nickel analogue is easier to oxidize and harder to reduce than the unsubstiuted Fischer–Palm cluster.

Acknowledgment. This research was made possible by financial support from the National Science Foundation. One of us (R. L.B.) is grateful to the Owens-Corning Fiberglas Corp. (Technical Center: Granville, Ohio) for a Research Fellowship during September 1983–August 1984. We also thank James A. Mahood for preparing a sample of $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ for electrochemical measurements.

Registry No. Ia, 53652-62-3; Ib, 103190-57-4; IIa, 103148-47-6; IIb, 103148-48-7; IIc, 103148-49-8; IIIa, 103190-58-5; IIIb, 103190-59-6; IV, 103148-50-1; Va, 103190-60-9; Vb, 103190-61-0; $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$, 12194-69-3; $Ni_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)_2$, 103148-51-2; $Ni_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$, 103148-52-3; Co, 7440-48-4; Ni, 7440-02-0.

Synthesis and Stereochemical–Electrochemical Investigations of the 49/48-Electron $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^n$ Series (x = 0, 1; n = 0, 1+): Bonding Analysis of a Marked Redox-Generated Change in Geometry of a Triangular Metal Cluster with π-Acceptor Nitrosyl and π-Donor Nitrene Capping Ligands

Robert L. Bedard and Lawrence F. Dahl*

Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706. *Received September 12, 1985*

Abstract: The isolation and structural characterization of the 49-electron $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (Vb) have been carried out in order to determine the redox-generated variations in geometry of a 49/48-electron trimetal cluster series with mixed π-acceptor and π-donor capping ligands. The preparation and spectral-electrochemical properties of the 49-electron $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ clusters (x = 0; Va; x = 1, Vb) containing π-acidic ON-capping and π-donor (nonhybridized) HN-capping ligands are described. These air-sensitive brownish black compounds were quantitatively obtained by one-electron reductions of their respective $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocations (x = 0, IIIa; x = 1, IIIb) with cobaltocene in THF. An X-ray diffraction investigation of the methylcyclopentadienyl derivative, Vb, has permitted an unequivocal differentiation between the two possible HOMOs (a_2 and e under C_{3v} symmetry) containing the unpaired electron. The striking structural change in the central $Co_3(NO)(NH)$ core upon the reduction of IIIb to Vb is that the pseudoequilateral cobalt triangle (of average length 2.406 Å) in IIIb undergoes a pronounced deformation in Vb to an isosceles cobalt triangle with *one* much longer Co–Co distance of 2.554 (3) Å and *two* slightly enlarged Co–Co distances of 2.414 (3) and 2.426 (3) Å. This particular distortion of the $Co_3(NO)(NH)$ core from an idealized C_{3v}—$3m$ geometry in IIIb to an idealized C_s—m geometry in Vb is rationalized in terms of a vibronically allowed first-order Jahn–Teller effect which splits the degeneracy of the ^2E ground state under C_{3v} symmetry. The preferential elongation of only one Co–Co bond necessitates that the unpaired electron in Vb occupies a nondegenerate HOMO (a'' under C_s symmetry) which is highly antibonding between the two mirror-related cobalt atoms and thereby ***antisymmetric*** with respect to the vertical mirror plane. The fact that the $Co\text{–}C_5H_4Me$(centroid) distances for these two mirror-related cobalt atoms are 0.03 Å longer than the third distance in Vb and 0.05 Å longer than the three corresponding distances in IIIb provides persuasive evidence that significant antibonding character between the two cobalt atoms and their attached C_5H_4Me ligands also exists in the HOMO of Vb. Of prime interest is the fact that the observed trimetal distortion in Vb is opposite to the one found in the 49-electron $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2]^+$ monoanion (crystallographically characterized both as the iodide and hexafluorophosphate salts) in which the isosceles cobalt triangle has *one* shorter and *two* longer Co–Co bonds. This latter distortion is consistent with the tricobalt antibonding electron being mainly localized between two of the three Co–Co bonds which requires that the half-filled nondegenerate HOMO in the bis(sulfido-capped) cluster is *symmetric* with respect to the vertical mirror plane. To our knowledge, *inverse* Jahn–Teller distortions have not been previously encountered in transition metal cluster chemistry. $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$: molecular weight 459.2; triclinic; $P\bar{1}$; a = 9.233 (3) Å, b = 23.750 (7) Å, c = 9.231 (2) Å, α = 96.96 (2)°; β = 119.26 (2)°, γ = 88.28 (3)°, V = 1748.5 (8) Å^3 at −60 °C; D(calcd) = 1.71 g/cm^3 for Z = 4. Anisotropic least-squares refinement converged at $R_1(F)$ = 8.86% and $R_2(F)$ = 10.32% for 3628 independent diffractometry data ($I > 3\sigma(I)$) with a data-to-parameter ratio of 15.1/1. The relatively high discrepancy factors are mainly a consequence of one of the two independent molecules possessing a crystal disorder involving a pseudomirror plane. Hence, the comparative analysis was based upon the "well-behaved" crystal-ordered molecule; the relatively precise structural parameters of its $Co_3(NO)(NH)$ core, which closely conform to C_s—m symmetry, are in accordance with the unambiguous location of the imido hydrogen atom from an electron-density difference map.

Systematic studies of the geometrical effects caused by changes in electronic configuration have been of prime importance in determining the nature of metal–metal bonding in a number of metal cluster systems. The major objective of such studies in our laboratories has been to relate observed structural changes with qualitative metal cluster bonding models possessing energy-level orderings which are dependent on the ligation about the metal cluster core.

Part of our research in this area has focused on the isolation and structural-bonding characterization of paramagnetic monocapped and bicapped triangular metal clusters in order to provide a basic understanding of their electron-transfer properties.

0002-7863/86/1508-5942$01.50/0

Specifically, we have correlated changes in geometry with changes in electronic configuration produced by oxidation and/or reduction of these clusters. The electronic structures and redox chemistry of a considerable number of electrochemically and/or chemically generated paramagnetic homonuclear and heteronuclear trimetal monoanions with a variety of capped ligands have been systematically probed via electrochemical and spectral techniques by others.[1-7]

The fact that the recently prepared 48-electron $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocations (x = 0, IIIa; x = 1, IIIb),[8] which are electronically equivalent (isolobal) to the 48-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$,[9] were found[10] to undergo two reversible one-electron reductions greatly aroused our interest in the possibility of determining the electronic configuration of the reduced 49-electron neutral system. From previous studies on other 49-electron systems, it was evident that the reduction-generated change in geometry of the 49-electron system would ideally discriminate between either of two possible configurations, viz., either an equilateral metal triangle corresponding to an a_2 HOMO or a markedly distorted isosceles metal triangle resulting from the geometry of the $Co_3(NO)(NH)$ core with an e HOMO under C_{3v} symmetry undergoing a vibronically allowed Jahn–Teller distortion to C_s—*m* symmetry in order to lift the orbital degeneracy of the ground state. Our decision to attempt a chemical isolation of the 49-electron methylcyclopentadienyl analogue (Vb) for a structural-bonding analysis was made because an X-ray structural determination of its 48-electron parent monocation (IIIb) had already been carried out.[8] Furthermore, it was hoped that the C_5H_4Me ligands would prevent crystal disorder and/or twinning problems (in the neutral reduced species) which had been previously encountered in X-ray crystallographic studies of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$[9] and $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$.[11]

Herein are presented the synthesis and characterization of the 49-electron $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ clusters (x = 0, Va; x = 1, Vb) together with their chemical behavior upon attempted methylation and protonation. An X-ray crystallographic determination of Vb has furnished the first structural characterization of a 49-electron bicapped trimetal cluster with mixed π-donor (nonhybridized) and π-acceptor ligands and has allowed an unequivocal assignment of its electronic configuration. Of prime importance is that the observed redox-imposed change of geometry for this mixed-bridged 48-electron (n = 1+)/49-electron (n = 0) series has also provided better insight into the contrasting redox properties between this and other related series (presented in the preceding paper[10]).

Experimental Section

General. All manipulations were carried out under dry N_2 in Schlenk-type glassware and/or in a Vacuum Atmospheres drybox. Solvents were dried over standard agents. FT-NMR spectra were recorded on a Bruker WP-200 instrument, and IR spectra were examined with a Beckman IR 4240 spectrometer.

The $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocations (x = 0, IIIa; x = 1, IIIb) were prepared as described previously.[8] Reagents used were procured from standard commercial sources.

Preparation of the Reduced $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ Clusters (x = 0, Va; x = 1, Vb). The syntheses of Va and Vb by reductions of IIIa and IIIb with cobaltocene are typified here by a description of the preparation of Va. Equimolar quantities of $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+[BF_4]^-$ (150 mg; 0.24 mmol) and cobaltocene (51 mg; 0.24 mmol) were stirred in 50 mL of THF at room temperature. The solution changed color immediately from red-brown with suspended black solid (Va) to dark brown, and in a short time a yellow-brown precipitate formed. At the end of 2 h, the solvent was removed under vacuum and the residue extracted into 50 mL of toluene. After filtration under N_2, the toluene was removed under vacuum. The crystalline black product, isolated in essentially quantitative yield, was found from spectroscopic analysis (coupled with an X-ray crystallographic characterization of the C_5H_4Me analogue) to be $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (Va). An infrared spectrum (KBr pellet) in the nitrosyl stretching region revealed that the absorption band pattern characteristic of the starting material (IIIa) with maxima at 1452 (s) and 1410 (m) cm^{-1} had disappeared and that a new band pattern with maxima at 1430 (m) and 1401 (s) cm^{-1} was present. An infrared spectrum (KBr pellet) of the methylcyclopentadienyl analogue (Vb) displayed characteristic infrared bands at 1365 (s), 1395 (sh), and 1349 (m) cm^{-1}. Due to the paramagnetic character of both Va and Vb, ^1H NMR spectra ($CDCl_3$) of these compounds did not exhibit proton resonances.

Reactions of the $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ Monocation (x = 0, IIIa; x = 1, IIIb) with Sodium Triethylborohydride. To a stirred THF solution of IIIb (107 mg; 0.2 mmol based upon a $[BF_4]^-$ counterion) was added a 1 M THF solution of $NaBHEt_3$ (210 μL; 0.21 mmol) via syringe. The initially red solution immediately changed to brown upon addition of this hydride reagent. Stirring was continued for 2 h, after which the THF was removed under vacuum. The crude product was extracted into several 10-mL portions of toluene. A ^1H NMR spectrum ($CDCl_3$) of the purified product showed no discernible resonances (due to its paramagnetism), while an IR spectrum (KBr pellet) displayed a broad nitrosyl absorption pattern with two discernible maxima characteristic of Vb.

A similar treatment of IIIa with $NaBHEt_3$ in THF solution also resulted in a quantitative one-electron reduction of the monocation to the toluene-soluble neutral product Va.

Attempted Methylation and Protonation Reactions of the Reduced Va. To a stirred CH_2Cl_2 solution of Va (160 mg; 0.35 mmol) was added CH_3I (21.8 μL; 0.35 mmol) in 20 mL of CH_2Cl_2; the solution was stirred for 3 h. A black residue was formed from the resulting mixture. Pumping off the CH_2Cl_2 and removing excess Va and CH_3I by extraction of the residue with toluene yielded black crystalline material. An infrared spectrum (KBr pellet) showed this compound to possess virtually identical bands to those of the oxidized $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (IIIa). Attempted protonation of Va with $HBF_4\cdot Et_2O$ also resulted in electron transfer to give the 48-electron monocation.

Electrochemical Measurements. A description of the electrochemical cell and the procedures utilized in the rigorous purification of both the solvents (CH_2Cl_2 and CH_3CN) and supporting electrolyte, tetrabutylammonium hexafluorophosphate ($TBAPF_6$), are given elsewhere.[10] Cyclic voltammograms, obtained via a BAS-100 Electrochemical Analyzer with the electrochemical cell located inside a Vacuum Atmospheres drybox, were *iR*-compensated.

Structural Determination of the Reduced $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ Cluster (Vb). Crystals of Vb suitable for X-ray diffraction measurements were obtained by slow evaporation of a THF solution. X-ray data were collected with Mo Kα radiation on a Nicolet (Syntex) $P\bar{1}$ diffractometer from a black parallelopiped-shaped crystal (of dimensions 0.12 × 0.36 × 0.44 mm) which had been mounted under argon inside a Lindemann glass capillary. Details of the crystal alignment, data collection, and data treatment together with crystallographic programs utilized are given elsewhere.[12] The dimensions and associated esd s for the chosen triclinic unit cell, which shows a near relationship to a hexagonal unit cell, were obtained from least-squares analysis of the setting angles for 15 well-centered reflections with $25° \leq 2\theta \leq 30°$; the symmetry of this unit cell was verified from axial photographs. The application of the cell-reduction program, TRACER,[13] also ruled out any possibility of higher crystal symmetry. Crystal data and data-collection

---

(1) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 405–410.

(2) Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410–415.

(3) (a) Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1000–1005. (b) Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1981**, *20*, 2540–2543.

(4) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1413–1417.

(5) (a) Colbran, S.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1361–1362. (b) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 943–951. (c) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 952–957.

(6) Lindsay, P. N.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Honrath, U.; Vahrenkamp, H.; Bond, A. M. *Organometallics* **1984**, *3*, 413–426.

(7) (a) Honrath, U.; Vahrenkamp, H. *Z. Naturforsch.* **1984**, *39b*, 545–554. (b) Honrath, U.; Vahrenkamp, H. *Z. Naturforsch.* **1984**, *39b*, 555–558. (c) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1981**, *114*, 505–512.

(8) Bedard, R. L.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.*, this issue, first paper in the series.

(9) Frisch, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 5082–5084.

(10) Bedard, R. L.; Dahl, L. F. *J. Am. Chem. Soc.*, this issue, second paper in the series.

(11) Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3763–3769.

(12) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277–284.

(13) Lawton, S. L.; Jacobson, R. A. *TRACER-The Reduced Cell and its Crystallographic Applications*; IS-1141, Ames Laboratory: Iowa State University, Ames, Iowa, 1965.

Table I. Crystal and Data Collection Parameters for $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$

A. Crystal Parameters	
formula	$C_{18}H_{22}N_2OCo_3$
a, Å	9.233 (3)
b, Å	23.750 (7)
c, Å	9.231 (2)
α, deg	96.96 (2)
β, deg	119.26 (2)
γ, deg	88.28 (3)
V, $Å^3$	1748.5 (8)
space group	$P\bar{1}$
crystallographic site symmetry; *Z*	C_1—1; 4
mol wt	459.21
d(calcd), g cm^{-3}	1.71
μ(calcd), cm^{-1}	25.73
dimensions, mm	0.12 × 0.36 × 0.44
crystal face indicies	(0,1,0); $(0,\bar{1},0)$; (1,0,1); $(\bar{1},0,\bar{1})$; $(\bar{2},\bar{1},2)$; $(\bar{2},1,\bar{2})$
B. Data Measurement Parameters	
data collection temp, °C	−60
scan mode	θ–2θ
scan speed, deg/min	variable (4–24)
scan range, deg above $\kappa\alpha_1$/below $\kappa\alpha_2$	1.1/1.1
2< limits, deg	3–55
std reflctns	$(2,\bar{3},2)$; $(0,\bar{4},1)$; $(\bar{1},\bar{2}.1)$; $(\bar{1},2,2)$
frequency of stds	4 per 46
reflctns measured	$\pm h,\pm k,l$
no. of unique reflctns	5766
cutoff for obsd data	$I > 3\sigma(I)$
no. of obsd. reflctns	3628
data/parameter ratio	15.1
anisotropic convergence, %	$R_1(F)$ = 8.86; $R_2(F)$ = 10.32
goodness-of-fit	2.83

parameters are given in Table I. The intensities of the four selected standard reflections (Table I) did not vary by more than 5% during data collection. An analytical absorption correction[14] was applied based upon an indexing of the crystal faces (Table I). Atomic scattering factors for neutral atoms were used together with anomalous dispersion corrections[15] for all non-hydrogen atoms.

The triclinic crystal structure of Vb was determined under centrosymmetric $P\bar{1}$ symmetry from direct methods by application of MULTAN[16] which provided initial coordinates for six independent cobalt atoms corresponding to two independent tricobalt molecules. The other 42 non-hydrogen atoms were located from successive Fourier syntheses. Blocked matrix least-squares refinement was carried out with RAELS[17] in which all non-hydrogen atoms not associated with the C_5H_4Me rings were anisotropically refined. Each of the six C_5H_4Me rings was constrained as a rigid group of C_{2v} symmetry with hydrogen positions internally generated by the RAELS program. The thermal librational-like motion of each rigid-group ring was treated with a TLX model (15 parameters) as described by Rae.[18]

Difficulties were encountered in the least-squares refinement because four of the five ring carbon atoms in the C_5H_4Me ligand coordinated to Co4 had nonpositive-definite thermal parameters. A Fourier difference map exhibited a significant amount of residual electron density in the vicinity of this C_5H_4Me ligand with the highest residual peak being approximately 0.4 Å from Co4. A detailed analysis revealed that the cause of this problem was a crystal disorder of the second independent molecule (with labeled Co4, Co5, and Co6 atoms) involving two unequally weighted orientations related by a mirror plane operation. An interpretation of the specific nature of this crystal-disordered model and its pronounced effect on the resulting averaged structure will be presented later. Since an attempt to use a crystal-disordered model for the second molecule did not lead to a noticeably improved refinement, it was ultimately decided to refine the crystal-disordered molecule as an ordered averaged structure. Although the relatively high final discrepancy factors (Table I) undoubtedly reflect the fact that the ordered averaged-structure model does not adequately describe the actual crystal disorder of the second molecule, we are satisfied with the refined crystal structure in that the atomic coordinates of the "well-behaved" crystal-ordered molecule are insensitive (within experimental error) to either the utilized averaged-structure model or the disordered-structure model. Furthermore, the well-behaved molecule possesses normal atomic thermal ellipsoids, and its geometry has entirely reasonable interatomic distances and bond angles which experimentally conform to assumed C_s—*m* symmetry. That the ordered molecule has relatively precise structural parameters is supported by the fact that the hydrogen atom bonded to the N2 atom of the capped nitrene ligand was unambiguously located from a final electron-density difference map at its anticipated position.

Table II. Interatomic Distances and Bond Angles in $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$

A. Distances (Å)			
Co1–Co2	2.414 (3)	Co1–C11	2.073 (12)
Co1–Co3	2.426 (3)	Co1–C12	2.071 (12)
Co2–Co3	2.554 (3)	Co1–C13	2.088 (10)
Co4–Co5	2.464 (3)	Co1–C14	2.092 (10)
Co4–Co6	2.498 (3)	Co1–C15	2.077 (11)
Co5–Co6	2.421 (3)	Co2–C21	2.100 (11)
Co1–N1	1.880 (11)	Co2–C22	2.111 (12)
Co2–N1	1.889 (12)	Co2–C23	2.128 (11)
Co3–N1	1.860 (12)	Co2–C24	2.125 (11)
Co1–N2	1.833 (11)	Co2–C25	2.107 (12)
Co2–N2	1.820 (12)	Co3–C31	2.139 (12)
Co3–N2	1.804 (13)	Co2–C32	2.131 (12)
N1–O1	1.230 (15)	Co3–C33	2.164 (11)
Co1–Cp′1[a]	1.71	Co3–C34	2.138 (11)
Co2–Cp′2	1.74	Co3–C35	2.089 (12)
Co3–Co′3	1.74		
B. Bond Angles (deg)			
Co1–N1–O1	130.8 (10)	N1–Co1–N2	78.9 (5)
Co2–N1–O1	129.5 (10)	N1–Co2–N2	78.4 (5)
Co3–N1–O1	131.4 (10)	N1–Co3–N2	79.9 (5)
Co1–N1–Co2	79.7 (5)	Co1–Co2–Cp′2	150.6
Co1–N1–Co3	80.9 (5)	Co2–Co1–Cp′1	149.3
Co2–N1–Co3	85.9 (5)	Co1–Co3–Cp′3	149.7
Co1–N2–Co2	82.7 (5)	Co3–Co1–Cp′1	146.7
Co1–N2–Co3	84.0 (6)	Co2–Co3–Cp′3	152.3
Co2–N2–Co3	89.2 (5)	Co3–Co2–Cp′2	150.9

[a] Cp′*n* denotes the centroid of the C_5H_4Me ligand attached to the Co*n* atom.

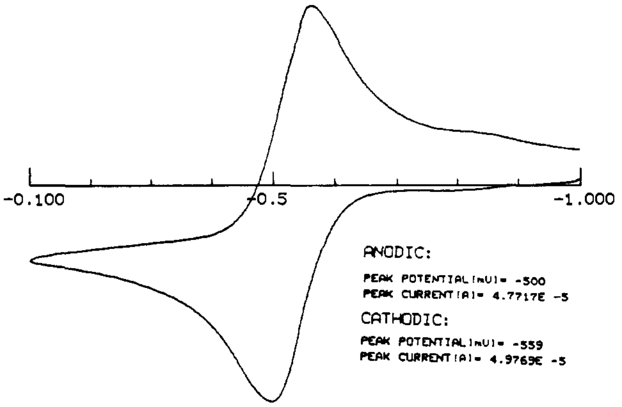

Figure 1. Cyclic voltammogram of $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (Vb) in CH_2Cl_2 at a platinum disk electrode with a scan rate of 200 mV/s. The observed reversible redox couple corresponds to the oxidation of the 49-electron neutral Vb to the 48-electron monocation (IIIb).

The positional and thermal parameters from the output of the final full-matrix least-squares cycle along with selected least-squares planes and interplanar angles are available as supplementary material. Interatomic distances and bond angles are presented in Table II. Observed and calculated structure factors are available as supplementary material. All configurations were computer-generated and computer-drawn with ORTEP II.[19]

---

(14) (a) Alcock, N. W. *Crystallographic Computing* (Ottawa Summer School), 1969. (b) DeMeulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

(15) Atomic scattering factors including anamolous dispersion corrections were taken from the following: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149, pp 155–157.

(16) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J.-P. MULTAN-78. Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(17) Rae, A. D. *RAELS—A Comprehensive Least-Squares Program*; University of New South Wales: Kensington, 1976. Adapted for a Harris/7 computer by A. D. Rae, University of Wisconsin, Madison, 1983.

(18) Rae, A. D. *Acta Crystallogr.* **1975**, *A31*, 570–574.

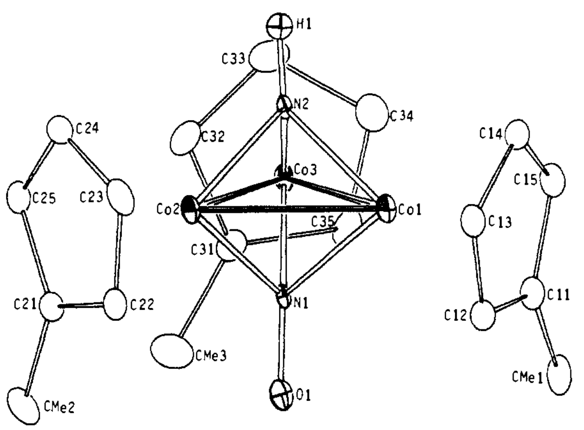

Figure 2. Molecular configuration of the crystal-ordered $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ molecule (Vb) which ideally possesses a vertical mirror plane passing through Co1, the NO and NH capping ligands, and the middle of the Co2–Co3 bond. The notable exception to this bilateral symmetry is the Co1-attached C_5H_4Me ligand with the methyl substituent rotated off the mirror plane by 36°.

Results and Discussion

Synthesis, Characterization, and Reactivity of Va and Vb. The toluene-soluble 49-electron $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ clusters ($x = 0$, Va; $x = 1$, Vb) are easily synthesized by treatment of the respective 48-electron monocations (IIIa and IIIb) in THF with a stoichiometric quantity of the reducing agent cobaltocene. Shown in Figure 1 is a cyclic voltammogram of the one-electron oxidation of Vb to IIIb in CH_2Cl_2. This voltammogram displays a 59-mV ΔE_p separation and essentially identical anodic and cathodic peak currents which substantiate the Nerntzian one-electron process for the reverse 48- to 49-electron reduction.

Reactions of IIIa or IIIb with $NaHBEt_3$ were carried out under the premise that either deprotonation to give (μ_3-N) or NO activation to give (μ_3-NOH) may initially occur with the resulting species possibly undergoing additional ligand transformations. Proton NMR spectra of the products of these reactions had no discernible resonances, indicating the formation of paramagnetic species. Furthermore, IR spectra showed that the nitrosyl bands were shifted to lower frequencies by ca. 50 cm^{-1} relative to the nitrosyl bands of the monocations. The same products resulted upon reactions of IIIa and IIIb with *n*-BuLi. It was then concluded from these spectral measurements that one-electron reductions of IIIa and IIIb to the 49-electron Va and Vb, respectively, had taken place.

Since previous work[20] showed that the (μ_3-NO) ligand in $Mn_3(\eta^5\text{-}C_5H_4Me)_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NO)$ undergoes protonation to give the $[Mn_3(\eta^5\text{-}C_5H_4Me)_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NOH)]^+$ cation, similar electrophilic additions to the (μ_3-NO) ligand in Va were attempted. However, reactions of Va with methyl iodide and $HBF_4\cdot Et_2O$ resulted in the oxidation of Va to IIIa.

Structural Features of the Reduced Vb. The molecular architecture of Vb (shown in Figure 2) lacks crystallographically imposed symmetry. This neutral compound crystallizes with two crystallographically independent molecules in the unit cell. The molecule shown in Figure 2 is "well-behaved" with normal atomic thermal ellipsoids, but the other independent molecule displays a previously described crystal disorder. The crystal-ordered species ideally conforms to a C_s—m geometry with the pseudo-vertical-mirror plane passing through Co1, the two tricapping ligands, and the midpoint of the Co2–Co3 bond. The notable exception to this approximate bilateral molecular symmetry is the Co1-coordinated C_5H_4Me ring, whose methyl substituent is rotated off of the psuedomirror by ca. 36° (Figure 2). Hence, the geometry of the tricobalt core of the ordered molecule closely approximates an isosceles triangle with one considerably larger Co–Co bond bisected by the pseudomirror plane and two mirror-related shorter Co–Co bonds.

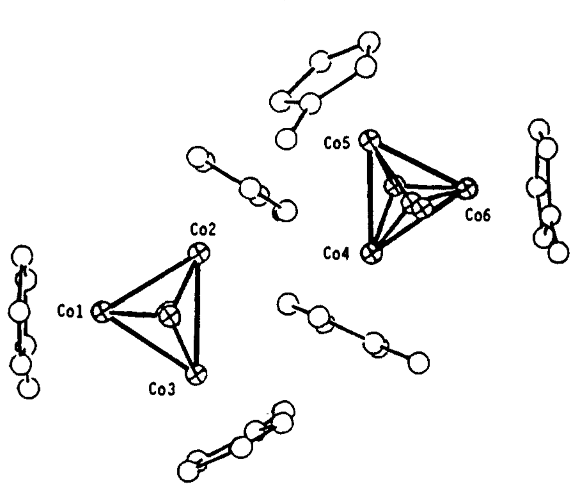

Figure 3. A view normal to the *b* axis of the relative orientations of the independent crystal-ordered molecule (Co1, Co2, Co3) and the independent crystal-disordered molecule (Co4, Co5, Co6) which has been refined as an averaged structure. The two independent molecules, which are related by an average center of symmetry, pack in a pseudohexagonal arrangement. The crystal-disordered molecule (Co4, Co5, Co6) is presumed to arise from a nonrandom distribution of an ordered molecule in two orientations due to a mirror-disordered plane passing through the midpoint of the normal Co5–Co6 bond and the averaged position of Co4.

The crystal-disordered molecule appears to arise from the non-superposition of two ordered molecules related by a false mirror plane which bisects one of the two shorter Co–Co bonds (viz., Co5–Co6) instead of the longer Co–Co bond. The result of this mirror-generated crystal disorder is that the other shorter and the longer Co–Co bonds (viz., Co4–Co5 and Co4–Co6) are noncoincident in an averaged structure. Although the resulting Co4–Co5 and Co4–Co6 distances (Table II) indicate that the crystal disorder is not an equal composite of the two orientation difference maps, the C_5H_4Me ligands in the averaged structure have the same relative orientations of their methyl substituents with respect to the false mirror plane as those in the ordered molecule (Figure 3).

The false mirror planes for the two molecules are rotated by 120° with respect to each other. In addition, there is a pseudocenter of symmetry at ca. $b/4$ which approximately relates the two independent molecules. The above observations, in addition to the observed lattice parameters, point to a pseudohexagonal packing for this crystal structure.

Experimental-Theoretical Analyses of 49-Electron Triangular Metal Clusters: (a) Previously Determined Species and Resulting Bonding Implications Concerning the Nature of the HOMO. An elucidation of the electronic structures of 49-electron bicapped trimetal clusters has been a major interest for a considerable period of time.[1-3,6,21-25] In their discussion of the bonding in $Co_3(CO)_9(\mu_3\text{-}S)$, Strouse and Dahl[21] proposed that the unpaired electron in the related Fischer–Palm 49-electron $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ cluster[25] is also contained in an in-plane nondegenerate trimetal antibonding orbital (of a_2' representation under D_{3h} symmetry). An operational test of this hypothesis was performed by the synthesis and X-ray crystallographic determinations of the 48-electron crystal-disordered $CoNi_2(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ and the corresponding crystal-ordered $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$, in which formal removal of the unpaired electron

---

(19) Johnson, C. K. *ORTEP-II, A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*; ORNL-5138, Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(20) Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727–3728.

(21) Strouse, C. E.; Dahl, L. F. *Discuss. Faraday Soc.* **1969**, *47*, 93–106.

(22) (a) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1229–1236. (b) Stevenson, D. L.; Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6027–6031.

(23) Strouse, C. E.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6032–6041.

(24) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456–3467.

(25) Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725–1731.

is achieved by the insertion of a cobalt atom in place of one nickel atom.[26] The virtually identical, highly significant decreases (of 0.031 and 0.033 Å) in the mean metal–metal distances of the 48-electron cobalt-dinickel clusters from that in the 49-electron Fischer–Palm cluster provided convincing evidence that the unpaired electron in the $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ parent is in a trimetal antibonding orbital. Further experimental analysis of the nature of the HOMO in the paramagnetic Fischer–Palm molecule involved the synthesis and stereochemical characterization of its 50-electron monoanion (in which the a_2' HOMO is filled) and of the 49-electron $[(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2]^-$ monoanion.[27] The nondegeneracy of the HOMO in the 50-electron trinickel Fischer–Palm monoanion (of idealized D_{3h} geometry) was demonstrated from magnetic susceptibility measurements at room temperature which showed the monoanion to be diamagnetic.[27] The cobalt–dinickel core of the 49-electron monoanion expectedly enlarged from the distorted C_{2v} core in the neutral parent to give equivalent Co–Ni and Ni–Ni distances which are experimentally the same as the symmetry-equivalent Ni–Ni distances in $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. The a_2' HOMO assignment of the unpaired electron from "experimental quantum mechanics" in these 49-electron systems is in agreement with theoretical MO treatments by Schilling and Hoffmann[24] and recently by Rives, You, and Fenske.[28]

In contrast, a comparative structural-bonding analysis of the bicapped 49-electron $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2]^+$ monocation (as the iodide salt), its neutral 50-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$ parent, and the 48-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$ by Frisch and Dahl[9] in 1972 furnished conclusive evidence that the unpaired electron in the 49-electron bis(sulfido-capped) tricobalt monocation occupied a doubly degenerate e′ MO (under D_{3h} symmetry) of trimetal antibonding character. This interpretation was based upon the following: (1) the Co_3S_2 core in the monocation being drastically distorted from D_{3h} symmetry toward C_{2v} symmetry with one *short* Co–Co distance of 2.474 (2) Å and two *long* Co–Co distances of 2.649 (1) Å; and (2) the mean Co–Co distance of 2.591 Å in the 49-electron monocation being 0.10 Å shorter than the symmetry-equivalent Co–Co distances of 2.687 (3) Å in the 50-electron neutral parent,[29–33] thereby indicating that an electron has been removed from a trimetal antibonding MO. A verification that this observed C_{2v} deformation in the Co_3S_2 core of the 49-electron monocation is electronically induced instead of being a consequence of crystalline packing effects was shown from an X-ray crystallographic determination of this same monocation as the hexafluorophosphate salt.[34] An analogous C_{2v} distortion was observed for the Co_3S_2 core with one short Co–Co bond length of 2.517 (4) Å and two long Co–Co bond lengths of 2.642 (3) Å. To date, this 49-electron bis(sulfido-capped) tricobalt cluster is the only example in which the unpaired electron occupies a HOMO of degenerate e′ symmetry under assumed D_{3h} symmetry. Molecular orbital calculations by Rives, You, and Fenske[28] on the 50-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$ showed the partially filled levels of the frontier a_2' and e′ orbitals to be very close in energy. On the basis of experimental data they proposed a triplet $^3E'$ $(a_2'^1e'^1)$ ground state for the 50-electron parent cluster at room temperature and a ^2E (e'^1) ground state for its 49-electron monocation. Their MO diagram for the (mixed ligand)-bicapped 48-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$ likewise showed the

Table III. Comparison of Distances (Å) and Bond Angles (deg) for $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ (IIIb)[a] and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (Vb)

	IIIb	Vb
Co–Co′	2.391 (2)	2.426 (3)
	2.399 (3)	2.414 (3)
	2.428 (3)	2.554 (3)
mean Co–Co′	2.406[b]	2.465[b]
mean Co–NH	1.835[b]	1.819[b]
mean Co–NO	1.869[b]	1.876[b]
mean Co–Cp′[c]	1.69[b]	1.73[b]
Co–N(H)–Co′	82.9 (4)	82.7 (5)
	80.9 (4)	84.0 (6)
	82.0 (4)	89.2 (5)
mean Co–N(H)–Co′	81.9[b]	85.3[b]
Co–N(O)–Co′	81.6 (4)	79.7 (5)
	79.0 (4)	80.9 (5)
	79.8 (4)	85.9 (5)
mean Co–N(O)–Co′	80.1[b]	82.2[b]
N–O	1.249 (11)	1.230 (15)

[a] $[BPh_4]^-$ salt, ref 8. [b] Means are calculated under assumed C_{3v} symmetry. [c] Cp′ denotes the centroid of the C_5H_4Me ring.

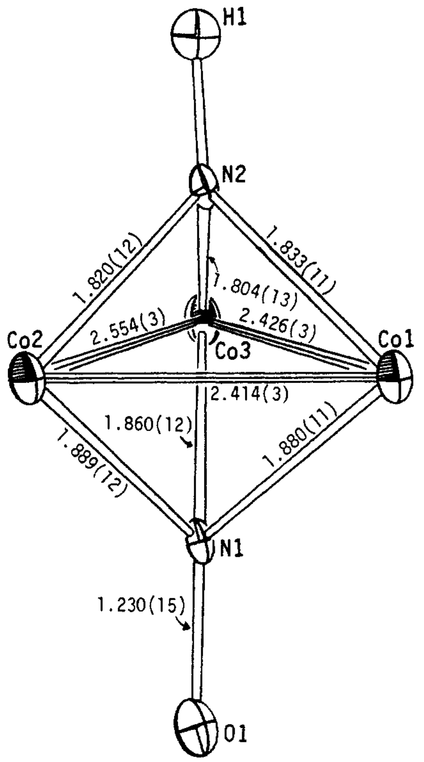

Figure 4. The Co$_3$(NO)(NH) core for the crystal-ordered molecule of the 49-electron $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (Vb). This core, which contains an isosceles cobalt triangle with *one* longer and *two* shorter Co–Co bonds, experimentally conforms to vertical mirror symmetry. The position of the hydrogen atom was determined from an electron-density difference map.

---

(26) Byers, L. R.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1981**, *103*, 1942–1951.

(27) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054–3063.

(28) Rives, A. B.; You, X.-Z.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286–2294.

(29) The 50-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$, which has two unpaired electrons at room temperature, undergoes a solid-state phase transition at 192 K, at which this paramagnetic cluster becomes diamagnetic.[30] Crystal structures of the room temperature phase and the low-temperature phase (at 130 K) were determined from X-ray diffraction measurements by Kamijo and Watanabē.[31] For the room temperature hexagonal crystals (which likewise were twinned) they invoked the same twinning model originally developed by Wei[32] and utilized in our laboratories to unravel and refine the crystal structures of the isostructural 53-electron $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$[33] and 48-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$[11] as well as the 50-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$[9] and 48-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$.[9] Their refined molecular parameters (including the independent Co–Co distance of 2.691 (4) Å for $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$, which has C_{3h}–$3/m$ site symmetry, are equivalent within experimental error to those obtained by Frisch and Dahl.[9] The low-temperature crystal structure of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$ was found by Kamijo and Watanabē[31] to be a twinned hexagonal superstructure of the room temperature modification. The Co_3S_2 core of C_1-1 site symmetry was determined from a bounded Fourier projection to be distorted from a regular D_{3h} geometry.

(30) Sorai, M.; Kosaki, A.; Suga, H.; Seki, S.; Yoshida, T.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2364–2371.

(31) Kamijo, N.; Watanabē, T. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2537–2542.

(32) (a) Wei, C. H.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 4792–4793. (b) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384–2397.

(33) Vahrenkamp, H.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1968**, *90*, 3272–3273.

(34) Teo, B. K. Ph.D. Thesis, University of Wisconsin—Madison, 1973.

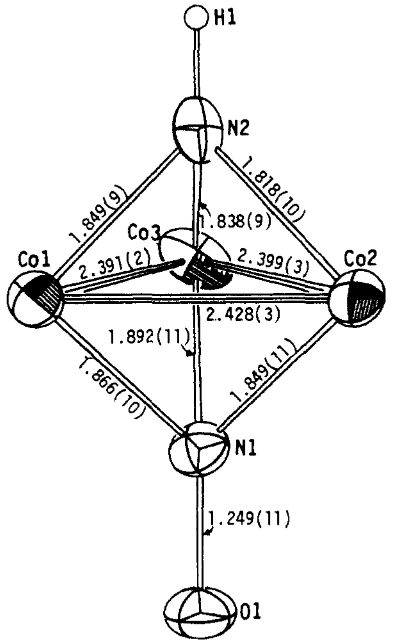

Figure 5. The $Co_3(NO)(NH)$ core of the 48-electron $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (IIIb) (as the $[BPh_4]^-$ salt; ref 8). This core, which contains a nearly equilateral cobalt triangle with three Co–Co bonds, approximates C_{3v}—$3m$ symmetry. The position of the hydrogen atom was ascertained from an electron-density difference map.

corresponding unoccupied a_2 and e levels (under assumed C_{3v} symmetry) to be nearly degenerate in energy. They also emphasized that the determined energy-level ordering in the MO correlation diagrams of the bicapped trimetal clusters are largely a consequence of the filled π-donor S-capped orbitals destabilizing the frontier e′ and e″ Mo's and of the empty π-acceptor OC-capped orbitals stabilizing them.

(b) Comparative Analysis of the Geometries of the 48/49-Electron $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^{1+,0}$ Series and Resulting Bonding Implications. (1) General. The one-electron reduction of the 48-electron monocation IIIb to the neutral 49-electron Vb gives rise to a significant distortion in the distances between the cobalt atoms and a small but noticeable increase in the Co–C(ring) distances for two of the three C_5H_4Me ligands in the ordered molecule. The overall distortion of the $Co_3(NO)(NH)$ core represents a clear-cut change from an idealized C_{3v}–$3m$ geometry to an idealized C_s—m geometry. The following detailed comparison of selected distances and bond angles (Table III) between IIIb and Vb is based upon the molecular parameters of the crystal-ordered Vb molecule (Figures 4 and 5).

(2) Co–Co Distances. Although the observed variations among the three Co–Co distances in IIIb indicate a small geometrical distortion from an equilateral triangle toward an isosceles triangle, the mean difference of 0.033 Å is not uncommon for other related 48-electron triangular metal clusters; hence, in this comparison, the $Co_3(NO)(NH)$ core in IIIb is assumed to conform to C_{3v} symmetry. This idealized equilateral cobalt triangle in IIIb undergoes a large distortion in Vb to an isosceles triangle with one *longer* Co–Co distance of 2.554 (3) Å and two *shorter* Co–Co distances of 2.414 (3) and 2.426 (3) Å. The *mean* Co–Co bond length of 2.465 Å in Vb is 0.059 Å longer than that of 2.406 Å in IIIb. The *mean* Co–Co distance of 2.461 Å for the averaged structure of the crystal-disordered molecule of Vb is virtually the same as that for the crystal-ordered molecule.

These reduction-induced geometrical changes are entirely consistent with the unpaired electron in Vb occupying the doubly degenerate e HOMO (under C_{3v} symmetry) which triggers a vibronic Jahn–Teller distortion of the equilateral metal triangle to the observed isosceles metal triangle. Since the alternative accommodation of the unpaired electron in the a_2 HOMO would lead to a simple dilation of the equilateral metal triangle (without distortion), this latter electronic configuration can be ruled out. On the basis of the observed distortion with the mean value of 2.420 Å for the two equivalent shorter Co–Co distances in Vb being only 0.014 Å longer than the mean Co–Co distance in IIIb but with the third Co–Co distance being 0.148 Å longer, it is evident that the unpaired electron in Vb is essentially localized on the two cobalt atoms associated with the longer Co–Co distance.

(3) Co–C_5H_4Me(centroid) Distances. The particular changes in these Co–Cp′ distances between IIIb and Vb also reflect localization of the unpaired electron on only two of the three cobalt atoms in Vb. The observed identical Co–Cp′ distances of 1.74 Å for the two cobalt atoms associated with the long Co–Co distance are significantly longer than the third Co–Cp′ distance of 1.71 Å in Vb and 0.05 Å longer than the mean value of 1.69 Å for the three Co–Cp′ distances in IIIb. This geometrical change provides persuasive evidence for there being significant antibonding character between the two cobalt atoms and their attached C_5H_4Me ligands in the HOMO of Vb.

(4) Co–(Ligand-Capped) Distances. The mean distances between the cobalt atoms and the (μ_3-NH) and (μ_3-NO) ligands do not show significant variations (viz., −0.016 and +0.007 Å, respectively) as a result of the one-electron reduction of IIIb to Vb. The relative constancy of these distances suggests that the HOMO containing the unpaired electron in Vb is largely composed of in-plane tricobalt d AO components which do not interact appreciably with the π-donor orbitals of the HN-capped ligand and the π-acceptor orbitals of the ON-capped ligand.

(5) Nature of the Half-Filled HOMO in Vb. A first-order Jahn–Teller distortion of the C_{3v} $Co_3(NO)(NH)$ core in Vb to a C_s—m geometry is vibronically allowed in order to lift the orbital degeneracy of the ^2E ground state due to the unpaired electron occupying an e MO under C_{3v} symmetry. Under the lower C_s symmetry, the e representation splits into an a′ and a″ set. The directional nature of the geometrical distortion, in which the unpaired electron is localized in an antibonding orbital combination between two cobalt atoms (thereby preferentially lengthening only one Co–Co bond), necessitates that the unpaired electron occupies the a″ MO which is antisymmetric with respect to the mirror plane.

From a valence-bond viewpoint, the metal–metal interactions (which in these triangular metal systems are particularly weak compared to metal–ligand interactions[28]) may be described in terms of a metal–metal bond order per pair of metal atoms. Under this representation of the metal–metal bonding, each of the metal–metal interactions in the equilateral metal triangle of the 48-electron IIIb corresponds to a bond order of 1.0. Localization of the added antibonding electron between only two cobalt atoms in the 49-electron Vb to give an isosceles metal triangle with one lengthened side and two essentially unaltered sides corresponds to a decrease in metal–metal bond order for only the long side to a value of 0.5.

The addition of a second electron to the a″ HOMO, which is presumed to be an experimentally accessible process based upon a cyclic voltammogram of IIIb exhibiting a second reversible one-electron reduction to give the 50-electron monoanion, would result in a nonbonding Co–Co distance with the other two Co–Co distances essentially unchanged. Crystallographically determined examples of such 50-electron triangular metal clusters possessing two bonding sides (each with bond order 1.0) and one nonbonding side (with bond order 0.0) include $Fe_3(CO)_9(\mu_3\text{-}X)_2$ (where X = S,[35] Se,[36] Te[37]), $Fe_3(CO)_9(\mu_3\text{-}NMe)_2$,[38] $Fe_3(CO)_9(\mu_3\text{-}AsPh)_2$,[39]

---

(35) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 493–499.

(36) Dahl, L. F.; Sutton, P. W. *Inorg. Chem.* **1963**, *2*, 1067–1069.

(37) Nelson, L. L. Ph.D. Thesis, University of Wisconsin—Madison, 1981.

(38) Doedens, R. J. *Inorg. Chem.* **1969**, *8*, 570–574.

(39) (a) Huttner, G.; Mohr, G.; Frank, A.; Schubert, U. *J. Organomet. Chem.* **1976**, *118*, C73–C77. (b) Jacob, M.; Weiss, E. *J. Organomet. Chem.* **1977**, *131*, 263–271.

Table IV. Structural Comparison of the Trimetal Frameworks for the $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^n$ Series (n = 1+, IIIb; n = 0, Vb) and Resulting Bonding Implications Concerning the Nature of the HOMO for Analogous 49- and 50-Electron Series

series	ref	no. of valence electrons	crystallographic site symmetry	framework idealized geometry	M–M′ distances (Å)	mean M–M′ distance	assumed HOMO[a]
$[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$	*b*	48	C_1—1	C_{3v}	[3] 2.406	2.406	
$Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$	*c*	49	C_1—1	C_s—*m*	[2] 2.420 [1] 2.554	2.465	e'^1
$[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2]^+$	*d*	49	C_s—*m*	C_{2v}	[2] 2.649 [1] 2.474	2.591	e'^1
$[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2]^+$	*e*	49	C_s—*m*	C_{2v}	[2] 2.642 [1] 2.517	2.600	e'^1
$Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$	*f*	50	C_{3h}—3/*m*	D_{3h}	[3] 2.687	2.687	e'^2
$CoNi_2(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$	*g*	48	C_{3h}—3/*m*	D_{3h}	[3] 2.358	2.358	
$Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$	*h*	49	C_{3h}—3/*m*	D_{3h}	[3] 2.389	2.389	$a_2'^1$
$[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2]^-$	*i*	50	C_1—1	D_{3h}	[3] 2.421	2.421	$a_2'^2$
$Co(\eta^5\text{-}C_5Me_5)Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$	*j*	48	C_1—1	C_{2v}	[2] 2.371 [1] 2.326	2.358	
$[Co(\eta^5\text{-}C_5Me_5)Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2]^-$	*k*	49	C_1—1	C_{2v}	[2] 2.391 [1] 2.388	2.390	$a_2'^1$
$Co_2Fe(CO)_9(\mu_3\text{-}S)$	*l*	48	C_1—1	C_{3v}	[3] 2.554	2.554	
$Co_3(CO)_9(\mu_3\text{-}S)$	*m*	49	C_1—1	C_{3v}	[3] 2.637	2.637	$a_2'^1$
$Co_2Fe(CO)_9(\mu_3\text{-}Se)$	*n*	48	C_1—1	C_{3v}	[3] 2.577	2.577	
$Co_3(CO)_9(\mu_3\text{-}Se)$	*o*	49	C_1—1	C_{3v}	[3] 2.616	2.616	$a_2'^1$

[a] Assumed D_{3h} symmetry. [b] $[BPh_4]^-$ salt, ref 8. [c] This work. [d] I^- salt, ref 9. [e] $[SbF_6]^-$ salt, ref 34. [f] Reference 9 and 31. [g] Reference 26. [h] Reference 26. [i] [K(2,2,2)-crypt)]$^+$ salt, ref 27. [j] Reference 26. [k] [K(2,2,2-crypt)]$^+$ salt, ref 27. [l] Reference 22b. [m] Reference 22a. [n] Reference 23. [o] Reference 23.

and $Fe_3(CO)_9(\mu_3\text{-}NR)(\mu_3\text{-}S)$ (where R = *p*-MeC_6H_4).[40]

Comparative Structure–Bonding Relationships of the 48-Electron (IIIb)/49-Electron (Vb) Series with Other 48-Electron/49-Electron and 49-Electron/50-Electron Series. Table IV gives a structural comparison of the trimetal frameworks for monocapped and bicapped triangular metal series containing 49-electron species. The observed variations in the mean metal–metal distances which arise from populating or depopulating the HOMO containing the unpaired electron in a 49-electron system range from 0.031 to 0.091 Å. Hence, the increase of 0.059 Å in the mean Co–Co distance of IIIb upon reduction to the 49-electron Vb is consistent with the observed changes of metal–metal distances in other series.

Table IV reveals that the only two series for which the 49-electron system has been shown to have a doubly degenerate HOMO (under threefold symmetry) are the 48/49-electron IIIb, Vb series and the 50/49-electron $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2]^n$ series (n = 0, 1+).[9] Both of these 49-electron systems undergo Jahn–Teller distortions to give isosceles metal triangles, but upon examination of Table IV it is seen that their distorted geometries are not analogous. In the 49-electron Vb there are *one* longer and *two* shorter Co–Co bonds, whereas in the 49-electron $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2]^+$ monocation there are *one* shorter and *two* longer Co–Co bonds. On the basis of this inverse distortion of the isosceles metal triangle, it is apparent that the nature of the HOMO in each of the two systems is different, one being antisymmetric with respect to the vertical mirror plane and the other being symmetric. It is tempting to speculate as to the origins of the opposite distortions for the two tricobalt clusters. There are two differences in terms of ligation between these two 49-electron species, viz., Ib possesses C_5H_4Me as opposed to the C_5H_2 ligands for the disulfido-capped system and Vb has a mixed π-acceptor and π-donor pair of capped ligands as opposed to the two π-donor ligands in the bis(sulfido-capped) monocation. An operational test to determine whether the C_5H_4Me ligands play an important role in dictating the type of isosceles metal triangle formed would involve the isolation and crystallographic characterization of the 49-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (Va) (with the hope that twinning-disorder problems would not arise).

Further examination of Table IV reveals that, except for the above two series, the other bicapped triangular metal series possess *two* π-acceptor OC-capped ligands. Since theoretical calculations[28] on several series of bicapped trimetal clusters showed (under D_{3h} symmetry) that two π-acceptor OC-capped ligands greatly stabilize the e′ and e″ MOs relative to the nondegenerate frontier a_2' MO whereas two π-donor S-capped ligands greatly destabilize these two sets of doubly degenerate MOs, it is clear that at least one or two π-donor (nonhybridized) capped ligands, such as (μ_3-NR) or (μ_3-S), are necessary for the unpaired electron in a 49-electron system to occupy a doubly degenerate HOMO, which thereby gives rise to a significantly deformed isosceles metal triangle. Current work in our laboratories involves systematic studies of the redox chemistry and structural-bonding features of the related $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}S)_2]^n$ series (n = 0, 1+, 2+)[41] and the $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)_2]^n$ series (x = 0, 1; n = 1−, 0, 1+).[42]

Acknowledgment. This research was generously supported by the National Science Foundation. One of us (R.L.B.) is pleased to acknowledge Owens-Corning Fiberglas Corp. (Technical Center: Granville, Ohio) for providing a Research Fellowship during September 1983–August 1984.

Registry No. IIIa, 103201-01-0; IIIb, 103201-03-2; Va, 103190-60-9; Vb, 103201-02-1; $NaBHEt_3$, 17979-81-6; Co, 7440-48-4; cobaltocene, 1277-43-6.

Supplementary Material Available: Tables presenting the atomic parameters and selected least-squares planes for the reduced $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)$ (6 pages); table of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

---

(40) Meij, R.; Stufkens, D. J.; Vrieze, K.; Brouwers, A. M. F.; Schagen, J. D.; Zwinselman, J. J.; Overbeek, A. R.; Stam, C. H. *J. Organomet. Chem.* **1979**, *170*, 337–354.

(41) (a) Pulliam, C. R.; Englert, M. H.; Dahl, L. F. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, Illinois, Sept. 8–13, 1985; American Chemical Society: Washington, DC, 1985. (b) Pulliam, C. R.; Englert, M. H.; Dahl, L. F., to be published.

(42) (a) Kubat-Martin, K. A.; Rae, A. D.; Dahl, L. F. *Organometallics* **1985**, *4*, 2221–2223. (b) Kubat-Martin, K. A.; Barr, M. E.; Spencer, B.; Dahl, L. F., to be published.