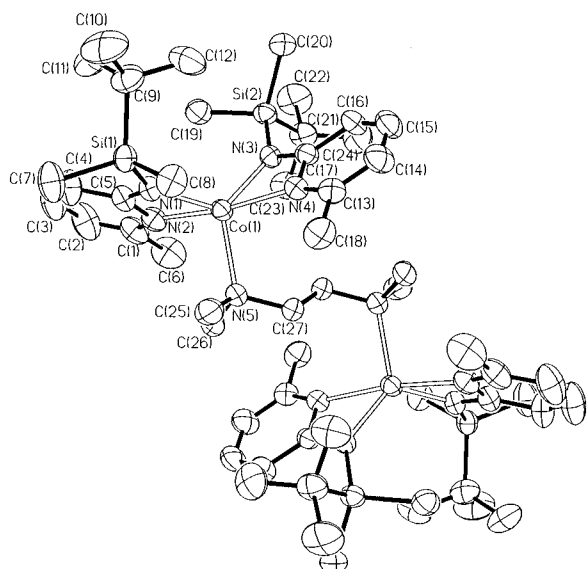


Figure 1. Molecular structure of $[(\text{CoL}_2)_2 \cdot (\text{TMEDA})]$ (**1**) (30% thermal ellipsoids) with the atomic labeling scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(\text{CoL}_2)_2 \cdot (\text{TMEDA})]$ (**1**)

Co(1)–N(1)	2.007(4)	Co(1)–N(3)	1.998(3)
Co(1)–N(2)	2.258(4)	Co(1)–N(4)	2.355(3)
Co(1)–N(5)	2.176(4)	C(5)–N(1)	1.359(5)
C(5)–N(2)	1.354(6)	C(17)–N(3)	1.362(5)
C(17)–N(4)	1.369(5)	N(1)–Si(1)	1.725(4)
N(3)–Si(2)	1.735(3)		
N(2)–Co(1)–N(1)	63.8(1)	N(4)–Co(1)–N(3)	62.7(1)
N(3)–Co(1)–N(1)	120.5(1)	N(4)–Co(1)–N(2)	172.6(1)
N(2)–Co(1)–N(5)	112.6(1)	N(4)–Co(1)–N(5)	126.7(1)
C(5)–N(2)–Si(1)	127.8(3)	C(5)–N(2)–Co(1)	96.8(3)
Si(1)–N(2)–Co(1)	135.0(1)	C(17)–N(4)–Si(2)	125.8(3)
C(17)–N(4)–Co(1)	99.6(2)	Si(2)–N(4)–Co(1)	133.0(1)

ligand. Examples of this type of unusual coordination mode for TMEDA have been reported for certain main-group metal alkyls and hydrides,²⁸ but are rarely observed in transition metal complexes.^{29,30} The TMEDA molecule might be expected to bind in a bidentate manner to the same cobalt atom, forming a six-coordinate mononuclear complex. Presumably, the large steric bulk of ligand L prevents the TMEDA molecule from ligating in a bidentate fashion in the present complex.

The Co–N_{pyridyl} distances [Co(1)–N(2), Co(1)–N(4)] of 2.258(4) and 2.355(3) Å in **1** are somewhat longer than the Co–N_{amine} distance [Co(1)–N(5)] of 2.176(4) Å. This is probably due to the presence of the highly strained four-membered metallacycle rings in **1**. The observed Co–N_{amido} bond distances in complex **1** [Co(1)–N(1) 2.007(4) Å, Co(1)–N(3) 1.998(3) Å] are much longer than those of 1.84(2) and 1.898(3)–1.904(3) Å in the monomeric Co[N(SiMe₃)₂]₂^{8e} and [Co{N(SiMePh₂)₂}]₂,⁹ respectively. They are also longer than the Co–N_{amido} distances

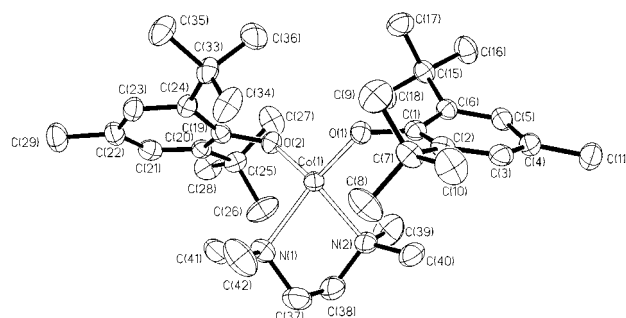


Figure 2. Molecular structure of $[\text{Co}(\text{OAr}^{\text{Me}})_2(\text{TMEDA})]$ (**2**) (30% thermal ellipsoids) with the atomic labeling scheme.

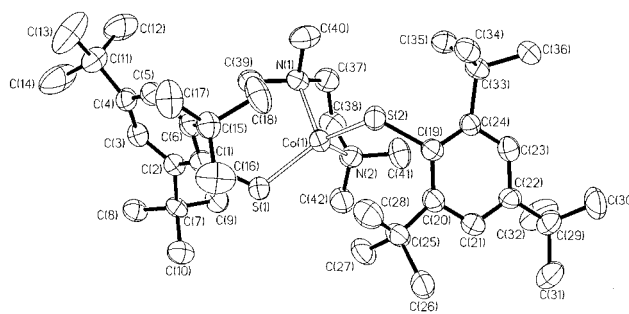


Figure 3. Molecular structure of $[\text{Co}(\text{SAr})_2(\text{TMEDA})]$ (**3**) (30% thermal ellipsoids) with the atomic labeling scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{Co}(\text{OAr}^{\text{Me}})_2(\text{TMEDA})]$ (**2**)

Co(1)–O(1)	1.907(3)	Co(1)–O(2)	1.893(3)
Co(1)–N(1)	2.223(4)	Co(1)–N(2)	2.183(4)
C(1)–O(1)	1.341(5)	C(19)–O(2)	1.349(5)
O(1)–Co(1)–O(2)	108.1(1)	N(1)–Co(1)–N(2)	83.0(1)
N(1)–Co(1)–O(1)	134.2(1)	N(1)–Co(1)–O(2)	104.5(1)
N(2)–Co(1)–O(1)	104.6(1)	N(2)–Co(1)–O(2)	122.8(1)
C(1)–O(1)–Co(1)	133.1(3)	C(19)–O(2)–Co(1)	138.1(3)

of 1.910(5)–1.922(5) Å for terminal ligands in the dimeric $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ ^{8d} and 1.89 Å (av) in $[\text{Co}(\text{NPh}_2)_2]_2$.¹⁰ The longer Co–N_{amido} distances in our current complex may be ascribed to a more crowded five-coordinate environment around the metal centers.

The amido nitrogen centers [N(1) and N(3)] exhibit a nearly trigonal planar geometry [sum of bond angles: 359.02° (av)], which is consistent with sp²-hybridized nitrogen atoms. The observed Si–N bond distances in **1** [1.725(4)–1.735(3) Å] are similar to the Si–N distances found in other silylamido complexes.^{5,8,10,18–22} Moreover, delocalization of the lone-pair electrons onto the pyridyl ring is evidenced by the short C_{pyridyl}–N_{amido} bond distances of 1.359(5)–1.362(5) Å in **1**. They are close to the observed C_{aromatic}–N_{amido} distances in other metal arylamido complexes, in which delocalization of electron density onto the aromatic substituents have been suggested.^{31,m,6,20,31} Apparently, ligand L behaves as a weak π-acceptor in complex **1**, and this may account for the stability of the complex.

The molecular structures of complexes **2** and **3** are shown in Figures 2 and 3, respectively. Selected bond distances and angles are listed in Tables 3 and 4. The metal center of the neutral monomeric bis(aryloxide) complex **2** is bound by two monodentate Ar^{Me}O ligands and a bidentate TMEDA ligand, resulting in a distorted tetrahedral N₂O₂ coordination geometry. The

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(30) Interestingly, an analogous iron(II) amido complex $[(\text{FeL}_2)_2 \cdot (\text{TMEDA})]$, which contains a TMEDA ligand ligating in a similar bridging coordination mode, has recently been prepared and structurally characterized in our laboratory and will be reported in a future article.

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Table 4. Selected Bond Distances (Å) and Angles (deg) for [Co(SAr)₂(TMEDA)] (**3**)

Co(1)–S(1)	2.277(4)	Co(1)–S(2)	2.276(3)
Co(1)–N(1)	2.138(8)	Co(1)–N(2)	2.148(9)
C(1)–S(1)	1.832(5)	C(19)–S(2)	1.826(5)
S(1)–Co(1)–S(2)	119.5(1)	N(1)–Co(1)–N(2)	85.9(4)
N(1)–Co(1)–S(1)	112.5(2)	N(1)–Co(1)–S(2)	106.7(2)
N(2)–Co(1)–S(1)	116.0(3)	N(2)–Co(1)–S(2)	110.9(3)
C(1)–S(1)–Co(1)	117.0(2)	C(19)–S(2)–Co(1)	116.7(2)

average Co–O distance of 1.90 Å in **2** is somewhat longer than those of 1.84 Å (av) and 1.85 Å (av) in the ionic cobalt(II) complexes [Co(Cl)(OC'Bu₃)₂·Li(THF)₃]^{32a} (**4**) and [Li(THF)_{4,5}]-[Co(Cl)(OC'Bu₃)₂]^{32a} (**5**), respectively. In comparison with other neutral cobalt(II) aryloxide complexes, the Co–O distances in **2** are much longer than the terminal Co–O distances of 1.78 Å (av) in the binuclear complex [Co{OC(C₆H₁₁)₃}₂]₂^{32b} (**6**), 1.81 Å (av) in [Co(OCPh₃)₂]₂^{32b} (**7**), and 1.85 Å (av) in [Co(OSiPh₃)₂(THF)]₂^{32b} (**8**), where the metal centers in complexes **4–8** exhibit a nearly trigonal planar geometry. The Co–O distance in **2** is slightly longer than that of 1.872(2) Å in the mononuclear four-coordinate complex [Co(OCPh₃)₂(THF)₂]^{32b} (**9**). The Co–O–C angles in **2**, viz., 133.1(3)–138.1(3)°, are large. Such large angles have been observed in a number of metal alkoxides and aryloxides, which may be attributed to a (d–p) π -interaction between the oxygen atom and the metal center.³²

The mononuclear dithiolate complex **3** exhibits a distorted tetrahedral geometry around the metal center. The Co–S bond distances of 2.276(3) and 2.277(4) Å in **3** are slightly shorter than that of 2.33(1) Å (av) for the anionic [Co(SPh)₄]^{2–}.³³ The small discrepancy in the bond lengths may be a consequence of the anionic charge on the latter complex. The Co–S bond distance in **3** is marginally longer than those of 2.228(1) (av) and 2.260(2) Å (av) in the mononuclear four-coordinate [Co(dppp)(SPh)₂] and [Co(bdpp)(SPh)₂], respectively.³⁴ It is also

slightly longer than the terminal Co–S bond distances of 2.222–(2) Å in the neutral binuclear complex [Co(SC₆H₂BU₃-2,4,6)₂]₂^{35a} and 2.191(5)–2.215(5) Å in the anionic [Co₂(SC₆H₂ⁱ-Pr₃-2,4,6)₅][–].³⁶

Magnetic Properties. The magnetic moments of **1–3** in benzene, viz., 3.06 μ_B per Co for **1**, 3.64 μ_B for **2**, 3.78 μ_B for **3**, have been measured by the Evans method. The reason for the relatively low value for **1** is unclear at this moment. We surmise that this may be ascribed to a mononuclear-to-binuclear type equilibrium for complex **1** in solution. The magnetic moments of complexes **2** and **3** are consistent with a high-spin d⁷ electronic configuration with three unpaired electrons.

Conclusions

The novel binuclear cobalt(II) amido complexes [(CoL₂)₂·(TMEDA)] (**1**) are readily prepared by treating anhydrous CoCl₂ with the lithium reagent [Li(L)(TMEDA)]. The solid-state structure of **1** contains two {CoL₂} moieties bridged by one TMEDA ligand. The latter binds in an unusual *N,N'*-bridging coordination mode, which is rarely observed in transition metal complexes. Each Co(II) center in **1** is bound by a pair of *N,N'*-chelating ligands L and an amino moiety of TMEDA, resulting in a trigonal bipyramidal coordination geometry around the metal center. Protolysis of **1** with Ar^{Me}OH and ArSH gave the neutral mononuclear cobalt(II) bis(aryloxide) [Co(OAr^{Me})₂(TMEDA)] (**2**) and dithiolate [Co(SAr)₂(TMEDA)] (**3**), respectively. The metal center in the latter two complexes adopts a distorted tetrahedral geometry. Studies on other late transition metal amido complexes derived from ligand L are currently under investigation in our laboratory.

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Supporting Information Available: Listings of X-ray crystallographic data, atomic coordinates, thermal parameters, and complete bond distances and angles for complexes **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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