Reaction of NO with $Cp^*_3Co_3(\mu\text{-}H)_4$ preserves the tricobalt cluster and produces $Cp^*_3Co_3(\mu_3\text{-}NO)_2$

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Abstract

$Cp^*_3Co_3(\mu\text{-}H)_4$ (**4**) reacts with NO to produce $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3**) which was characterized by X-ray crystallography. **3** is a diamagnetic 48 electron tricobalt cluster in which an equilateral triangular array of cobalt atoms ($Co\text{–}Co_{av} = 2.423(2)$ Å) is capped on each face by a μ_3-NO ligand ($Co\text{–}\mu_3\text{-}NO_{av} = 1.863(7)$ Å).

Introduction

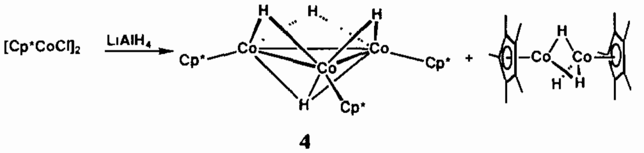
In bicapped trimetal clusters, changes in metal–metal bond distances occur as valence electrons are added to or removed from the system. Trimetallic clusters with 48 valence electrons are diamagnetic and have metal–metal bond orders of 1.0. The HOMOs for 48 electron trimetallic clusters are a degenerate pair of e″ orbitals which are metal–metal antibonding. As electrons are removed to form 47 or 46 electron clusters, bond orders are expected to increase and bond lengths are anticipated to shorten. Symmetric trimetallic clusters with 46 valence electrons are anticipated to be paramagnetic species with a triplet ground state and a net metal–metal bond order of 1.3. As part of an extensive study on the redox behavior of cyclopentadienyl tricobalt clusters, Dahl and co-workers recently reported the synthesis and X-ray crystal structure of the 46 electron tricobalt cluster $Cp^*_3Co_3(\mu_3\text{-}CO)_2$ (**1**) [1] which had a shorter mean Co–Co distance (2.370 Å) than in the analogous 48 electron cation $[(C_6H_6)_3Co_3(\mu_3\text{-}CO)_2]^+PF_6^-$ (**2**) (2.399 Å) [2] in accord with theoretical predictions [3]. However, due to the greater steric requirements of the Cp* ligands of **1** relative to the benzene ligands of **2**, it was not possible to quantitatively assess the shortening of the Co–Co distance of **1** that resulted solely from a decrease in the number of antibonding electrons. A better comparison would be between the 46 electron **1** and its 48 electron dianion $[Cp^*_3Co_3(\mu_3\text{-}CO)_2]^{-2}$ (**A**). However, since **A** remains unknown, we set out to synthesize $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3**) which is a sterically equivalent 48 electron analog of **1**.

Recently, in collaboration with Theopold and co-workers, we reported the synthesis of the unusual trinuclear tetrahydride cluster $Cp^*_3Co_3(\mu\text{-}H)_4$ (**4**) formed along with the dinuclear trihydride complex, $Cp^*_2Co_2(\mu\text{-}H)_3$, from the reaction of $[Cp^*CoCl]_2$ with $LiAlH_4$ (Scheme 1) [4]. Since **4** is a reactive, electron deficient 46 electron complex and has no bridging atoms other than hydrogen, we thought that **4** might react directly with NO to form the desired bis μ_3-NO capped cluster **3**. Here we report that hydride **4** reacts cleanly with NO to form **3** (see Scheme 2) and that the Co–Co distances in the 48 electron complex **3** are 0.052 Å longer than in the 46 electron complex **1**.

Experimental

$Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (3)

On a high vacuum line, NO (0.55 mmol) was condensed at 77 K into an 8 ml thick-walled flask containing a suspension of **4** (43 mg, 0.073 mmol) in 3 ml pentane. The flask was sealed at 77 K and the slurry was stirred at room temperature for 2 min to give **3** as a red suspension. Excess NO was removed at −80 °C under high vacuum, the solid was filtered, washed with pentane, and dried to give $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3**) (28 mg, 54%) as a red powder. ^1H NMR (C_6D_6, 200 MHz) δ 1.48;



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Scheme 1.

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IR ($CHCl_3$) 1328 cm^{-1}; HRMS(EI) calc. for $C_{30}H_{45}N_2O_2Co_3$: 642.1477, found: 642.1606. *Anal.* Calc. for $C_{30}H_{45}N_2O_2Co_3$: C, 56.08; H, 7.06; N, 4.36. Found: C, 55.75; H, 7.05; N, 4.09%.

X-ray crystallography of Cp$_3$Co$_3$(μ_3-NO)$_2$ (3)*

A three-fold excess of hexane was added to a saturated solution of **3** in $CHCl_3$. Slow evaporation in an inert atmosphere glovebox gave black crystals of **3** suitable for X-ray analysis. Diffraction data were collected on a Siemens P4RA diffractometer. The 8291 reflections collected produced 6062 independent, observed reflections ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by full-matrix least-squares methods employing SHELXTL plus software. Crystallographic data (Table 1), atomic coordinates (Table 2), selected bond lengths and selected bond angles (Table 3) are presented.

Results and discussion

Synthesis of Cp$_3$Co$_3$(μ_3-NO)$_2$ (3)*

A black pentane suspension of $Cp^*_3Co_3(\mu\text{-}H)_4$ (**4**) reacted with excess NO at room temperature in less than a minute to form $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3**), which was isolated in 54% yield as a red powder. ^1H NMR analysis of the reaction in C_6D_6 with C_6Me_6 as an internal standard showed quantitative (103 ± 10%) formation of **3**. Gas chromatography[†] of the gases over solution showed the presence of H_2 and comparison with standard mixtures indicated a **4**:H_2 ratio of

TABLE 1. Crystal structure data for $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (3)

Empirical formula	$C_{30}H_{45}Co_3N_2O_2$
Color, habit	black, block
Crystal size (mm)	0.2×0.2×0.2
Crystal system	orthorhombic
Space group	*Pna*2$_1$
Unit cell dimensions	
a (Å)	28.552(5)
b (Å)	11.444(2)
c (Å)	17.842(4)
Volume (Å^3)	5835(2)
Peaks to determine cell	20
2θ Range of cell peaks	4.0–45
Z	8
Formula weight	642.5
Density (calc.) (g cm^{-3})	1.463
Absorption coefficient (mm^{-1})	1.715
F(000)	2688
R(*F*) (%)	4.56
$R_w(F)$ (%)	4.91

TABLE 2. Atomic coordinates for $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (3)

	x	y	z	U_{eq}[a]
Co(1A)	9708(1)	1948(1)	8585	31(1)
Co(2A)	10104(1)	3644(1)	9095(1)	31(1)
Co(3A)	10022(1)	3431(1)	7754(1)	29(1)
N(1A)	9569(2)	3541(6)	8497(5)	34(3)
O(1A)	9190(2)	4065(5)	8532(4)	42(2)
N(2A)	10320(2)	2484(5)	8457(5)	29(2)
O(2A)	10701(2)	1941(5)	8434(4)	40(2)
C(1A)	9068(3)	1166(8)	8893(6)	44(4)
C(2A)	9432(4)	687(9)	9347(6)	55(4)
C(3A)	9760(4)	174(9)	8862(7)	55(4)
C(4A)	9611(3)	296(8)	8097(6)	43(4)
C(5A)	9176(3)	946(8)	8142(5)	38(4)
C(6A)	8644(3)	1800(9)	9175(7)	66(4)
C(7A)	9427(5)	588(12)	10190(7)	83(6)
C(8A)	10212(4)	−459(9)	9097(8)	77(5)
C(9A)	9847(4)	−155(9)	7414(7)	68(5)
C(10A)	8873(3)	1222(10)	7483(7)	66(4)
C(11A)	9986(3)	5118(8)	9777(6)	37(3)
C(12A)	10452(4)	5144(9)	9517(6)	48(4)
C(13A)	10686(3)	4124(10)	9772(6)	44(4)
C(14A)	10350(3)	3427(10)	10178(6)	47(4)
C(15A)	9916(3)	4096(10)	10175(5)	40(4)
C(16A)	9606(4)	6034(10)	9629(7)	69(5)
C(17A)	10699(4)	6202(10)	9168(7)	75(5)
C(18A)	11182(3)	3807(10)	9637(6)	65(4)
C(19A)	10463(5)	2304(11)	10581(8)	81(6)
C(20A)	9456(3)	3736(10)	10547(6)	55(4)
C(21A)	9716(3)	4276(9)	6826(6)	42(4)
C(22A)	9921(3)	3233(9)	6556(6)	42(4)
C(23A)	10415(3)	3278(9)	6761(5)	38(4)
C(24A)	10502(3)	4332(9)	7125(5)	39(3)
C(25A)	10066(4)	5002(9)	7153(6)	46(4)
C(26A)	9212(4)	4609(10)	6725(7)	67(5)
C(27A)	9695(4)	2305(10)	6097(7)	70(5)
C(28A)	10764(4)	2331(10)	6588(6)	58(4)
C(29A)	10982(3)	4735(9)	7376(6)	58(4)
C(30A)	9994(4)	6203(8)	7446(6)	60(4)
Co(1B)	7729(1)	7641(1)	8433(1)	30(1)
Co(2B)	7349(1)	5898(1)	7959(1)	28(1)
Co(3B)	7438(1)	6175(1)	9296(1)	28(1)
N(1B)	7126(2)	7070(6)	8595(5)	31(3)
O(1B)	6733(2)	7605(5)	8626(4)	45(2)
N(2B)	7888(2)	6076(5)	8555(4)	25(2)
O(2B)	8275(2)	5583(5)	8526(4)	38(2)
C(1B)	6767(3)	5320(8)	7333(5)	39(3)
C(2B)	7024(3)	4341(8)	7598(5)	39(3)
C(3B)	7493(3)	4430(9)	7310(5)	39(3)
C(4B)	7519(4)	5432(9)	6866(5)	43(4)
C(5B)	7072(4)	6004(9)	6888(5)	41(4)
C(6B)	6258(3)	5620(10)	7505(7)	63(4)
C(7B)	6815(3)	3301(8)	7982(6)	55(4)
C(8B)	7886(3)	3561(9)	7460(6)	59(4)
C(9B)	7950(4)	5810(11)	6436(6)	66(5)
C(10B)	6922(4)	7091(10)	6502(7)	62(5)
C(11B)	7070(4)	6399(10)	10309(6)	48(4)
C(12B)	7559(4)	6429(9)	10458(5)	42(4)
C(13B)	7748(3)	5347(9)	10231(5)	42(4)
C(14B)	7380(3)	4644(9)	9918(5)	42(4)
C(15B)	6962(4)	5318(10)	9985(5)	51(4)
C(16B)	6722(4)	7361(11)	10444(7)	68(5)

(*continued*)

[†] Gas chromatography was performed on a Varian Vista 6000 thermal conductivity instrument using a 5 Å molecular sieve column (6′ × 1/8″, 30 °C, N_2 carrier gas).

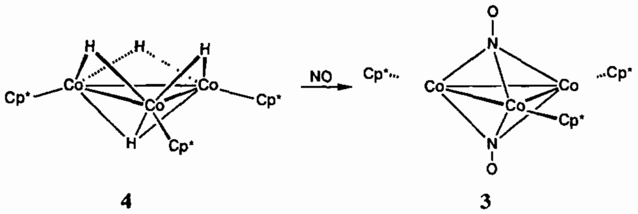
TABLE 2. (*continued*)

	x	y	z	U_{eq}[a]
C(17B)	7823(4)	7332(10)	10911(6)	60(4)
C(18B)	8255(3)	4934(10)	10275(6)	57(4)
C(19B)	7426(5)	3411(9)	9661(6)	70(5)
C(20B)	6472(4)	4946(12)	9753(7)	76(5)
C(21B)	7648(4)	9434(9)	8150(8)	63(5)
C(22B)	7969(4)	8907(9)	7651(6)	55(4)
C(23B)	8346(3)	8448(8)	8053(6)	42(3)
C(24B)	8276(3)	8662(8)	8815(6)	41(4)
C(25B)	7832(4)	9297(8)	8883(7)	53(4)
C(26B)	7195(4)	10031(11)	7990(11)	120(8)
C(27B)	7942(6)	9012(12)	6828(7)	103(7)
C(28B)	8765(4)	7806(11)	7752(8)	77(5)
C(29B)	8607(4)	8311(10)	9450(7)	67(5)
C(30B)	7623(5)	9776(10)	9581(8)	90(6)

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

TABLE 3. Selected bond lengths (Å) and angles (°) for $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3a**)

Co(1)–Co(2)	2.423(2)	Co(1)–N(1)–O(1)	130.7(5)
Co(1)–Co(3)	2.425(2)	Co(2)–N(1)–O(1)	131.0(6)
Co(2)–Co(3)	2.416(2)	Co(3)–N(1)–O(1)	132.6(7)
Co(1)–N(1)	1.872(7)	Co(1)–N(2)–O(2)	130.8(5)
Co(1)–N(2)	1.865(6)	Co(2)–N(2)–O(2)	131.6(6)
Co(2)–N(1)	1.867(7)	Co(3)–N(2)–O(2)	131.5(7)
Co(2)–N(2)	1.854(7)	N(1)–Co(1)–N(2)	82.4(3)
Co(3)–N(1)	1.857(8)	N(1)–Co(2)–N(2)	82.9(3)
Co(3)–N(2)	1.863(8)	N(1)–Co(3)–N(2)	82.9(3)
N(1)–O(1)	1.238(8)	Co(1)–N(1)–Co(2)	80 8(3)
N(2)–O(2)	1.254(8)	Co(1)–N(1)–Co(3)	81.1(3)
Co(1)–$Cp_{(cent)}$	1 716	Co(2)–N(1)–Co(3)	80.9(3)
Co(2)–$Cp_{(cent)}$	1.715	Co(1)–N(2)–Co(2)	81.3(3)
Co(3)–$Cp_{(cent)}$	1.718	Co(1)–N(2)–Co(3)	82.1(3)
		Co(2)–N(2)–Co(3)	81.1(3)



Scheme 2.

1:2.3 ± 0.5. When a C_6D_6 solution of **4** was exposed to <2 equiv. of NO, ^1H NMR analysis revealed signals for **4** (δ 62) and **3** (δ 1.48); no intermediates were detected. It is noteworthy that while **4** reacted with CO at room temperature to produce mononuclear $Cp^*Co(CO)_2$ and H_2 [4], the reaction of **4** with NO preserves the cluster and leads to the formation of the trinuclear complex **3** (Scheme 2).

While the reactions of NO with mononuclear metal hydride complexes to form terminal nitrosyl complexes are well known [5], no analogous reaction of NO with a hydrido metal cluster to form a μ_2- or μ_3-NO complex has been reported. Due in part to the lack of straightforward synthetic strategies, only a few trimetal clusters containing a μ_3-NO ligand have been reported. Examples include $Cp_3Mn_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NO)$ (**5**) [6], $Cp'_3Mn_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NO)$ [7], $Cp_3Co_3(\mu_3\text{-}NO)_2$ (**6**) [8], $Cp'_3Co_3(\mu_3\text{-}NO)_2$ (**7**) [8b], $Cp_3Rh_3(\mu_3\text{-}NO)_2$ [9], $[Cp'_3Co_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^n$ ($n = 0$ (**8**), 1 (**8**$^+$)) [10, 11], $Cp_3Co_2Fe(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ [12], $Cp'_3Co_2Fe(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ [13], $Cp'MnCp_2Fe_2(\mu_2\text{-}CO)_2(\mu_2\text{-}NO)(\mu_3\text{-}NO)$ [14], $Cp'_3Fe_3(\mu_2\text{-}CO)_3(\mu_3\text{-}NO)$ [15] and $Cp^*_3Fe_3(\mu_2\text{-}CO)_3(\mu_3\text{-}NO)$ [15].

In the mass spectrum of **3**, the parent peak at $m/z = 642$ was the most intense peak in the spectrum. In the IR spectrum ($CHCl_3$) of **3**, a single μ_3-NO absorbance was observed at 1328 cm^{-1} in the range seen for other μ_3-NO complexes[†]. Cluster **3** is sparingly soluble in aliphatic hydrocarbons, but dissolves readily in halocarbons, aromatic hydrocarbons and THF to form deep red solutions.

X-ray crystal structure of $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (3)

The structure of **3** was determined by X-ray crystallography (Fig. 1, Table 3) and shown to consist of a equilateral triangular array of three cobalt atoms symmetrically capped on each face by a μ_3-NO ligand. One methyl group of each Cp* ligand lies in the Co_3 plane and the Cp* ligands are arranged in a head to tail manner about the cobalt triangle. There are two crystallographically independent molecules **3a** and **3b** in the unit cell which differ from one another only in the thermal motion of the Cp* ligands. Molecule **3a** possesses less distortion and is shown in Fig. 1.

The average Co–Co distances in **3a** (2.423(2) Å) and **3b** (2.422(2) Å) are not significantly different, and the variation among the three individual Co–Co distances is <0.01 Å in both **3a** and **3b**. The highly symmetric tricobalt core of **3** is unusual since distortions away from a symmetric equilateral triangle are often observed in similar trimetal clusters[††]. The Co–Co distance in **3** (2.423(2) Å) is very similar to the Co–Co distances observed in the 48 electron $Cp^*_3Co_3$ clusters $Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (2.428 Å) [16] and $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2.437 Å) [17].

Molecular orbital calculations performed on both $Cp_3Co_3(\mu\text{-}CO)_2$ (**1**) [3a] and $Cp_3Rh_3(\mu\text{-}CO)_2$ [3b] assign the HOMO of these symmetric 46 electron clusters to a doubly degenerate e″ orbital that is net trimetal

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[†] Values for $\nu(\mu_3\text{-}NO)$ range from 1290 cm^{-1} in $Cp^*_3Fe_3(\mu_2\text{-}CO)_3(\mu_3\text{-}NO)$ [15] to 1400 cm^{-1} in $Cp_3Co_3(\mu_3\text{-}NO)_2$ [8].

[††] Variations in individual Co–Co distances have been observed in clusters **7** (0 019 Å) [8b], **8**$^+$ (0.037 Å) [11], **2** (0 041 Å) [2] and $Cp'_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (0.032 Å) [11].

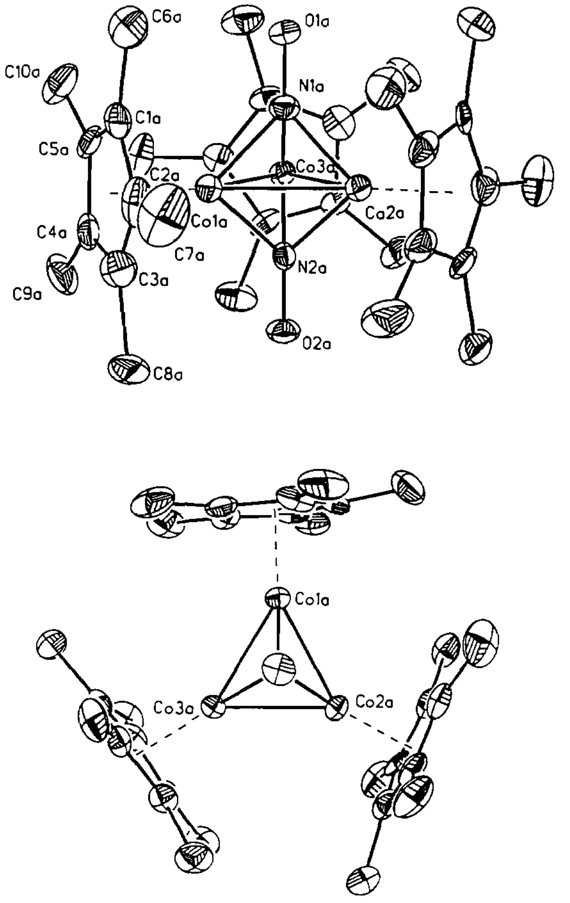

Fig. 1. X-ray crystal structure of $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3a**).

antibonding in character. In the 46 electron complex **1**, the two degenerate e″ orbitals are each half filled, while in the 48 electron complex $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3**), both degenerate e″ orbitals are completely filled. This predicts a lower overall Co–Co bond order in **3**, and hence longer Co–Co distances in **3** relative to **1**. In agreement with this theoretical prediction, the mean Co–Co distance of 2.423(2) Å in **3** is significantly longer (0.052 Å) than the mean Co–Co distance in the 46 electron complex **1**. However, the Co–Co distance in **3** is only 0.014 Å longer than in the 47 electron cation $[Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]^+$, possibly due to the substitution of the electron donating μ_3-NH ligand for the electron accepting μ_3-NO ligand. The 0.052 Å longer Co–Co distance between 46 electron **1** and 48 electron **3** is similar to a 0.03 Å/electron lengthening of the M–M distances observed in the 48/49/50 electron series, $Cp_3CoNi_2(\mu_3\text{-}CO)_2$ (2.356 Å) [18], $Cp_3Ni_3(\mu_3\text{-}CO)_2$ (2.389 Å) [18], and $[Cp_3Ni_3(\mu_3\text{-}CO)_2]^-$ $[K(2,2,2\text{-crypt})]^+$ (2.421 Å) [19].

Olson and Dahl noted that substitution of the bulky Cp* ligand for a ‘sterically innocent’ ligand such as Cp, Cp′ and C_6H_6 in a tricobalt cluster normally results in an approximately 0.025 Å increase in the Co–Co distance due to Cp*–Cp* repulsion [2]. However, the Co–Co distance in $Cp^*_3Co_3(\mu_3\text{-}CO)_2$ (**1**) is actually 0.020 Å shorter than the Co–Co distance in the recently synthesized Cp analog $Cp_3Co_3(\mu_3\text{-}CO)_2$ (**9**) [20]. In contrast, the Co–Co distance in **3** is consistently longer than in the non-Cp* clusters summarized in Table 4. For example, the mean Co–Co distance in **3** is 0.024 Å longer the mean Co–Co distance in the benzene complex $[(C_6H_6)_3Co_3(\mu_3\text{-}CO)_2]^+PF_6^-$ (**2**), 0.020 Å longer than in the Cp′ cluster $Cp'_3Co_3(\mu_3\text{-}NO)_2$ (**7**), and 0.024 Å longer than in the Cp analog $Cp_3Co_3(\mu_3\text{-}NO)_2$ (**6**).

The Co–NO distances in **3a** and **3b** have the same mean value of 1.863 Å and range from 1.848(7) to 1.882(7) Å. This Co–NO distance of 1.863 Å in **3** is somewhat smaller than the 1.929 Å Mn–(μ_3-NO) distance in **5**, but is similar to the values observed in other μ_3-NO cobalt complexes (Table 4), which range from 1.843 to 1.869 Å. The similarity of the Co–(μ_3-NO) distances in **3** and the various μ_3-NO clusters in Table 4 suggests that bonding of the NO ligand is not

TABLE 4. Comparison of bond lengths (Å) for Co_3 clusters

Complex	No electrons	Co–Co mean	Co–$Cp_{(cent)}$	Co–μ_3-NO	Co–μ_3-CO	π-Ligand
$Cp^*_3Co_3(\mu_3\text{-}NO)_2$ (**3**)	48	2.423	1.715	1.863		C_5Me_5
$Cp'_3Co_3(\mu_3\text{-}NO)_2$ (**7**)	48	2.403	1.71	1.863		C_5H_4Me
$Cp_3Co_3(\mu_3\text{-}NO)_2$ (**6**)	48	2 399	1.67	1.843		C_5H_5
$Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)^a$	48	2.428	1.72		1.930	C_5Me_5
$[Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]^+PF_6^{-\,b}$	47	2.409	1.72		1.979	C_5Me_5
$Cp^*_3Co_3(\mu_3\text{-}CO)_2$ (**1**)	46	2.370	1.73		1.951	C_5Me_5
$Cp_3Co_3(\mu_3\text{-}CO)_2$ (**9**)	46	2.390	1.70		1.973	C_5H_5
$Cp'_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NCONH_2)^a$	48	2.400	1.69		1.953	C_5H_5
$[Cp'_3Co_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+BPh_4^-$ (**8+**)	48	2 406	1.69	1.869		C_5H_4Me
$Cp'_3Co_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (**8**)	49	2.465	1.73	1.848		C_5H_4Me
$[(C_6H_6)_3Co_3(\mu_3\text{-}CO)_2]^+PF_6^-$ (**2**)	48	2 399	1.61		1.930	C_6H_6

[a] Ref. 11. [b] Ref. 16.

significantly perturbed by the presence of the bulky Cp* ligands.

The average Co–Cp*(centroid) distances for both **3a** and **3b** are 1.715 Å, which is similar to those seen in related tricobalt clusters (Table 4). However, the Cp* ligands of both **3a** and **3b** show substantial differences in the Co–C(ring) distances of up to 0.12 Å within an individual Cp* ring. In addition, the Cp* methyl groups show significant out of plane distortions. For example, the C(7) methyl carbon, which is in the Co_3 plane, is bent out of Cp* plane by 7.3°. Similar deformations in related molecules have been attributed to intramolecular interactions between neighboring Cp* ligands (for example see complex **1** and $Cp^*_3Ni_3(\mu_3\text{-}CO)_2$ [18]).

Supplementary material

Tables of structure determination data, positional and anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, idealized atomic parameters for hydrogen atoms, and observed and calculated structure factor amplitudes for **3** are available from the authors upon request.

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