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New Cobalt Complexes Incorporating Thioether Chelation and Base-Induced Homolog-Selective Transformations Thereof

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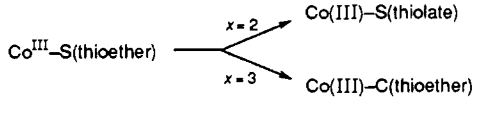
The reaction of cobalt(II) acetate tetrahydrate with dithiaalkyl-substituted triazene 1-oxides $[MeN(O)NNHC_6H_4S]_2(CH_2)_x$, H_2MexL (x = 2, 3) affords $Co^{II}(MexL)$ (**2**), which undergoes facile oxidation by hydrogen peroxide, furnishing $[Co^{III}(MexL)]ClO_4{\cdot}CH_2Cl_2$ (**3**). In these complexes the ligands act in a hexadentate manner, and the coordination spheres are of the type $CoS_2N_2O_2$. When $Co(Me2L)^+$ is treated with base, the green complex $Co^{III}(Me1)(Me1')$ (**4**) is formed through cleavage of the coordinated ligand into two tridentate parts via scission of a C–S bond. The coordination sphere is Co(SNO)(SNO), one sulfur site being thioether and the other being thiolate. On the other hand a similar treatment of $Co(Me3L)^+$ affords the organocobalt(III) complex $Co^{III}(Me3L')$ (**5**) formed by the displacement of a thioether site by a carbanionic site in the coordination sphere which becomes $CoSCN_2O_2$. The same reactions can be achieved by reacting Co(Me*x*L) with alkali in the presence of oxygen. These remarkable homolog-selective transformations have been rationalized, and other examples fitting into the rationale are also presented. Cleavage occurs when the thioether chelate ring activated via α-methylene deprotonation is five-membered and an organocobalt(III) complex is formed when it is six-membered. The complexes have been characterized with the help of spectroscopy (UV–vis, ^1H NMR) and X-ray crystallography. The X-ray structures of four complexes are reported: (i) Co(Me3L), crystal system orthorhombic, space group $P2_12_12_1$, a = 7.871(2) Å, b = 9.777(4) Å, c = 25.942(10) Å, V = 1996(1) Å^3, Z = 4, R = 5.02%, R_w = 5.19%; (ii) $[Co(Me3L)]ClO_4{\cdot}CH_2Cl_2$, crystal system triclinic, space group $P\bar{1}$; a = 9.849(5) Å, b = 11.666(6) Å, c = 13.354(7) Å; α = 102.33(4)°, β = 103.24(4)°, γ = 108.47(4)°, V = 1346(1) Å^3, Z = 2, R = 4. 54%, R_w = 4.38%; (iii) Co(Me1)(Me1'), crystal system monoclinic; space group $P2_1/n$, a = 9.445(5) Å, b = 18.650(8) Å, c = 11.284(6) Å, β = 100.90(4)°, V = 1952(1) Å^3, Z = 4, R = 4.74%, R_w = 4.72%; (iv) $Co(Me3L'){\cdot}CHCl_3$, crystal system monoclinic, space group $P2_1/n$, a = 12.818(7) Å, b = 14.597(8) Å, c = 13.194(6) Å, β = 97.67(4)°, V = 2447(2) Å^3, Z = 4, R = 4.03%, R_w = 4.07%.

Introduction

The selective transformation of organic groups via metal binding is an abiding theme of chemical research. The concern of this work is the thioether function coordinated to bivalent and trivalent cobalt. Herein we report new complexes of coordination type $CoS_2N_2O_2$ derived from hexadentate ligands incorporating homologous dithiaalkyl fragments, $-S(CH_2)_xS-$ (x = 2, 3). Alkali activates the thioether group in the cobalt(III) species but a remarkable x-dependent product selectivity is observed, eqs 1 and 2. In eq 1 a C–S bond is cleaved, and in eq 2 metal binding simply shifts from sulfur to carbon. All relevant species have been isolated and structurally characterized. A rationale for the x-dependence of products is proposed on the basis of the present findings taken collectively with other results from this laboratory and elsewhere.



(1)
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Results and Discussion

Ligands, Parent Complexes, and Transformed Complexes. The thioether function is a relatively weak donor, and polydentate ligation is a useful tool for ensuring viable metal–thioether binding.[1-4] This principle has been utilized in the present work. The two concerned hexadentate ligands H_2MexL (x = 2, 3) (**1**) belong to the dithiaalkyl-substituted triazene 1-oxide family.[5-12] These and the complexes derived therefrom are shown in Scheme 1 along with the synthetic and transformation steps. The reaction of H_2MexL with cobalt(II) acetate tetrahydrate in a methanol–dichloromethane mixture affords the red cobalt(II) complexes of type Co(Me*x*L) (**2**), which undergo facile oxidation by hydrogen peroxide in the same mixed solvent furnishing the purple cobalt(III) analogs of type **3** isolated as solvated perchlorate salts, $[Co(MexL)]ClO_4{\cdot}CH_2Cl_2$.

The $Co(MexL)^+$ complexes are indefinitely stable in the solid state and in neutral solutions. However, they are activated in alkaline media (Scheme 1) but *the products are entirely different for the otherwise very similar homologous chelates* $Co(Me2L)^+$ *and* $Co(Me3L)^+$. When $Co(Me2L)^+$ is treated with methanolic potassium hydroxide in acetonitrile solution, the color rapidly changes from purple to green, and from the reaction mixture the

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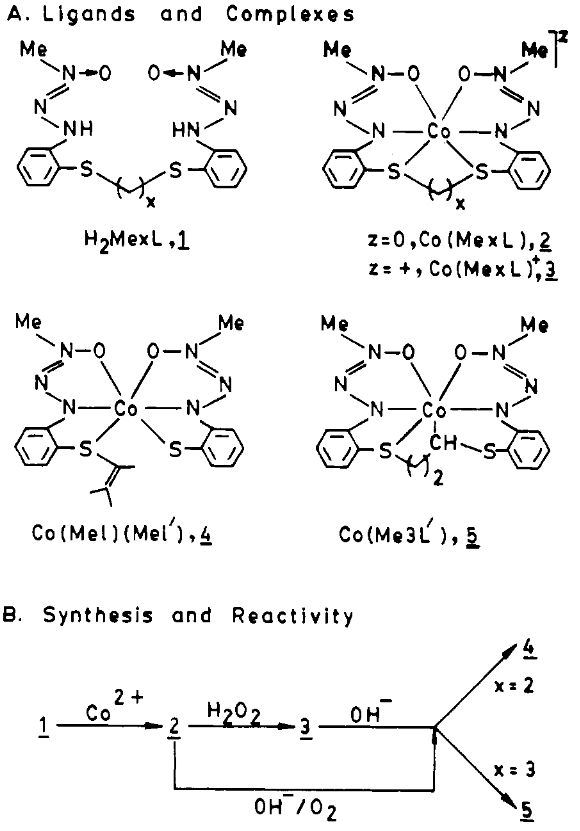
Scheme 1



green cobalt(III) complex Co(Me1)(Me1′) (**4**) is isolated in good yield. A similar treatment of Co(Me3L)$^+$ afforded the green organocobalt(III) complex Co(Me3L′) (**5**), which was isolated as a crystalline 1:1 chloroform adduct. The transformations Co-(Me2L)$^+$ → Co(Me1)(Me1′) and Co(Me3L)$^+$ → Co(Me3L′) respectively illustrate the reaction types of eqs 1 and 2.

The above-noted formation of complexes **4** and **5** occur equally well in air or under inert atmosphere. When the cobalt(II) complexes of type Co(Me*x*L) are similarly treated with alkali no reaction is discernible under pure nitrogen. However, in air and even better under pure oxygen **4** and **5** are formed smoothly from Co(Me2L) and Co(Me3L) respectively (Scheme 1).

The reactivity of the coordinated thioether function has received attention[13-20] in recent years, and some of the reported results have special relevance to the present work; *vide infra*.

Magnetism, Spectra, and Reduction Potentials. The Co(Me*x*L) complexes are high spin ($S = 2$), the magnetic moments of the solids at 300 K being 4.20 μ_B ($x = 2$) and 4.22 μ_B ($x = 3$). All the other complexes are diamagnetic as expected (cobalt(III)). Electronic spectral data (360–1600 nm) are collected in Table 1, and representative cobalt(III) spectra are shown in Figure 1. The low symmetry of the metal coordination sphere as revealed by X-ray crystallography (*vide infra*) causes observable splitting of octahedral ligand-field transitions: (i) in Co(Me*x*L) two components[12] of $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ in the region 800–1300 nm and (ii) in Co(Me*x*L)$^+$ and Co(Me1)(Me1′) two components[21] of $^1A_{1g} \rightarrow {}^1T_{1g}$ in the region 500–900 nm. Splitting of the corresponding transition (620 nm) in Co(Me3L′) is not resolved.

The aliphatic ^{1}H NMR resonances of the cobalt(III) complexes in $CDCl_3$ are listed in Table 1. The two NMe groups are equivalent in Co(MexL)$^+$ but not in Co(Me1)(Me1′) and Co-(Me3L′) as expected. The vinyl group in Co(Me1)(Me1′) gives rise to the splitting pattern shown in Figure 2 (assignment in Table 1). The aliphatic chain in Co(Me3L′) has a complex spectrum. Fortunately the CoCH proton occurs as an isolated multiplet of correct intensity at a relatively low-field as expected for a cobalt(III)-coordinated alkyl function forming part of a polydentate frame.[6,22] The splitting pattern (Figure 2) is qualitatively consistent with its coupling to the two inequivalent methylene protons.

In acetonitrile solution a quasi-reversible (cyclic voltammetric peak-to-peak separation 80–100 mV) Co(Me*x*L)$^+$–Co(Me*x*L) couple can be observed starting from either Co(Me*x*L) (initial scan anodic) or Co(Me*x*L)$^+$ (initial scan cathodic). At 298 K the $E_{1/2}$ values are 0.04 V ($x = 2$) and 0.07 V ($x = 3$) versus saturated calomel electrode (SCE). Coulometric oxidation of Co(Me*x*L) at 0.30 V quantitatively affords Co(MexL)$^+$ with the liberation of one electron. The original cobalt(II) complex is fully regenerated upon reduction of the oxidized solution at −0.20 V. Unlike Co(Me*x*L)$^+$, the complexes Co(Me1)(Me1′) and Co-(Me3L′) are not electroactive in acetonitrile in the voltage region +0.4 to −1.5 V, showing that the trivalent state is better stabilized in the latter two species.[23]

The facile oxidation of Co(Me*x*L) to Co(Me*x*L)$^+$ by hydrogen peroxide is consistent with the relatively low $E_{1/2}$ values of the Co(Me*x*L)$^+$–Co(Me*x*L) couple. Aerial oxygen may also be expected (thermodynamically speaking) to bring about this oxidation. In practice this does not occur in neutral media, but in alkaline solution oxidation does occur, affording the transformed cobalt(III) species (Scheme 1).

Crystal and Molecular Structure. The X-ray structures of four species have been determined: Co(Me3L), [Co(Me3L)]ClO_4·CH_2Cl_2, Co(Me1)(Me1′), and Co(Me3L′)·$CHCl_3$. Molecular views are shown in Figures 3–6, and selected bond parameters are collected in Tables 2–4. In the first three complexes, the distorted octahedral coordination sphere is of the type $CoS_2N_2O_2$, and in Co(Me3L′), it is $CoSCN_2O_2$. All the N,O- and N,S-coordinating five-membered chelate rings are planar. The other rings are puckered. The trend of N–N lengths is consistent with the triazene 1-oxide formulation of the nitrogeneous part of the ligand, O—N=N—N—$^-$.

Between Co(Me3L) and [Co(Me3L)]ClO_4·CH_2Cl_2 the average Co–S lengths decrease by a remarkable ~0.3 Å, consistent with the large contraction of metal radius upon oxidation and spin-pairing. To our knowledge, this is the first example where the Co–S(thioether) lengths for the high-spin bivalent and low-spin trivalent metal has been compared in the same ligand environment. Cases where both metal oxidation states are low spin in

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(23) The complex Co(Me1)(Me1′) however displays a quasi-reversible one-electron oxidation with $E_{1/2} = 0.56$ V (peak-to-peak separation, 80 mV). On the other hand Co(Me3L′) is irreversibly oxidized (anodic peak, 0.56 V). No attempts were made to characterize the products of oxidation.

Table 1. Electronic and ^{1}H NMR Spectral Data

complex	UV–vis data^a λ_{max}, nm (ϵ, M^{-1} cm^{-1})	^{1}H NMR data in CDCl$_3$: group	^{1}H NMR data in CDCl$_3$: δ,^{c} ppm
Co(Me2L)	1270 (15), 800 (20), 470^b (620)		
Co(Me3L)	1220 (15), 850 (30), 500^b (430)		
[Co(Me2L)]ClO$_4$·CH$_2$Cl$_2$	800 (420), 550 (570)	–CH$_3$	3.90 (s)
		–CH$_2$–CH$_2$–	3.16 (m)
[Co(Me3L)]ClO$_4$·CH$_2$Cl$_2$	800 (400), 540 (450)	–CH$_3$	3.89 (s)
		–CH$_2$–CH$_2$–CH$_2$–	2.58 (t),^{d} 1.89 (m)
Co(Me1)(Me1′)	750 (300), 550 (380)	–CH$_3$	3.87 (s), 3.75 (s)
		–CH═CH$_2$	6.07 (dd),^{e} 5.66 (dd),^{f} 5.60 (dd)^g
Co(Me3L′)·CHCl$_3$	620 (320)	–CH$_3$	4.03 (s), 3.88 (s)
		CoCH–	4.50 (m)
		–CH$_2$–CH$_2$–	2.04 (m)

^{a} Solvent is dichloromethane. ^{b} Shoulder. ^{c} Meaning of letters given in parentheses are as follows: s, singlet; t, triplet; dd, doublet of doublet; m, multiplet. ^{d} Terminal methylene protons; J^{13} = 10.3 Hz. ^{e} Methine proton; $J_{cis}{}^{13}$ = 9.0 Hz and $J_{trans}{}^{13}$ = 16.8 Hz. ^{f} Methylene proton cis to methine proton; $J_{cis}{}^{13}$ = 9.0 Hz; J^{12} = 0.5 Hz. ^{g} Methylene proton trans to methine proton; $J_{trans}{}^{13}$ = 16.8 Hz; J^{12} = 0.5 Hz.

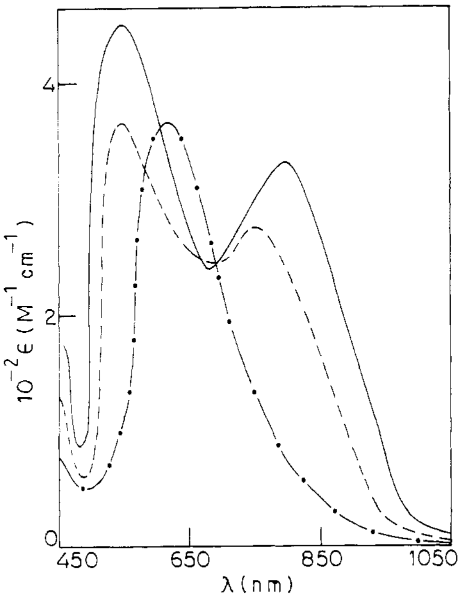

Figure 1. Electronic spectra of [Co(Me3L)]ClO$_4$·CH$_2$Cl$_2$ (—), Co(Me1)(Me1′) (- - -) and Co(Me3L′)·CHCl$_3$ (–·–).

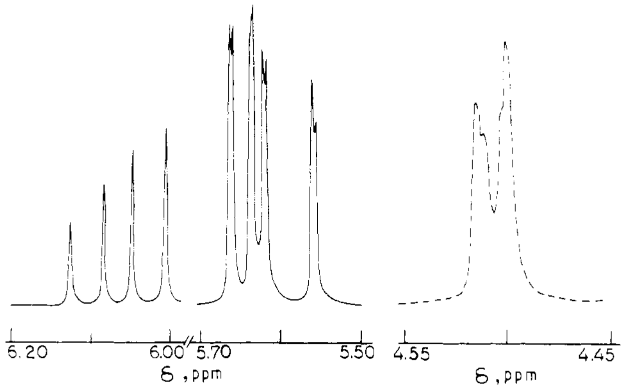

Figure 2. ^{1}H NMR spectra of the vinylic region (—) of Co(Me1)(Me1′) and the CoCH region (- - -) of Co(Me3L′)·CHCl$_3$.

macrocyclic environments have been documented.[3] As a consequence of the contraction of metal radius upon oxidation, there is a significant increase in chelate bite angles between Co(Me3L) and Co(Me3L)$^+$. The cummulative effect of two adjacent chelate rings results in a relatively large increase (in going from Co(Me3L) to Co(Me3L)$^+$) in the angles subtended at the metal by donor sites located at mutually trans positions (Table 2).

In Co(Me1)(Me1′) the lengths of Co(III)–S(thioether) and Co–S(thiolate) are equal within experimental error, 2.228(2) Å. The vinylic C═C length is 1.294(13) Å and the nonbonded Co···S(1) distance is 3.105(2) Å. The Co–C length, 1.969(5) Å, in

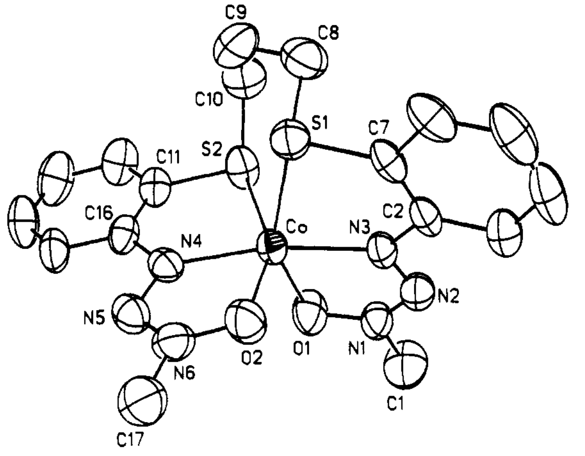

Figure 3. ORTEP plot and labeling scheme for Co(Me3L) with all atoms represented by their 50% probability ellipsoids.

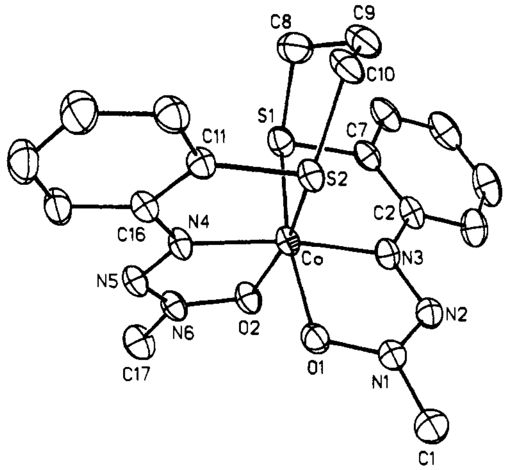

Figure 4. ORTEP plot and labeling sheme for Co(Me3L)$^+$ in [Co(Me3L)]ClO$_4$·CH$_2$Cl$_2$ with all atoms represented by their 50% probability ellipsoids.

Co(Me3L′) lies within the range 1.94–2.05 Å found in organocobalt(III) species where the coordinated alkyl carbon is part of a polydentate ligand chain.[15,16,24] The Co–O(1) bond lying trans to Co–C in Co(Me3L′) is ~0.08 Å longer than the Co–O(2) length. The chemistry of alkylcobalt(III) species is of general interest in the context of vitamin B$_{12}$ and related chemistry.[25]

Origin of Transformation Selectivity. A plausible rationale for the remarkable difference in base-induced transformations of the homologs Co(Me2L)$^+$ and Co(Me3L)$^+$ (Scheme 1) is given

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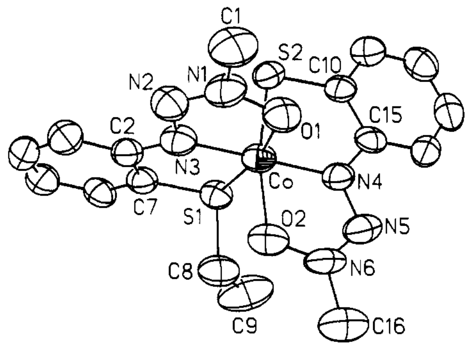


Figure 5. ORTEP plot and labeling scheme for Co(Me1)(Me1′) with all atoms represented by their 50% probability ellipsoids.

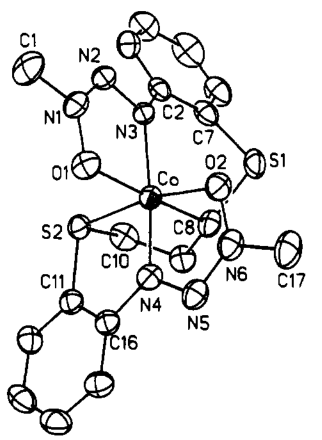


Figure 6. ORTEP plot and labeling scheme for Co(Me3L′) in chloroform adduct with all atoms represented by their 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Co(Me3L) and [Co(Me3L)]ClO_4·CH_2Cl_2

	Co(Me3L)	[Co(Me3L)]ClO_4· CH_2Cl_2
	Distances	
Co–S(1)	2.526(3)	2.227(2)
Co–S(2)	2.541(3)	2.251(1)
Co–O(1)	2.091(7)	1.923(4)
Co–O(2)	2.085(6)	1.929(2)
Co–N(3)	2.037(7)	1.864(4)
Co–N(4)	2.015(7)	1.870(4)
O(1)–N(1)	1.312(10)	1.352(5)
O(2)–N(6)	1.319(11)	1.348(5)
N(1)–N(2)	1.275(12)	1.267(6)
N(2)–N(3)	1.317(10)	1.315(6)
N(4)–N(5)	1.327(10)	1.320(4)
N(5)–N(6)	1.280(11)	1.271(5)
	Angles	
O(1)–Co–O(2)	103.0(3)	90.9(1)
O(1)–Co–N(3)	74.4(3)	80.9(2)
O(1)–Co–N(4)	100.5(3)	93.9(2)
O(1)–Co–S(1)	151.0(2)	167.8(1)
O(1)–Co–S(2)	86.0(2)	85.2(1)
O(2)–Co–N(3)	95.5(3)	91.5(1)
O(2)–Co–N(4)	75.2(3)	81.1(1)
O(2)–Co–S(1)	90.2(2)	87.3(1)
O(2)–Co–S(2)	154.1(2)	166.3(1)
N(3)–Co–N(4)	168.4(3)	171.0(1)
N(3)–Co–S(1)	78.8(2)	87.1(1)
N(3)–Co–S(2)	110.3(2)	100.8(1)
N(4)–Co–S(1)	107.8(2)	97.7(1)
N(4)–Co–S(2)	79.3(2)	86.0(1)
S(1)–Co–S(2)	93.1(1)	99.2(1)

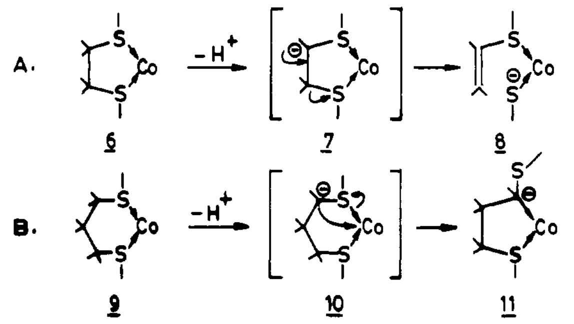
Table 3. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Co(Me1)(Me1′)

	Distances		
Co–S(1)	2.226(2)	O(1)–N(1)	1.341(9)
Co–S(2)	2.228(2)	O(2)–N(6)	1.339(10)
Co–O(1)	1.940(5)	N(1)–N(2)	1.280(10)
Co–O(2)	1.969(6)	N(2)–N(3)	1.309(8)
Co–N(3)	1.864(6)	N(4)–N(5)	1.316(9)
Co–N(4)	1.875(6)	N(5)–N(6)	1.286(11)
		C(8)–C(9)	1.294(13)
	Angles		
O(1)–Co–O(2)	89.9(2)	O(2)–Co–S(2)	167.8(2)
O(1)–Co–N(3)	80.4(2)	N(3)–Co–N(4)	175.6(3)
O(1)–Co–N(4)	96.0(2)	N(3)–Co–S(1)	87.2(2)
O(1)–Co–S(1)	167.5(2)	N(3)–Co–S(2)	95.3(2)
O(1)–Co–S(2)	91.7(2)	N(4)–Co–S(1)	96.4(2)
O(2)–Co–N(3)	96.8(3)	N(4)–Co–S(2)	87.4(2)
O(2)–Co–N(4)	80.5(3)	S(1)–Co–S(2)	87.3(1)
O(2)–Co–S(1)	93.7(2)		

Table 4. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Co(Me3L′)·$CHCl_3$

	Distances		
Co···S(1)	3.105(2)	O(1)–N(1)	1.319(5)
Co–S(2)	2.203(2)	O(2)–N(6)	1.339(6)
Co–O(1)	2.019(4)	N(1)–N(2)	1.279(7)
Co–O(2)	1.935(3)	N(2)–N(3)	1.326(5)
Co–N(3)	1.941(4)	N(4)–N(5)	1.324(6)
Co–N(4)	1.857(4)	N(5)–N(6)	1.281(6)
Co–C(8)	1.969(5)		
	Angles		
O(1)–Co–O(2)	89.5(1)	O(2)–Co–C(8)	89.2(2)
O(1)–Co–N(3)	79.8(2)	N(3)–Co–N(4)	171.0(2)
O(1)–Co–N(4)	91.4(2)	N(3)–Co–S(2)	93.9(1)
O(1)–Co–S(2)	92.1(1)	N(3)–Co–C(8)	98.8(2)
O(1)–Co–C(8)	177.8(2)	N(4)–Co–S(2)	87.8(1)
O(2)–Co–N(3)	97.4(2)	N(4)–Co–C(8)	90.1(2)
O(2)–Co–N(4)	80.9(2)	S(2)–Co–C(8)	89.6(2)
O(2)–Co–S(2)	168.6(1)		

Scheme 2



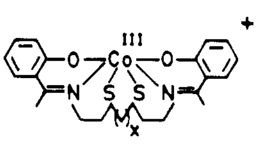
in Scheme 2. where only the reactive zone, viz., the chelated $-S(CH_2)_xS-$ fragment, is shown. The base-induced deprotonation of an α-methylene group implicated in the processes **6** → **7** and **9** → **10** has been documented in related species.[13,17] The affinity of the metal cation for the carbanionic site created by deprotonation is believed to drive the transformation of the six-membered ring **10** to the five-membered metallacycle **11**. In this process a Co–S bond is cleaved and a Co–C bond is formed (Scheme 2B). In the case of the five-membered ring in **7**, such a process would force a four-membered metallacycle. This unfavorable situation is bypassed via an effective migration of the anionic charge to a coordinated sulfur site leading to **8**. Here a C–S bond is heterolytically cleaved and the order of a C–C bond increases from 1 to 2 (Scheme 2A).

We have also examined the effect of alkali on the cobalt(III) complexes of types **12** and **13**, and the details will be reported elsewhere. For the present we only note that also in these cases the $CoS_2(CH_2)_x$ chelate rings display base-induced reactivity and the products are x-dependent as in the case of Co(MexL)$^+$. Some instances of coordinated thioether reactivity reported in literature also fit into this pattern. First, several d^6-metal (including cobalt(III)) complexes of 1,4,7-trithiacyclononane are documented[13,14] to undergo C–S bond cleavage: **14** → **15**. This can be compared with the process Co(Me2L)$^+$ → Co(Me1)(Me1′) (**6** → **8** in

Table 5. Crystallographic Data for Co(Me3L), [Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$, Co(Me1)(Me1') and Co(Me3L')·$CHCl_3$

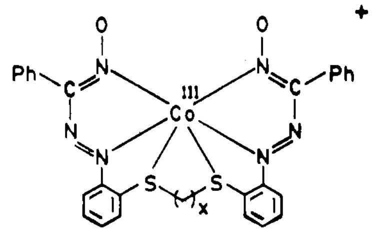
	Co(Me3L)	[Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$	Co(Me1)(Me1')	Co(Me3L')·$CHCl_3$
chem formula	$C_{17}H_{20}N_6O_2S_2Co$	$C_{18}H_{22}N_6O_6S_2Cl_3Co$	$C_{16}H_{17}N_6O_2S_2Co$	$C_{18}H_{20}N_6O_2S_2Cl_3Co$
fw	463.4	647.6	448.4	583.8
space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	7.871(2)	9.849(5)	9.445(5)	12.818(7)
b, Å	9.777(4)	11.666(6)	18.650(8)	14.597(8)
c, Å	25.942(10)	13.354(7)	11.284(6)	13.194(6)
α, deg	90.00	102.33(4)	90.00	90.00
β, deg	90.00	103.24(4)	100.90(4)	97.67(4)
γ, deg	90.00	108.47(4)	90.00	90.00
V, $Å^3$	1996(1)	1346(1)	1952(1)	2447(2)
Z	4	2	4	4
T, °C	23	23	23	23
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.542	1.535	1.526	1.585
μ, cm^{-1}	10.95	10.36	11.17	12.28
transm coeff	0.2298–0.4402	0.6958–0.7747	0.6082–0.6472	0.6952–0.7341
R,[a] %	5.02	4.54	4.74	4.03
R_w,[b] %	5.19	4.38	4.72	4.07
GOF[c]	0.84	0.99	0.75	0.70

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; g = 0.0001 for Co(Me3L), 0.00005 for [Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$ and Co(Me1)(Me1'), and 0.0002 for Co(Me3L')·$CHCl_3$. [c] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.



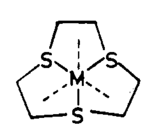
x = 2,3

12

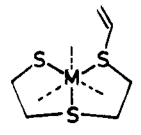


x = 2,3

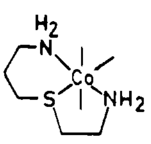
13



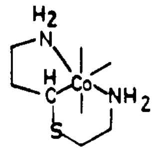
14



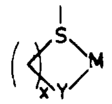
15



16



17



18

Scheme 2A). Second, the base-induced transformation **16** → **17** occurs in certain cobalt(III) complexes of 1,6-diamino-3-thiahexane.[15-17] This is analogous to the process Co(Me3L)$^+$ → Co(Me3L') (**9** → **11** in Scheme 2B).

Thus there is a general correlation between the size of the base-activated chelate ring and the type of transformation it undergoes. *When the ring is five-membered, the transformation corresponds to cobalt(III)–thiolate formation via C–S bond cleavage and when it is six-membered, the transformed complex is an organocobalt(III) species.* Examples of the former are Co(Me2L)$^+$, **12** (x = 2), **13** (x = 2), and **14** and those of the latter are Co(Me3L)$^+$, **12** (x = 3), **13** (x = 3), and **16**. We can now comment on the role of site Y in the reactive chelate ring generalized as **18**. In the x = 3 type transformation the carbanionic center (formed by α-methylene deprotonation) gets bound to the metal and the nature of Y is not critical. Thus it is amine N in **16** but thioether S in the other examples. In the x = 2 type of transformation, the Y–C bond is cleaved which therefore should not be particularly strong. Further Y^- should be able to act as a stable anionic coordination site. Species where Y is an N-function are thus expected to be unreactive. Examples are the five-membered N,S-coordinating chelate rings in **12** (x = 2, 3) and **16**.

Concluding Remarks

The main findings of this work will now be stated. The dithiaalkyl substituted triazene 1-oxide ligands of type H_2Me*x*L (x = 2, 3) (**1**) have afforded high-spin cobalt(II) (z = 0) and low-spin cobalt(III) (z = +) complexes of type Co(Me*x*L)^z (**2**, **3**) which have distorted octahedral $CoS_2N_2O_2$ coordination spheres. One thioether function in each Co(Me*x*L)$^+$ complex is subject to base-induced activation via α-methylene deprotonation. The otherwise very similar homologous complexes Co(Me2L)$^+$ and Co(Me3L)$^+$ are strongly differentiated in terms of the products furnished. For x = 2, the coordinated ligand is cleaved into two parts via scission of a C–S bond affording Co^{III}(Me1)(Me1') (**4**), which has Co(SNO)(SNO) type coordination sphere involving both thioether and thiolate coordination. For x = 3, the organocobalt(III) complex Co^{III}(Me3L') (**5**) with $CoSCN_2O_2$ coordination sphere is formed.

Collective scrutiny of these and some other available results on d^6-ion-promoted thioether activation via base attack has revealed a general rationale for the observed selectivity of transformations. Cleavage occurs when the activated chelate ring is five-membered, and organocobalt(III) is formed when it is six-membered. In the latter case the carbanionic center formed by deprotonation simply displaces a thioether site from the coordination sphere, forming a five-membered metallacycle. In the former case the possible formation of a four-membered metallacycle is bypassed via migration of anionic charge to a sulfur site with concomitant ligand cleavage. Studies directed toward augmenting the scope of the ideas developed in the present work are in progress.

Experimental Section

Materials. The purification of acetonitrile and dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as before.[26] All other chemicals and solvents were of analytical grade and used as received.

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(26) Chandra, S. K.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 760–765.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Co(Me3L)[a]

atom	*x*	*y*	*z*	*U*(eq)
Co	2659(1)	262(1)	1187(1)	44(1)
S(1)	1564(3)	2548(3)	1497(1)	52(1)
S(2)	−255(3)	−507(3)	880(1)	59(1)
O(1)	3633(11)	−997(6)	606(3)	67(3)
O(2)	4654(8)	369(8)	1714(3)	66(2)
N(1)	4416(10)	−278(9)	251(3)	54(2)
N(2)	4513(11)	1023(8)	260(3)	52(3)
N(3)	3729(9)	1551(7)	662(3)	44(2)
N(4)	2088(9)	−1143(7)	1728(3)	46(2)
N(5)	3202(10)	−1377(8)	2102(3)	54(2)
N(6)	4477(9)	−567(9)	2076(3)	57(3)
C(1)	5247(19)	−1019(12)	−157(5)	88(5)
C(2)	3900(11)	2967(8)	717(3)	45(3)
C(3)	4970(13)	3800(10)	416(4)	57(3)
C(4)	5041(16)	5185(11)	513(4)	72(4)
C(5)	4087(17)	5789(10)	897(5)	74(4)
C(6)	3049(12)	5001(8)	1195(4)	61(3)
C(7)	2936(12)	3568(7)	1109(3)	50(3)
C(8)	−479(13)	2875(10)	1177(5)	75(4)
C(9)	−1791(14)	1811(14)	1340(5)	82(4)
C(10)	−1987(13)	670(12)	945(4)	74(4)
C(11)	−612(12)	−1728(9)	1376(3)	48(3)
C(12)	−2046(14)	−2539(11)	1368(4)	71(3)
C(13)	−2312(19)	−3546(11)	1734(4)	88(4)
C(14)	−1117(18)	−3744(11)	2105(4)	80(4)
C(15)	323(14)	−2952(10)	2129(3)	62(3)
C(16)	616(12)	−1963(9)	1750(3)	47(3)
C(17)	5787(14)	−657(15)	2460(4)	81(4)

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

Physical Measurements. Spectra were recorded on the following equipments: UV–vis, Hitachi 330 spectrophotometer; IR spectra, Perkin-Elmer 783 IR spectrophotometer; NMR spectra, Varian XL 200-MHz FT NMR spectrometer. Magnetic susceptibilities of solids were measured with a Model 155 PAR vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (CHN). Electrochemical measurements were performed under nitrogen atmosphere on a PAR 370-4 electrochemistry system as reported earlier.[26] All potentials reported in this work are uncorrected for junction contribution. Solution (~10^{-3} M) electrical conductivities were measured with the help of a Philips PR 9500 bridge.

Preparation of Compounds. Ligands. These were synthesized by coupling diazolized solutions of 1,2-bis((2-aminophenyl)thio)ethane and 1,3-bis((2-aminophenyl)thio)propane with *N*-methylhydroxylamine.[5b,12,27,28]

[1,3-Bis[(*o*-(3′-oxo-3′-methyltriazeno)phenyl)thio]propane]cobalt(II), Co(Me3L). To a dichloromethane solution (15 mL) of H$_2$Me3L (0.2 g, 0.49 mmol) was added a methanolic solution (5 mL) of KOH (0.055 g, 0.98 mmol), and the mixture was stirred at room temperature for 0.5 h. A methanolic solution (10 mL) of Co(CH$_3$COO)$_2$·4H$_2$O (0.122 g, 0.49 mmol) was then added. Stirring was continued for a further period of 0.5 h. The deposited red crystalline solid was filtered off, washed with methanol and water, and finally dried in vacuo over P$_4$O$_{10}$. Yield: 0.203 g (89%). Anal. Calcd for C$_{17}$H$_{20}$N$_6$O$_2$S$_2$Co: C, 44.06; H, 4.32; N, 18.14. Found: C, 44.08; H, 4.35; N, 18.11.

The complex Co(Me2L) was similarly prepared starting from H$_2$-Me2L. Anal. Calcd for C$_{16}$H$_{18}$N$_6$O$_2$S$_2$Co: C, 42.77; H, 4.01; N, 18.71. Found: C, 42.69; H, 4.03; N, 18.75.

Table 7. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Co(Me3L)ClO$_4$·CH$_2$Cl$_2$[a]

atom	*x*	*y*	*z*	*U*(eq)
Co	751(1)	3386(1)	2984(1)	35(1)
Cl(1)	−7199(1)	−1858(1)	989(1)	56(1)
Cl(2)	−3262(2)	−2997(1)	−7669(2)	90(2)
Cl(3)	−3842(2)	−2437(2)	−5713(1)	88(2)
S(1)	1961(1)	2067(1)	3029(1)	45(1)
S(2)	−1629(1)	1950(1)	2141(1)	39(1)
O(1)	−82(3)	4621(3)	2730(2)	43(1)
O(2)	2604(3)	4713(3)	3986(2)	46(1)
O(3)	−7266(6)	−3100(4)	611(5)	111(3)
O(4)	−7006(5)	−1491(5)	2111(3)	90(2)
O(5)	−8576(4)	−1787(5)	423(4)	93(2)
O(6)	−5956(4)	−986(4)	802(3)	76(2)
N(1)	177(4)	4892(3)	1839(3)	45(1)
N(2)	955(4)	4448(3)	1357(3)	44(1)
N(3)	1361(4)	3655(3)	1803(3)	40(1)
N(4)	298(3)	3390(3)	4270(2)	38(1)
N(5)	1337(4)	4209(3)	5176(2)	42(1)
N(6)	2508(4)	4855(3)	4993(3)	43(1)
C(1)	−530(7)	5692(5)	1434(4)	65(2)
C(2)	2412(4)	3210(4)	1493(3)	43(2)
C(3)	3117(5)	3559(5)	744(4)	59(2)
C(4)	4132(6)	3025(7)	518(4)	73(3)
C(5)	4445(5)	2167(6)	1004(4)	69(3)
C(6)	3770(5)	1828(5)	1747(4)	57(2)
C(7)	2768(4)	2368(4)	1998(3)	43(2)
C(8)	677(6)	401(5)	2395(4)	61(2)
C(9)	−503(6)	123(5)	1329(4)	61(2)
C(10)	−1900(5)	337(4)	1412(4)	55(2)
C(11)	−2092(4)	1755(4)	3328(3)	38(2)
C(12)	−3472(5)	887(4)	3278(4)	52(2)
C(13)	−3814(6)	859(5)	4218(4)	65(2)
C(14)	−2793(6)	1704(5)	5206(4)	65(2)
C(15)	−1418(5)	2564(4)	5272(3)	51(2)
C(16)	−1050(4)	2592(4)	4327(3)	39(2)
C(17)	3830(5)	5799(5)	5877(4)	60(2)
C(18)	−4405(8)	2788(7)	7082(8)	130(11)

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

[1,3-Bis-[(*o*-(3′-oxo-3′-methyltriazeno)phenyl)thio]propane]cobalt(III) Perchlorate, Dichloromethane Adduct, [Co(Me3L)]ClO$_4$·CH$_2$Cl$_2$. The cobalt(II) complex Co(Me3L) (0.2 g, 0.43 mmol) was dissolved in 25 mL of a mixture of dichloromethane and methanol (3:2). Hydrogen peroxide solution (30%) was then added dropwise to the stirred ice-cold solution till the color changed to deep purple. Sodium perchlorate (0.063 g, 0.43 mmol) was then added and the mixture was stirred for 2 h. The solution was then evaporated and the precipitate formed was washed with water and then dried in vacuo over P$_4$O$_{10}$. The residue was crystallized from dichloromethane. Yield: 0.204 g (83%). Anal. Calcd for C$_{18}$H$_{22}$N$_6$O$_6$S$_2$Cl$_3$Co: C, 33.28; H, 3.39; N, 12.94. Found: C, 33.19; H, 3.32; N, 13.01.

The complex [Co(Me2L)]ClO$_4$·CH$_2$Cl$_2$ was similarly prepared starting from Co(Me2L). Anal. Calcd for C$_{17}$H$_{20}$N$_6$O$_6$S$_2$Cl$_3$Co: C, 32.13; H, 3.15; N, 13.23. Found: C, 32.19; H, 3.07; N, 13.31. Both the complexes behave as 1:1 electrolytes in acetonitrile solution with Λ = 130–135 Ω^{-1} cm^2 M^{-1}.

[((*o*-(3-Oxo-3-methyltriazeno)phenyl)thio)ethylene][*o*-(3′-oxo-3′-methyltriazeno)benzenethiolato]cobalt(III), Co(MeL)(MeL′). (a) The complex [Co(Me2L)]ClO$_4$·CH$_2$Cl$_2$ (0.4 g, 0.73 mmol) was dissolved in acetonitrile (20 mL), and a methanolic solution (100 mL) of KOH (1 M) was added. The reaction mixture was stirred at room temperature for 2 h, and the color became greenish. It was then completely evaporated, and the residue was washed with water and dried in vacuo over P$_4$O$_{10}$. The solid was then extracted with dichloromethane and chromatographed on silica gel with a (1:25, v/v) benzene–acetonitrile mixture as eluent. The green band was collected and upon evaporation afforded the complex, which was dried in vacuo. Yield: 0.17 g (60%). Anal. Calcd for C$_{16}$H$_{17}$N$_6$O$_2$S$_2$Co: C, 42.86; H, 3.79; N, 18.75. Found: C, 42.90; H, 3.81; N, 18.71.

(b) The complex Co(Me2L) (0.2 g, 0.44 mmol) was dissolved in dichloromethane (20 mL), and a methanolic solution (100 mL) of KOH (1 M) was added. The reaction mixture was stirred at room temperature for 2 h under oxygen when the color became brownish green. The residue left upon evaporation was washed with water and dried in vacuo over P$_4$O$_{10}$. It was then purified by chromatography as in method a. Yield: 0.11 g (58%). Anal. Found: C, 42.79; H, 3.92; N, 18.63.

[1,3-Bis[*o*-3′-oxo-3′-methyltriazeno)phenyl)thio]propyl]cobalt(III), Chloroform Adduct, Co(Me3L′)·CHCl$_3$. (a) To a solution of [Co(Me3L)]-ClO$_4$·CH$_2$Cl$_2$ (0.2 g, 0.35 mmol) in acetonitrile (20 mL) was added a methanolic solution (100 mL) of KOH (1 M), and the reaction mixture was stirred at room temperature for 2 h. The greenish solution was then evaporated, and the residue was washed with water and dried in vacuo over P$_4$O$_{10}$. The solid was then extracted with dichloromethane and chromatographed on silica gel with a (1:24, v/v) benzene–acetonitrile

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(27) Unger, O. *Chem. Ber.* **1897**, *30*, 607.

(28) Mukkanti, K.; Bhoon, Y. K.; Pandeya, K. B.; Singh, R. P. *J. Indian Chem. Soc.* **1982**, *59*, 830–832.

Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Co(Me1)(Me1′)[a]

atom	*x*	*y*	*z*	*U*(eq)
Co	7614(1)	1624(1)	8911(1)	48(1)
S(1)	9283(2)	943(1)	10038(2)	51(1)
S(2)	7262(2)	725(1)	7589(2)	52(1)
O(1)	5873(5)	2105(3)	8110(5)	57(2)
O(2)	8201(6)	2496(3)	9860(5)	61(2)
N(1)	4776(6)	1869(4)	8604(7)	59(3)
N(2)	4958(6)	1446(4)	9513(6)	57(2)
N(3)	6326(6)	1286(3)	9845(6)	53(2)
N(4)	8835(6)	2032(3)	7965(5)	51(2)
N(5)	9496(6)	2635(4)	8340(7)	64(3)
N(6)	9141(8)	2852(3)	9326(7)	66(3)
C(1)	3362(7)	2152(5)	8068(8)	74(3)
C(2)	6703(7)	773(4)	10767(6)	51(3)
C(3)	5784(8)	472(5)	11453(7)	66(3)
C(4)	6327(9)	−15(5)	12333(8)	74(4)
C(5)	7753(9)	−234(5)	12527(7)	69(3)
C(6)	8664(8)	62(4)	11848(7)	56(3)
C(7)	8153(7)	567(4)	10971(6)	49(3)
C(8)	10460(9)	1494(5)	11071(8)	73(3)
C(9)	11814(10)	1483(7)	11007(11)	122(6)
C(10)	8388(7)	1058(4)	6632(7)	50(3)
C(11)	8560(8)	702(5)	5586(7)	61(3)
C(12)	9470(9)	981(5)	4868(8)	69(3)
C(13)	10188(9)	1606(6)	5156(8)	67(3)
C(14)	10018(7)	1983(4)	6177(7)	56(3)
C(15)	9106(7)	1712(4)	6912(6)	47(2)
C(16)	9757(13)	3502(6)	9879(10)	109(5)

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

mixture as eluent. The greenish band was collected and evaporated, affording the green complex which was dried in vacuo and recrystallized from chloroform. Yield: 0.11 g (59%). Anal. Calcd for $C_{18}H_{20}N_6O_2S_2Cl_3Co$: C, 37.05; H, 3.44; N, 14.41. Found: C, 37.16; H, 3.39; N, 14.45.

(b) To a dichloromethane solution (25 mL) of Co(Me3L) (0.3 g, 0.64 mmol) was added a methanolic solution (100 mL) of KOH (1 M), and the reaction mixture was stirred at room temperature for 2.5 h under oxygen. The brownish green solution was evaporated; the residue was washed with water and dried in vacuo over P_4O_{10}. It was finally purified chromatographically as in method a. Yield: 0.22 g (58%). Anal. Found: C, 37.31; H, 3.07; N, 14.28.

X-ray Structure Determination. Unless otherwise indicated the same description applies to all the four complexes. Cell parameters of Co(Me3L) (crystal size, 0.20 × 0.24 × 0.64 mm^3), [Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$ (0.36 × 0.39 × 0.60 mm^3), and Co(Me1)(Me1′) (0.14 × 0.15 × 0.58 mm^3) grown (298 K) by slow diffusion of hexane into dichloromethane solutions and of Co(Me3L′)·$CHCl_3$ (0.22 × 0.38 × 0.44 mm^3) grown (298 K) by slow diffusion of hexane into chloroform solution were determined by least-squares fit of 25 machine-centered reflections (2θ, 18–30°). Systematic absences led to the following space group identifications: $P2_12_12_1$ for Co(Me3L); $P2_1/n$ for Co(Me1)(Me1′) and Co(Me3L′)·$CHCl_3$. In the case of triclinic [Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$ the structure was successfully solved in space group $P\bar{1}$. Data were collected by the ω-scan method (2θ, 3–52°) on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Two check reflections measured after every 98 reflections showed no significant intensity reduction during the ~24 h (Co(Me3L)), ~49 h ([Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$), ~35 h (Co(Me1)(Me1′)), and ~42 h (Co(Me3L′)·$CHCl_3$) of exposure to X-rays. Data were corrected for Lorentz–polarization effects, and an empirical absorption correction was done on the basis of azimuthal scan of six reflections.[29] Of the 2712 (Co(Me3L)), 5654 ([Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$), 3853 (Co(Me1)(Me1′)) and 4750 (Co(Me3L′)·$CHCl_3$) reflections collected, 2649, 5326, 3454, and 4344 were respectively unique of which 1585, 3560, 1644, and 2438 satisfying $I > 3\sigma(I)$ were respectively used for structure solutions.

Table 9. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Co(Me3L′)·$CHCl_3$[a]

atom	*x*	*y*	*z*	*U*(eq)
Co	2363(1)	595(1)	1975(1)	42(1)
Cl(1)	4575(3)	1100(6)	−1020(4)	162(2)
Cl(2)	4022(3)	2827(2)	−317(1)	154(2)
Cl(3)	2538(3)	1693(2)	−1726(2)	129(1)
S(1)	828(1)	753(1)	3600(1)	68(1)
S(2)	2946(1)	−826(1)	2058(1)	50(1)
O(1)	3711(3)	1065(2)	1527(3)	56(1)
O(2)	1712(3)	1772(2)	1639(3)	56(1)
N(1)	4338(3)	1321(3)	2353(4)	51(1)
N(2)	4091(3)	1266(3)	3259(3)	50(1)
N(3)	3132(3)	936(2)	3289(3)	43(1)
N(4)	1795(3)	363(3)	631(3)	50(1)
N(5)	1182(3)	993(3)	136(4)	56(2)
N(6)	1166(3)	1704(3)	703(4)	56(2)
C(1)	5352(4)	1697(4)	2200(5)	72(2)
C(2)	2968(4)	676(3)	4279(4)	47(2)
C(3)	3798(4)	559(4)	5072(4)	56(2)
C(4)	3618(6)	287(4)	6031(5)	78(3)
C(5)	2613(8)	110(5)	6221(6)	91(3)
C(6)	1783(6)	216(4)	5461(6)	77(3)
C(7)	1943(4)	499(3)	4489(4)	58(2)
C(8)	1047(4)	178(3)	2445(4)	52(2)
C(9)	924(4)	−862(3)	2438(5)	62(2)
C(10)	1965(5)	−1328(4)	2761(5)	65(2)
C(11)	2470(4)	−1139(3)	774(4)	50(2)
C(12)	2671(4)	−2001(3)	381(5)	60(2)
C(13)	2328(5)	−2184(4)	−635(5)	69(2)
C(14)	1808(5)	−1523(4)	−1258(5)	70(2)
C(15)	1603(4)	−670(4)	−879(4)	59(2)
C(16)	1927(3)	−468(3)	147(4)	49(2)
C(17)	556(5)	2505(4)	333(6)	75(2)
C(18)	3568(6)	1725(5)	−711(6)	85(3)

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

The structures were solved by direct methods. All non-hydrogen atoms were made anisotropic, and hydrogen atoms were added at calculated position with fixed *U* = 0.08 Å^2 in the last cycle of refinement. All refinements were performed by full matrix least-squares procedures. The highest residuals were 0.50 e/Å^3 (Co(Me3L)), 0.52 e/Å^3 ([Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$), 0.34 e/Å^3 (Co(Me1)(Me1′), and 0.39 e/Å^3 (Co(Me3L′)·$CHCl_3$). All calculations were done on a MicroVAX II Computer with the programs of SHELXTL-PLUS.[30] Significant crystal data are listed in Table 5. Atomic coordinates and isotropic thermal parameters are collected in Tables 6–9.

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Supplementary Material Available: For Co(Me3L), [Co(Me3L)]$ClO_4 \cdot CH_2Cl_2$, Co(Me1)(Me1′), and Co(Me3L′)·$CHCl_3$ tables of complete bond distances (Tables S1, S5, S9 and S13) and angles (Tables S2, S6, S10, and S14), anisotropic thermal parameters (Tables S3, S7, S11, and S15), and hydrogen atom positional parameters (Tables S4, S8, S12, and S16) (16 pages). Ordering information is given on any current masthead page.

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