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Reactions of $Cp^*_3Co_3(\mu_2\text{-H})_3(\mu_3\text{-H})$ with Carbon Dioxide, Carbon Disulfide, and Phenyl Isocyanate

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The tetrahydride tricobalt cluster $Cp^*_3Co_3(\mu_2\text{-H})_3(\mu_3\text{-H})$ (**1**) reduces CO_2 at 120 °C to form the dicobalt dicarbonyl complex $[Cp^*Co(\mu\text{-CO})]_2$ (**2**) in 45% yield by ^1H NMR. **1** reacted with CS_2 at room temperature to form the thiocarbonyl cluster $Cp^*_3Co_3(\mu_3\text{-CS})(\mu_3\text{-S})$ (**3**) in 19% isolated yield. **3** was characterized by X-ray crystallography and shown to consist of a triangle of cobalt atoms $[Co{-}Co_{(ave)} = 2.495$ Å] capped on one face by a μ_3-sulfide ligand $[Co{-}\mu_3\text{-}S_{(ave)} = 2.129$ Å] and on the opposite face by a μ_3-thiocarbonyl ligand $[Co{-}\mu_3\text{-}C_{(ave)} = 1.949$, $\mu_3\text{-}C{-}S = 1.634(5)$ Å]. **1** reacted with phenyl isocyanate at 55 °C to form the *N,N'*-diphenylureylene complex $Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-PhNCONPh})$ (**5**), the dicarbonyl tricobalt cluster $Cp^*_3Co_3(\mu_3\text{-CO})_2$ (**6**), and the carbonyl dimer **2**. **5** was isolated in 13% yield and characterized by X-ray crystallography, which revealed that each nitrogen atom of the η^2-N,N'-diphenylureylene ligand was symmetrically bonded to both cobalt atoms $[Co{-}Co = 2.456(1)$, $Co{-}\mu_2\text{-}N_{(ave)} = 1.959$ Å].

Introduction

We have been exploring the reactions of the unusual trinuclear tetrahydride cluster $Cp^*_3Co_3(\mu_2\text{-H})_3(\mu_3\text{-H})$ (**1**)[1] with small unsaturated molecules in an effort to form new tricobalt derivatives. For example, we have shown that **1** reacts rapidly with NO at room temperature to form the bicapped nitrosyl cluster $Cp^*_3Co_3(\mu_3\text{-NO})_2$.[2] **1** reacted rapidly with CO at room temperature to form the dicarbonyl dihydride cluster $Cp^*_3Co_3(\mu_3\text{-CO})(\mu_2\text{-CO})(\mu\text{-H})_2$ (Scheme 1).[3] Cluster **1** reacted with *tert*-butyl isocyanide at low temperature to form the bis(isocyanide) cluster $Cp^*_3Co_3(\mu_3\text{-CNCMe}_3)(\mu_2\text{-CNCMe}_3)(\mu\text{-H})_2$, which undergoes rapid isocyanide insertion into a Co−H bond to produce the formimidoyl cluster $Cp^*_3Co_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC{=}NCMe}_3)$.[3]

We have also shown that **1** reacts with acetylene to form the mono(ethylidyne) clusters $Cp^*_3Co_3(\mu_3\text{-CCH}_3)(\mu_2\text{-H})_3$ and $Cp^*_3Co_3(\mu_3\text{-CCH}_3)(\mu_3\text{-H})$; these mono(ethylidyne) clusters react further with acetylene to ultimately yield the bis(ethylidyne) cluster $Cp^*_3Co_3(\mu_3\text{-CCH}_3)_2$ (Scheme 2).[4] The mono(ethylidyne) clusters interconvert quantitatively via reversible H_2 addition.

Carbon dioxide can be reduced by H_2 over heterogeneous catalysts. Depending on reaction conditions and catalyst, methane, methanol, or CO can be obtained.[5] In addition, homogeneous transition metal complexes and clusters have been studied as potential catalysts for the water-gas shift reaction[6] and for the hydrogenation of CO_2 to formic acid.[7] The stoichiometric reaction of CO_2 with metal hydrides to produce metal formate complexes has been reported.[8] The reaction of CO_2 and other heterocumulenes with metal hydride clusters is therefore of interest as an analog of catalytic CO_2 reduction. Because tetrahydride cluster **1** displayed interesting reduction chemistry with both acetylene and *tert*-butyl isocyanide, we investigated the reaction of **1** with CO_2 and its analogs CS_2 and PhNCO.

Results

Reaction of 1 with CO_2. A black C_6D_6 solution of the tetrahydride **1** was heated at 120 °C under 5 atm carbon dioxide and monitored periodically by ^1H NMR spectroscopy. Cluster **1** reacted slowly ($t_{1/2} = 6.2$ h) over 44 h to form a bright green

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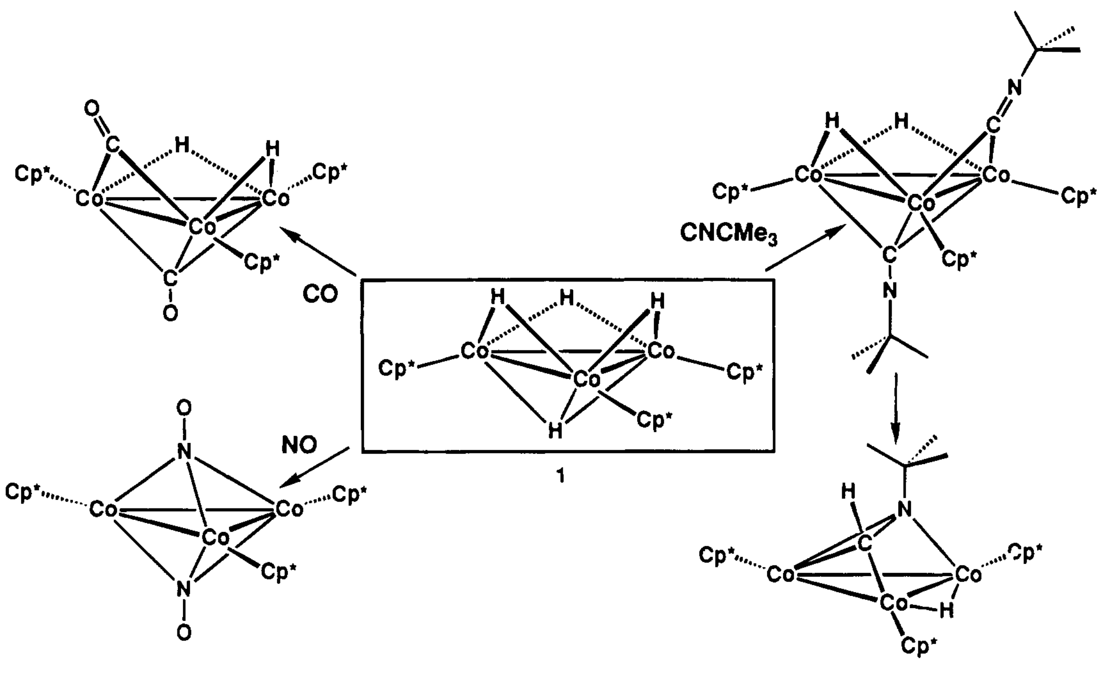
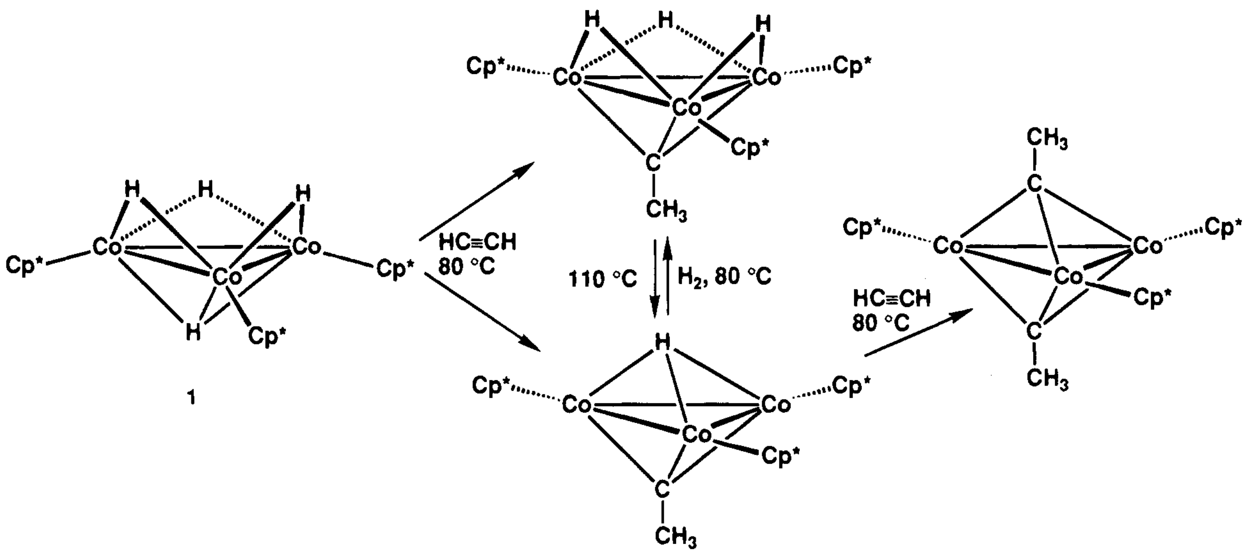
Scheme 1



Scheme 2

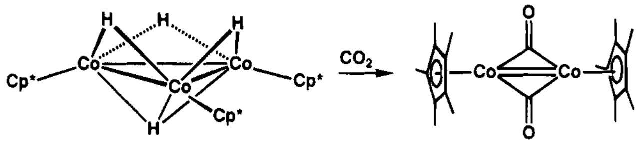


solution of the dicobalt dicarbonyl complex $[Cp^*Co(\mu\text{-}CO)]_2$ (**2**) in 45% yield by NMR (Scheme 3). **2** was identified on the basis of its ^1H NMR spectrum (δ 1.41) and IR spectrum (hexane, 1758 cm^{-1}).[9]

The formation of **2** from **1** and CO_2 is of interest because the transformation involves the reduction of CO_2 by a metal cluster compound. However, the forcing conditions required for the transformation precluded the isolation of any tricobalt intermediates. We therefore studied the reaction of **1** with the more reactive CO_2 analogs CS_2 and phenyl isocyanate in an effort to isolate new tricobalt derivatives.[10]

Reaction of 1 with CS_2. When a black benzene solution of **1** was stirred with excess CS_2 for 15 min at room temperature, the solution turned brown. ^1H NMR analysis of the crude reaction mixture indicated a mixture of three products that accounted for greater than 95% of the Cp* resonances. A Cp* resonance at δ 1.51 accounted for 15% of the total Cp* peaks and was shown to be the thiocarbonyl sulfide cluster $Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**3**) by spectroscopy and by X-ray crystallography (see below). A second Cp* resonance at δ 1.55 accounted for 20% of the Cp* peaks. When solvent was evaporated and the crude reaction mixture heated in C_6D_6 for 15 min at 80 °C, the compound with the δ 1.55 resonance was converted to **3** (δ 1.51). We have not been able to obtain further structural information on the δ 1.55 intermediate. The third compound, **4**, had three resonances that always appeared in the same ratio; two Cp* resonances at δ 1.73 and 1.72 in a 2:1 ratio accounted

Scheme 3



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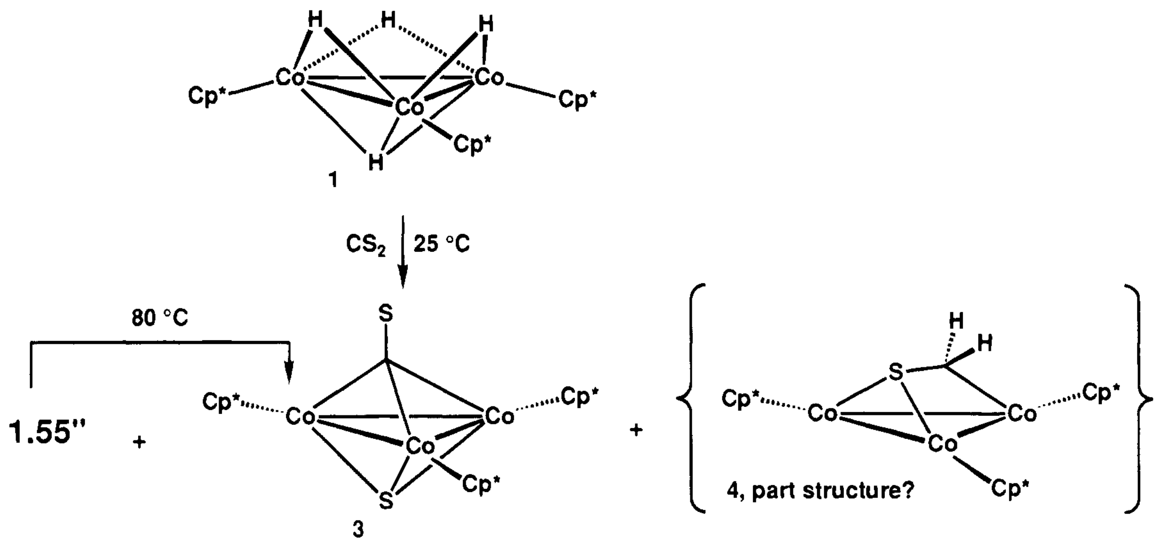
Scheme 4



for 65% of the total Cp* resonances, and a two-proton resonance at δ 2.48 was observed. No metal hydride resonance was seen. The δ 2.48 resonance is at too low a frequency for a μ-CH_2 group but is consistent with a μ-thioformaldehyde ligand.[11] Cluster **4** was exceedingly soluble in hydrocarbon solvents and decomposed rapidly upon attempted low-temperature silica gel chromatography. As a result, **4** could be purified only by careful hexane extraction of a mixture of **3** and **4** to give **4** as an oily black solid which contained ~15% **3** by ^1H NMR analysis. The molecular formula of **4** could not be determined from the mass spectrum of a mixture of **4** and **3**. We suggest a partial structure for **4** consisting of a 46-electron $Cp^*_3Co_3(\mu\text{-}CH_2S)$ unit; other unobserved ligands, possibly a μ-S or a μ-CS, might provide the additional two electrons needed for a coordinatively saturated 48-electron tricobalt cluster (Scheme 4).

Cluster **3** was obtained by heating the initial product mixture in benzene, which converted the δ 1.55 intermediate to **3**. The residue was washed with pentane and crystallized from toluene to provide pure **3**. The IR spectrum of **3** displayed two bands at 1040 and 1021 cm^{-1}, similar to the spectrum of the C_5H_4Me analog $Cp'_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$, which displayed bands at 1069 and 1059 cm^{-1}.[12]

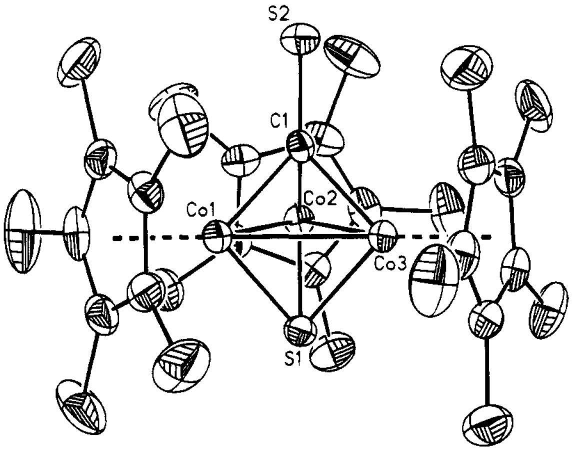


Figure 1. X-ray crystal structure for $Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**3**). Thermal ellipsoids are shown at the 35% probability level.

Table 1. Crystal Structure Data for $Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**3**) and $Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (**5**)

	3	5
empirical formula	$C_{31}H_{45}S_2Co_3$	$C_{33}H_{40}N_2OCo_2$
color; habit	black block	black wedge
crystal size, mm	0.5 × 0.3 × 0.3	0.5 × 0.3 × 0.2
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	8.5651(5)	10.964(1)
b, Å	17.9536(15)	15.5496(6)
c, Å	19.574(2)	18.112(2)
β, deg	91.368(6)	99.615(8)
V, $Å^3$	3009.2(2)	3044.6(4)
peaks to determine cell	41	40
2θ range of cell peaks, deg	10.0−25.0	10.0−25.0
Z	4	4
fw	658.6	598.5
density (calc), g cm^{-3}	1.454	1.306
abs. coeff., mm^{-1}	1.78	1.113
F(000)	1376	1256
R(*F*),[a] %	3.79	6.12
$R_w(F)$,[b] %	4.52	8.28

[a] $R(F) = |\Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$. [b] $R_w(F) = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$ where $w = (\sigma^2(F) + 0.0006F^2)^{-1}$.

X-ray Crystallography of 3. The structure of **3** was determined by X-ray crystallography (Figure 1, Tables 1 and 2) and shown to consist of an equilateral triangle of cobalt atoms capped on one face by a μ_3-sulfide ligand and on the opposite face by a μ_3-thiocarbonyl ligand. Dahl has noted that in bicapped trimetallic clusters, the M−M distances lengthen upon substitution of bulky Cp* ligands for the less sterically demanding Cp ligand.[13] In accord with this observation, the average Co−Co distance for **3** [2.495 Å] is ~0.05 Å longer than the Co−Co distances in the Cp analog $Cp_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ [2.43(1) and 2.44(1) Å for two independent molecules].[14] In addition, the M−M distances in bicapped trimetal clusters typically lengthen as the size of the capping atoms increases.[15] As a result, the Co−Co distance in cluster **3**, which possesses a single apical sulfur atom, is somewhat longer than the Co−Co distances observed for the 48-electron $(Cp^*Co)_3$ clusters Cp^*_3-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**3**)

Co(1)−Co(2)	2.491(1)	Co(1)−Co(2)−Co(3)	59.9(1)
Co(1)−Co(3)	2.492(1)	Co(1)−Co(3)−Co(2)	59.8(1)
Co(2)−Co(3)	2.503(1)	Co(2)−Co(1)−Co(3)	60.3(1)
Co(1)−S(1)	2.129(1)	Co(1)−C(1)−S(2)	131.8(3)
Co(2)−S(1)	2.128(1)	Co(2)−C(1)−S(2)	133.5(3)
Co(3)−S(1)	2.130(1)	Co(3)−C(1)−S(2)	131.6(3)
Co(1)−C(1)	1.958(5)	C(1)−Co(1)−S(1)	89.4(1)
Co(2)−C(1)	1.936(5)	C(1)−Co(2)−S(1)	90.0(1)
Co(3)−C(1)	1.949(5)	C(1)−Co(3)−S(1)	89.6(1)
C(1)−S(2)	1.634(5)	Co(1)−C(1)−Co(2)	79.6(2)
Co(1)−$Cp_{(cent)}$	1.723	Co(1)−C(1)−Co(3)	79.3(2)
Co(2)−$Cp_{(cent)}$	1.731	Co(2)−C(1)−Co(3)	80.2(2)
Co(3)−$Cp_{(cent)}$	1.732	Co(1)−S(1)−Co(2)	71.6(1)
		Co(1)−S(1)−Co(3)	71.6(1)
		Co(2)−S(1)−Co(3)	72.0(1)

$Co_3(\mu_3\text{-}CCH_3)_2$ [2.437(1) Å],[16] $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ [2.423(2) Å],[2] and $Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}CCH_3)(\mu_2\text{-}H)$ [2.425(1) Å],[17] which possess only carbon or nitrogen atoms at the apical positions.

Reaction of 1 with Phenyl Isocyanate. Tetrahydride **1** reacted with a low concentration of phenyl isocyanate [0.3 M] at 55 °C in C_6D_6 to form a 65:28:7 ratio of the *N,N'*-diphenylureylene dicobalt complex $Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (**5**), the known dicarbonyl tricobalt cluster $Cp^*_3Co_3(\mu_3\text{-}CO)_2$ (**6**),[18] and the dicobalt dicarbonyl complex **2** (Scheme 5). The ratio of the carbonyl products **6**:**2** decreased at higher concentration of PhNCO. For example, when **1** and PhNCO [2.1 M] were heated at 55 °C in C_6D_6 for 20 min, a 65:4:31 ratio of **5**:**6**:**2** was obtained.

The known cluster **6** was characterized on the basis of its unusual paramagnetic chemical shift in the ^1H NMR spectrum (δ 3.39 in C_6D_6) and from the IR spectrum (1681 cm^{-1} in hexane).

In a preparative experiment, **5** was isolated in 13% yield from reaction of **1** and phenyl isocyanate [2.5 M] in benzene at 55 °C. Recrystallization from pentane gave **5** as green blocks which readily dissolved in benzene to form yellow-brown solutions. In the ^1H NMR spectrum, a singlet at δ 1.45 and aromatic resonances at δ 7.25−8.04 established the 1:1 ratio of Cp* ligands to phenyl groups. The IR spectrum displayed a strong carbonyl stretch at 1695 cm^{-1}; ν_{CO} values for ureylene complexes range from 1608 to 1698 cm^{-1}.[19]

X-ray Crystallography of $Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (5). The structure of **5** was determined by X-ray crystallography and consists of a pair of cobalt atoms bonded to a $\mu_2,\mu_2\text{-}\eta^2$-N,N'-diphenylureylene ligand (Figure 2, Tables 1 and 3). The Cp* ligand bonded to Co(1) was highly disordered and was therefore modeled as a rigid body with partial occupancy in two orientations; the major orientation (55%) is depicted in Figure 2. Each nitrogen atom of the *N,N'*-diphenylureylene ligand is bonded symmetrically to both cobalt atoms. The Co−Co distance of 2.456(1) Å is consistent with a Co−Co single bond which is required for a closed-shell, 18-electron configuration at each metal. The centroids of the Cp* ligands lie in the Co(1)−C(1)−Co(2) plane but are displaced ~25° from the Co−Co axis away from the *N,N'*-diphenylureylene ligand [Co(1)−Co(2)−$Cp^*_{[centroid]}$ = 153.3°, Co(2)−Co(1)−$Cp^*_{[centroid]}$ = 155.3°]. The structure of the dicobalt core and bridging atoms of **5** closely resembles the core structures of the related dicobalt di-*tert*-butylureylene complex $Cp_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}Me_3CNCONCMe_3)$[20] and the diiron complexes $Fe_2(CO)_6(\mu_2,\mu_2\text{-}\eta^2\text{-}RNCONR)$ [R = Ph,[21] Me[22]].

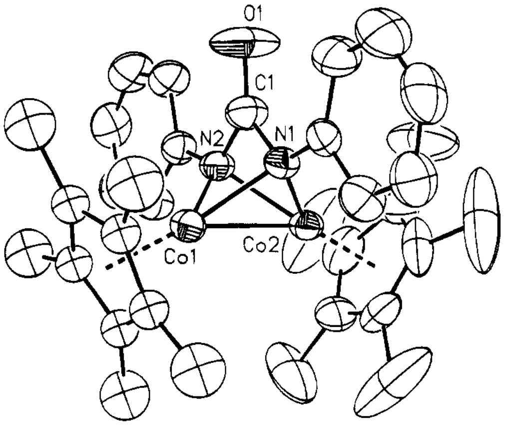

Figure 2. X-ray crystal structure for $Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (**5**). Thermal ellipsoids are shown at the 35% probability level. The minor orientation of the disordered Cp* ligand has been removed for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (**5**)

Co(1)−Co(2)	2.456(1)	Co(1)−N(1)−Co(2)	77.5(1)
Co(1)−N(1)	1.965(4)	Co(1)−N(2)−Co(2)	77.8(2)
Co(1)−N(2)	1.949(5)	Co(1)−C(1)−Co(2)	63.2(2)
Co(2)−N(1)	1.962(4)	N(1)−C(1)−N(2)	99.4(4)
Co(2)−N(2)	1.961(4)	N(1)−C(1)−O(1)	129.8(6)
C(1)−N(1)	1.413(7)	N(2)−C(1)−O(1)	130.8(6)
C(1)−N(2)	1.396(7)	C(1)−N(2)−C(8)	124.2(4)
C(1)−O(1)	1.217(8)		

Discussion

The reaction of CO_2 with tetrahydride **1** reduces CO_2 and forms the dicobalt dicarbonyl complex $[Cp^*Co(\mu\text{-}CO)]_2$ (**2**); the fate of the oxygen atom which is cleaved from CO_2 is not known. The deoxygenation of CO_2 by electron-rich mononuclear metal complexes employing a range of stoichiometric reducing agents has been previously demonstrated.[5c,23]

In the reduction of CS_2 with tetrahydride **1**, the sulfide thiocarbonyl cluster **3** serves as the sulfide acceptor. The reaction of tetrahydride **1** with CS_2 (25 °C, 15 min) is more facile than the reaction of **1** with CO_2 (120 °C, 44 h); this is consistent with both the higher reactivity of CS_2 relative to CO_2 and the often better ligating properties of the softer S atoms of CS_2 compared to the hard O atoms of CO_2.[10] The cleavage of a C═S bond of CS_2 either by a metal cluster or in the formation of a metal cluster has been previously observed. For example, the tricobalt thiocarbonyl sulfide cluster $Cp_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ is formed both in the thermolysis of the η^2-CS_2 cobalt adduct $CpCo(PMe_3)(\eta^2\text{-}CS_2)$[14] and in the thermolysis of the dicarbonyl complex $CpCo(CO)_2$ in the presence of CS_2.[12] Similarly, the thiocarbonyl cluster $Os_3(CO)_{10}(CS)(S)$ is formed in the reaction of the triosmium cluster $Os_3(CO)_{12}$ with CS_2.[24] The reaction of CS_2 with the triosmium dihydride clusters $Os_3H_2(CO)_{10}$ and

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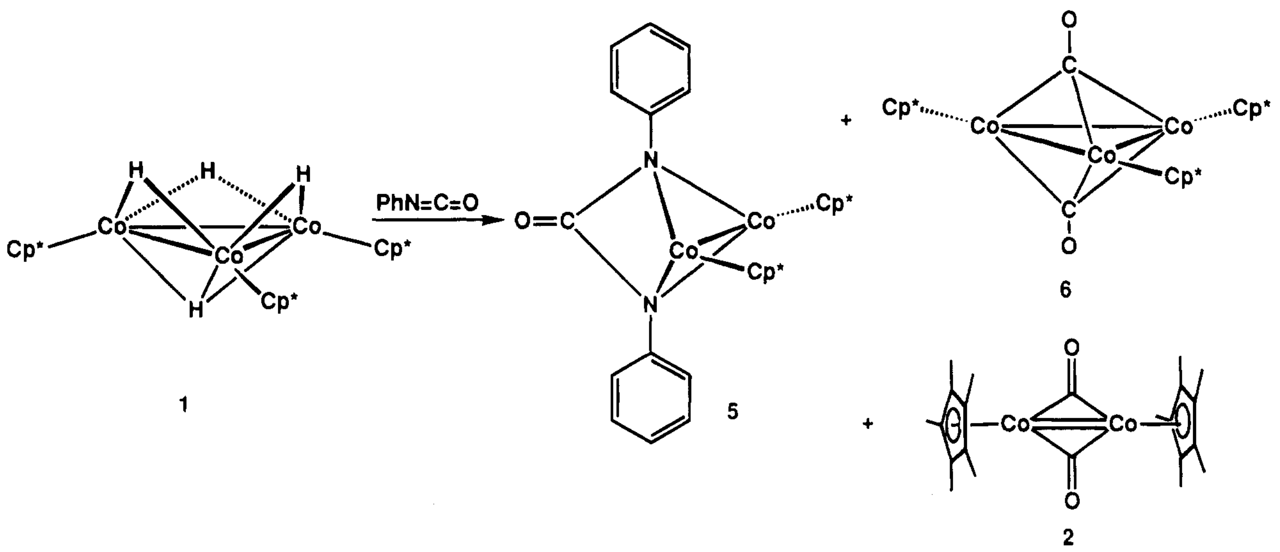
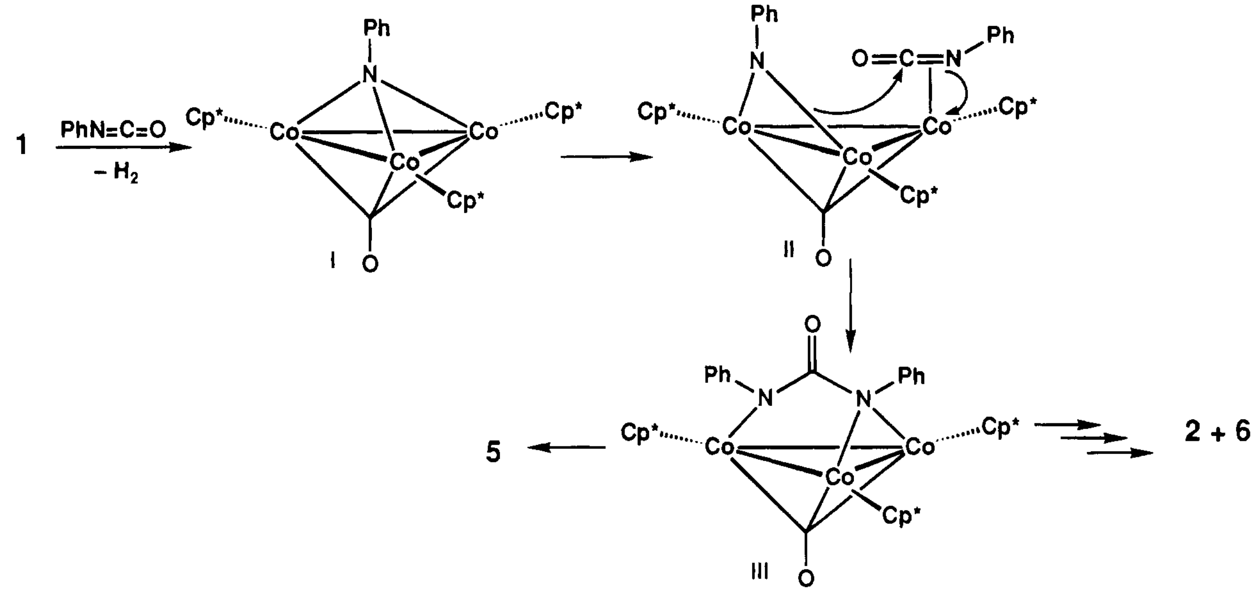
Scheme 5



Scheme 6



$Os_3H_2(CO)_9(PMe_2Ph)$ produced a range of clusters including the μ-methanedithiolate cluster $[HOs_3(CO)_{10}]_2(\mu\text{-}S_2CH_2)$, the dithioformyl cluster $Os_3(\mu\text{-}S_2CH)(\mu\text{-}H)(CO)_9(PMe_2Ph)$, and the μ-sulfide μ-thioformaldehyde cluster $Os_3(\mu_3\text{-}\eta^2\text{-}SCH_2)(\mu_3\text{-}S)(CO)_8(PMe_2Ph)$.[11]

The cleavage of a C=X [X = N, O, S] bond of isocyanates and isothiocyanates by metal clusters has also been observed. For example, the reaction of phenyl isocyanate with the triruthenium cluster $Ru_3(CO)_{12}$ formed the μ_3-nitride cluster $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$.[25] Reaction of the triosmium dihydride cluster $Os_3H_2(CO)_{10}$ with methyl or phenyl isocyanate gave the formamide clusters $Os_3(CO)_{10}(\mu\text{-}H)(\mu_2\text{-}\eta^2\text{-}RNCHO)$ [R = CH_3[26] (**7**), *p*-tolyl[27]]. Thermolysis of **7** cleaved the C−N bond and formed the μ_3-nitride dihydride cluster $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}NCH_3)$.[26] Similarly, the reaction of the bis(phosphine)cobalt complex $CpCo(PPh_3)_2$ with isothiocyanates such as PhNCS formed the μ_3-sulfide μ_3-isocyanide cluster $Cp_3Co_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)$.[28] The reaction of $Os_3H_2(CO)_{10}$ with aryl isothiocyanates such as PhNCS led initially to the formation of the $\mu_2\text{-}\eta^1$-thioformamide cluster $HOs_3(\mu_2\text{-}\eta^1\text{-}SC(H){=}NPh)(CO)_{10}$, which was photolyzed to form the $\mu_3\text{-}\eta^2$-thioformamide cluster $HOs_3(\mu_3\text{-}\eta^2\text{-}SC(H){=}NPh)(CO)_9$ (**8**). Thermolysis of **8** cleaved a C−S bond to give the sulfide formimidoyl cluster $HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}NPh)(CO)_9$.[29]

Reductive disproportionation of phenyl isocyanate upon reaction with tetrahydride **1** formed the diphenylureylene complex **5** and the carbonyl compounds **2** and **6**. The 65:35 ratio of **5**:(**2** + **6**) observed at both low and high isocyanate concentrations is consistent with the 2:1 ratio of **5**:(**2** + **6**)

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficents (Å^2 $\times$ 10^3) for $Cp^*{}_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**3**)

	x	*y*	*z*	*U*(eq)
Co(1)	1751(1)	8184(1)	3433(1)	33(1)
Co(2)	1684(1)	6800(1)	3514(1)	35(1)
Co(3)	2677(1)	7559(1)	4505(1)	34(1)
S(1)	344(2)	7552(1)	4102(1)	38(1)
C(1)	3453(5)	7469(3)	3580(2)	32(1)
S(2)	5226(2)	7438(1)	3292(1)	48(1)
C(2)	989(9)	8672(3)	2500(3)	57(2)
C(3)	140(7)	8968(3)	3055(3)	57(2)
C(4)	1230(8)	9308(3)	3507(3)	49(2)
C(5)	2726(7)	9228(3)	3236(3)	42(2)
C(6)	2576(8)	8839(3)	2608(3)	47(2)
C(7)	233(11)	8361(4)	1856(3)	124(4)
C(8)	−1603(8)	8975(5)	3109(5)	120(4)
C(9)	808(9)	9739(3)	4130(3)	93(3)
C(10)	4250(8)	9522(4)	3510(3)	83(3)
C(11)	3867(9)	8687(4)	2124(3)	97(3)
C(12)	1661(8)	5622(3)	3625(3)	53(2)
C(13)	177(8)	5874(3)	3441(3)	47(2)
C(14)	265(7)	6247(3)	2795(3)	43(2)
C(15)	1830(8)	6216(3)	2592(3)	48(2)
C(16)	2717(8)	5822(3)	3104(4)	59(3)
C(17)	2046(9)	5118(3)	4220(3)	90(3)
C(18)	−1325(8)	5754(4)	3820(3)	75(3)
C(19)	−1140(7)	6544(4)	2401(3)	69(3)
C(20)	2499(8)	6501(4)	1932(3)	77(3)
C(21)	4404(8)	5610(4)	3061(4)	90(3)
C(22)	3474(8)	8239(3)	5337(3)	51(2)
C(23)	2303(7)	7752(3)	5550(3)	47(2)
C(24)	2834(8)	7004(3)	5441(3)	47(2)
C(25)	4333(8)	7047(3)	5155(3)	50(2)
C(26)	4718(8)	7808(4)	5094(3)	54(2)
C(27)	3474(9)	9072(3)	5445(3)	86(3)
C(28)	794(7)	7964(4)	5887(3)	75(3)
C(29)	1942(9)	6321(3)	5649(3)	79(3)
C(30)	5375(8)	6411(4)	4975(3)	90(3)
C(31)	6284(7)	8113(5)	4872(3)	92(3)

predicted by the stoichiometry of the conversion, 2PhNCO → PhNC(O)NPh + CO. The reductive disproportionation of an isocyanate to a ureylene ligand has been observed in a number of mononuclear compounds[30] and in several polynuclear complexes. For example, the reaction of triiron decacarbonyl $[Fe_3(CO)_{10}]$ with phenyl isocyanate formed a dinuclear species which was initially formulated as the bis(isocyanate) hexacarbonyl complex $Fe_2(CO)_6(PhNCO)_2$.[21b,c] However a subsequent X-ray crystallographic study revealed the complex was actually the diphenylureylene compound $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}PhNC(O)NPh)$.[21a] Likewise, reaction of the highly reduced titanium carbonyl complex $Cp_2Ti(CO)_2$ with PhNCO initially formed the trinuclear complex $(Cp_2Ti)_3(PhNC(O)NPh)_2$ which fragmented upon thermolysis to form the dinuclear ureylene complex $(Cp_2Ti)_2(PhNC(O)NPh)$ and the mononuclear ureylene complex $Cp_2Ti(PhNC(O)NPh)$.[31] Reaction of PhNCO with the cobalt salen complex [Co(salen)Na(THF)] gave the dicobalt ureylene complex $[Co(salen)Na]_2(PhNC(O)NPh)$ along with $[Co(CO)_4]^-$, formed from the reaction of CO with the starting complex.[32]

Formation of the diphenylureylene ligand of **5** from the reaction of **1** and phenyl isocyanate presumably requires the cleavage of an isocyanate C=N bond and insertion of a coordinated isocyanate into a Co−N bond. A plausible mechanism which incorporates these transformations is depicted in Scheme 6. Although Scheme 6 employs tricobalt intermediates, the formation of **5** from **1** and PhNCO could be equally well explained using mono- or dinuclear intermediates. Coordination of phenyl isocyanate to **1** followed by cleavage of the C=N bond and loss of H_2 would give the μ_3-nitride μ_3-carbonyl intermediate $Cp^*{}_3Co_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)$, **I**. Formation of intermediate **I** is supported by analogy to formation of **3** from **1** and CS_2. Coordination of a second isocyanate would give the μ_2-nitride isocyanate intermediate **II**. Insertion of the isocyanate C=N bond into a Co−N bond would form the diphenylureylene carbonyl intermediate **III**; the insertion of a coordinated isocyanate into a M−N bond has been previously observed.[19,30] Intermediate **III** could then undergo fragmentation to give **5** directly and a [Cp*Co(CO)] fragment which could eventually form compounds **2** and **6**.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficents (Å^2 $\times$ 10^3) for $Cp^*{}_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (**5**)

	x	*y*	*z*	*U*(eq)
Co(1)	8553(1)	9022(1)	1493(1)	64(1)
Co(2)	7392(1)	9304(1)	2516(1)	62(1)
C(1)	8430(6)	7990(4)	2409(4)	83(2)
N(1)	9037(4)	8788(3)	2568(2)	62(1)
N(2)	7407(4)	8268(3)	1900(2)	64(1)
O(1)	8723(5)	7275(3)	2649(4)	156(3)
C(2)	10153(5)	8885(4)	3044(3)	68(2)
C(3)	10845(7)	8246(5)	3431(4)	107(3)
C(4)	11942(8)	8419(7)	3874(5)	131(4)
C(5)	12369(7)	9213(7)	3985(4)	114(4)
C(6)	11731(7)	9881(6)	3636(4)	107(3)
C(7)	10626(6)	9722(5)	3162(4)	91(3)
C(8)	6442(5)	7715(4)	1547(3)	71(2)
C(9)	6412(6)	6848(4)	1708(4)	88(3)
C(10)	5425(8)	6368(5)	1298(5)	115(4)
C(11)	4518(8)	6743(6)	823(5)	113(4)
C(12)	4543(7)	7580(6)	676(5)	113(3)
C(13)	5523(6)	8080(5)	1028(4)	97(3)
C(14)	9326(13)	8483(8)	608(7)	72(1)
C(15)	10122(11)	9121(9)	1021(7)	72(1)
C(16)	9472(12)	9890(8)	961(7)	72(1)
C(17)	8360(12)	9822(8)	540(7)	72(1)
C(18)	8177(12)	8927(9)	325(6)	72(1)
C(19)	9570(15)	7531(11)	534(10)	132(2)
C(20)	11419(15)	8908(12)	1403(9)	132(2)
C(21)	9958(17)	10727(11)	1222(10)	132(2)
C(22)	7224(16)	10409(12)	250(10)	132(2)
C(23)	7174(15)	8458(12)	−176(9)	132(2)
C(14′)	10049(14)	9685(11)	1114(8)	72(1)
C(15′)	8962(15)	10093(10)	845(8)	72(1)
C(16′)	8091(13)	9508(11)	409(8)	72(1)
C(17′)	8769(16)	8674(10)	410(8)	72(1)
C(18′)	10001(15)	8766(10)	882(8)	72(1)
C(19′)	11138(18)	10200(14)	1558(11)	132(2)
C(20′)	8740(20)	11031(13)	902(12)	132(2)
C(21′)	6943(18)	9713(15)	−47(11)	132(2)
C(22′)	8352(19)	7842(14)	60(11)	132(2)
C(23′)	11079(19)	8210(14)	1108(11)	132(2)
C(24)	6449(10)	9328(6)	3414(5)	112(4)
C(25)	5635(7)	9502(6)	2732(5)	110(4)
C(26)	6045(8)	10245(5)	2421(4)	100(3)
C(27)	7064(8)	10522(4)	2878(5)	98(3)
C(28)	7343(7)	9990(8)	3469(4)	123(4)
C(29)	6339(15)	8660(9)	3952(8)	263(10)
C(30)	4503(10)	8976(10)	2489(10)	285(12)
C(31)	5350(13)	10658(10)	1741(6)	254(9)
C(32)	7714(13)	11373(7)	2751(10)	272(11)
C(33)	8372(10)	10086(12)	4137(6)	316(12)

Experimental Section

General Methods. All manipulations were performed under a nitrogen atmosphere in an inert-atmosphere glovebox or by standard high-vacuum techniques. ^1H NMR spectra were obtained on a Bruker WP200 or AM300 spectrometer, and ^{13}C NMR spectra were obtained on a Bruker AM500 (126 MHz) spectrometer. Infrared spectra were

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recorded on a Mattson Genesis FT-IR spectrometer. Mass spectra were determined on a Kratos MS-80 spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Diethyl ether, hexane, pentane, and benzene were distilled from sodium and benzophenone; toluene was distilled from sodium. Benzene-d_6 was distilled from sodium and benzophenone or from sodium−potassium alloy. CO_2 (Matheson), CS_2 (Aldrich), and PhNCO (Aldrich) were used as received.

Reaction of 1 with CO_2. A 1.9 mL thick-walled resealable NMR tube containing **1** (4 mg, 0.007 mmol) and CO_2 (0.34 mmol) in C_6D_6 was heated at 120 °C, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. Concentrations were determined by integrating the Cp* resonances for **1** (δ 62) and **2** (δ 1.41) relative to the residual proton signal of C_6D_6 (δ 7.15). After 44 h, the Cp* resonance for **1** could no longer be detected and the Cp* resonance for **2** accounted for 45% of the Cp* resonances in solution. Other unidentified Cp* resonances were observed at δ 47.9 (19%) and 1.70 (17%). A linear plot of ln[**1**] versus time gave a first-order rate constant for the disappearance of **1** of $k_{obs} = 3.1 \times 10^{-5}$ s^{-1}.

$Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (3). Carbon disulfide (1.3 g, 17 mmol, 0.8 M) was added to a solution of **1** (250 mg, 0.43 mmol) in benzene (20 mL) and was stirred for 20 min. After benzene and unreacted CS_2 were evaporated under vacuum, the residue was redissolved in benzene and the solution was heated at 80 °C for 15 min. Evaporation of benzene gave a black residue consisting of a 2:1 mixture of **4** and **3** by ^{1}H NMR analysis. The residue was washed with hexane until the filtrate changed color from black to brown. The precipitate was collected and dried to give $Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**3**) (54 mg, 19%) as a black powder which contained ~5% **4** by ^{1}H NMR analysis. **3** was further purified by crystallization from toluene at −20 °C: ^{1}H NMR (C_6D_6, 200 MHz) δ 1.51; $^{13}C\{^1H\}$ NMR [C_6D_6, 126 MHz, 0.007 M Cr(acac)$_3$] δ 93.05 (C_5Me_5), 10.2 (C_5Me_5), μ_3-CS carbon not observed; IR (CS_2) 1040, 1021 cm^{-1}; HRMS (EI) calcd (found) for $C_{31}H_{45}CoS_2$, 658.0956 (658.0988). Although samples of **3** were homogeneous and >95% pure by ^{1}H NMR analysis, elemental analyses for C were consistently low.

$Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (5). A solution of **1** (250 mg, 0.43 mmol) and phenyl isocyanate (3 g, 34 mmol, 2.5 M) in benzene (10 mL) was stirred at 55 °C for 50 min. Benzene and unreacted PhNCO were evaporated under vacuum, and the residue was extracted with hexane. Evaporation of hexane under vacuum and crystallization from pentane at −20 °C gave **5** as green crystals (33 mg, 13%): ^{1}H NMR (300 MHz, C_6D_6) δ 8.25 (d, J = 7 Hz, *ortho*-H), 7.26 (t, J = 7 Hz, *meta*-H), 7.06 (t, J = 7 Hz, *para*-H), 1.45 (Cp*); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 147.6, 125.4, 123.8, 120.1 (NC_6H_5), 83.4 (C_5Me_5), 10.0 (C_5Me_5), NCON carbon not observed; IR (hexane) 1695 cm^{-1}; HRMS (EI) calcd (found) for $C_{33}H_{40}N_2OCo_2$, 598.1805 (598.1796). Anal. Calcd (found) for $C_{33}H_{40}N_2OCo_2$: C, 66.22 (65.56); H, 6.74 (6.60); N, 4.70 (4.63).

X-ray Crystallographic Determinations and Refinements. Each crystal was coated with epoxy and mounted on the tip of a thin glass fiber. Diffraction data were obtained with graphite-monochromated Mo Kα radiation on a Siemens P4RA diffractometer at 295 K. Automatic indexing of 40 well-centered reflections determined the unit cell; precise unit cell dimensions were determined by least-squares refinement of 25 well-centered, high-angle reflections (25° < 2θ < 30°). Empirical absorption corrections were applied to each data set. Initial positions for Co atoms were found by direct methods, and all non-hydrogen atoms were located from successive difference Fourier maps. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed at idealized positions with isotropic thermal parameters of U = 0.08 Å^2. Crystallographic computations were performed employing SHELXTL-PLUS[33] software on VAX computers.

X-ray Crystallography of $Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (3). Slow cooling of a saturated toluene solution to −20 °C gave black crystals of **3** suitable for X-ray analysis. The 6893 reflections collected produced 2937 independent, observed reflections ($|F| > 4.0\sigma(F)$). The largest residual on the final difference map was 0.45 e Å^{-3}. Crystallographic data (Table 1), selected bond lengths and bond angles (Table 2), and atomic coordinates (Table 4) are presented.

X-ray Crystallography of $Cp^*_2Co_2(\mu_2,\mu_2\text{-}\eta^2\text{-}PhNCONPh)$ (5). Slow evaporation of a toluene solution gave black crystals of **5** suitable for X-ray analysis. The Cp* ligand bonded to Co(1) was disordered; the best fit of the data was obtained with a model which assigned the Cp* ligand partial occupancy over two independent orientations. In the major orientation (55%), the Co(1) Cp* ligand was eclipsed relative to the Co(2) Cp* ligand, and in the minor orientation (45%), the Co(1) Cp* ligand was staggered relative to the Co(2) Cp* ligand. Standard reflections showed no significant variations throughout data acquisition. The 6705 reflections collected produced 3828 independent, observed reflections ($|F| > 4.0\sigma(F)$). The largest residual on the final difference map was 0.64 e Å^{-3}. Crystallographic data (Table 1), selected bond lengths and bond angles (Table 3), and atomic coordinates (Table 5) are presented.

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Supplementary Material Available: ORTEP diagrams and tables of structure determination data, anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, and idealized atomic parameters for hydrogen atoms for compounds **3** and **5** (27 pages). Ordering information is given on any current masthead page.

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[33] SHELXTL-PLUS, Siemens Analytical X-Ray Instruments, Inc.