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Synthesis, Stereochemical Analysis, and Ligand-Transformation Reactions of New Classes of Bicapped Tricobalt Clusters, $[\mathrm{Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)}]^n$ (x = 0, 1, 5), Containing Mixed π-Acceptor X and π-Donor Y Capping Ligands (X = CO, NO; Y = $\mathrm{NSiMe_3}$, $\mathrm{NC(O)NH_2}$, NH): A Rational Preparative Route to Nitrene (μ_3-NH) Clusters and the Unprecedented Direct Exchange of an Isoelectronic μ_3-$\mathrm{NO^+}$ Ligand for a μ_3-CO Ligand

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Abstract: The initial objective of this work was to prepare triangular metal clusters with capping $\mathrm{NSiMe_3}$ ligands and to use these clusters in subsequent ligand transformation reactions involving N–Si bond cleavage in order to produce an unprecedented "bare" pyramidal nitrido (μ_3-N) cluster as well as to generate a high-yield pathway to nitrene (μ_3-NH) clusters. The reactions of trimethylsilyl azide with $\mathrm{Co(\eta^5\text{-}C_5H_{5-x}Me_x)(CO)_2}$ (x = 0, 1, 5) furnished the desired OC, $\mathrm{Me_3SiN}$-bicapped $\mathrm{Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)}$ clusters (x = 0, Ia; x = 1, Ib) and unexpectedly gave the OC, formamidonitrene-bicapped $\mathrm{Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)}$ cluster (IV) and OC, HN-bicapped $\mathrm{Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)}$ cluster (IIc); the isolation of the nitrene-capped IIc rather than the $\mathrm{Me_3SiN}$-capped $\mathrm{Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)}$ cluster was attributed to intramolecular steric effects of the bulky pentamethylcyclopentadienyl ligands. The nitrene-capped $\mathrm{Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)}$ clusters (x = 0, IIa; x = 1, IIb) were subsequently obtained in >90% yields by cleavage of the N–Si bond with fluoride ion. Attempted oxidations of Ia and Ib with $\mathrm{NOBF_4}$ instead gave rise in quantitative yields to the ON, HN-bicapped $[\mathrm{Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)}]^+$ monocations (x = 0, IIIa; x = 1, IIIb); the formation of IIIa and IIIb involves both a N–Si bond cleavage of the μ_3-$\mathrm{NSiMe_3}$ ligand by the tetrafluoroborate anion to form the μ_3-NH ligand and a "simple" substitution of an isoelectronic μ_3-$\mathrm{NO^+}$ ligand for the μ_3-CO ligand. This unprecedented exchange (presumably via an association mechanism) of a $\mathrm{NO^+}$ capping ligand for a CO capping ligand was also shown to occur quantitatively when the OC, HN-bicapped clusters, IIa and IIb, were reacted with $\mathrm{NOBF_4}$. However, the HN-capped ligands in IIa and IIb were resistant to attempted hydrogen atom extraction and deprotonation transformations. Characterization of these 48-electron $\mathrm{Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)}$ clusters with mixed π-acceptor X and π-donor (nonhybridized) Y ligands was achieved by IR, ^{1}H NMR, mass spectral, and electrochemical measurements. X-ray diffraction studies were carried out on $\mathrm{Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)}$ (IIc), the $[\mathrm{Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)}]^+$ monocation (IIIb) as the tetraphenylborate salt, and the novel formamidonitrene-capped $\mathrm{Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)}$ (IV). A comparative structural-bonding analysis of these three clusters allowed a detailed assessment of the relative steric-bonding effects of the terminal $\mathrm{C_5H_{5-x}Me_x}$ ligands (x = 0, 1, 5) and the trimetal-capping ligands on the central $\mathrm{Co_3(\mu_3\text{-}X)(\mu_3\text{-}Y)}$ cores. $\mathrm{Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)}$ (IIc); molecular weight 625.6; monoclinic; $P2_1/m$; a = 10.516 (5) Å, b = 17.859 (9) Å, c = 8.443 (4) Å, β = 111.76 (5)°, V = 1473 (1) Å^3 at 22 °C; d(calcd) = 1.39 g/cm^3 for Z = 2. Anisotropic least-squares refinement (with RAELS) of IIc, which possesses crystallographic C_s—m site symmetry, converged at $R_1(F)$ = 6.50%, $R_2(F)$ = 8.03% for 772 independent reflections ($I > 3\sigma(I)$) with a data-to-parameter ratio of 10.3/1; despite a definite indication from the large elongated atomic thermal ellipsoids of a pronounced rotational-type crystal disorder of the $\mathrm{C_5Me_5}$ rings, the normal atomic thermal ellipsoids observed for the $\mathrm{Co_3(CO)(NH)}$ core are consistent with its reasonable molecular parameters which closely comply with C_{3v} symmetry. $[\mathrm{Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)}]^+[\mathrm{BPh_4}]^-$ ($[\mathrm{IIIb}]^+[\mathrm{BPh_4}]^-$): formula weight 764.4; monoclinic; $P2_1/c$; a = 11.092 (3) Å, b = 10.666 (5) Å, c = 30.022 (12) Å, β = 94.70 (3)°, V = 3540 (2) Å^3 at −30 °C; d(calcd) = 1.44 g/cm^3 for Z = 4. Anisotropic least-squares refinement of $[\mathrm{IIIb}]^+[\mathrm{BPh_4}]^-$ converged at $R_1(F)$ = 6.73%, $R_2(F)$ = 6.98% for 2239 independent reflections ($I > 3\sigma(I)$) with a data-to-parameter ratio of 8.2/1. $\mathrm{Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)}$ (IV): molecular weight 500.2; monoclinic; $P2_1/c$; a = 9.204 (4) Å, b = 15.165 (4) Å, c = 14.267 (5) Å, β = 98.87 (3)°, V = 1968 (1) Å^3 at −50 °C; d(calcd) = 1.66 g/cm^3 for Z = 4. Anisotropic least-squares refinement converged at $R_1(F)$ = 3.24; $R_2(F)$ = 4.09% for 3392 reflections ($I > 3\sigma(I)$) with a data-to-parameter ratio of 13.9/1.

Prior to the work described herein, only a limited number of triangular metal cyclopentadienyl clusters possessing triply bridging organonitrene (μ_3-NR)[2-4] or nitrene (μ_3-NH)[5,6] ligands have been reported. Our interest in this area was stimulated by a study of Abel, Blackmore, and Whitley,[4] who described the high-yield syntheses of $\mathrm{Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)}$, $\mathrm{Rh_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)}$, and $\mathrm{Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)}$ by reaction of $\mathrm{SiMe_3N_3}$ with $\mathrm{Co(\eta^5\text{-}C_5H_5)(CO)_2}$, $\mathrm{Rh_3(\eta^5\text{-}C_5H_5)_3(\mu_2\text{-}CO)_3}$, and $\mathrm{Ru_3(CO)_{12}}$, respectively. Their synthetic strategy, originally used by Koerner von Gustorf

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and Wagner[3a] to produce $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ from $Fe_2(CO)_9$, resulted in 50–60% yields of the Me_3SiN-capped tricobalt and trirhodium products.

We noted the possibility of reactivity within the (μ_3-$NSiMe_3$) part of these clusters. Our initial objective was the synthesis of unprecedented pyramidal nitrido (μ_3-N) clusters via heterolytic N–Si bond cleavage with reagents such as the fluoride anion. Another goal was the rational synthesis of nitrene (μ_3-NH) clusters by N–Si bond cleavage with concomitant protonation. Only a few such complexes[4,5] had been previously obtained and those only in relatively low yields; of these, structural determinations had been carried out on the 48-electron $FeCo_2(CO)_9(\mu_3\text{-}NH)$,[5b] the 48-electron $[Mn_3(\eta^5\text{-}C_5H_4Me)_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NH)]^+$ monocation,[6] and the 48-electron $W_3(O\text{-}i\text{-}Pr)_6(\mu_2\text{-}O\text{-}i\text{-}Pr)_3(\mu_3\text{-}O\text{-}i\text{-}Pr)(\mu_3\text{-}NH)$.[7]

Since prior electrochemical investigations of other X,Y-bicapped $M_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)$ clusters ($M_3 = CoNi_2$, X = Y = CO;[8] $M_3 = Ni_3$, X = Y = CO;[9,10] $M_3 = Co_3$, X = Y = CR;[11a] $M_3 = Co_3$, X = Y = CPh;[11b] $M_3 = Co_3, Ni_3$, X = Y = S;[10] $M_3 = Co_3$, X = S, Y = CS[10]) revealed that these triangular metal systems have a rich redox chemistry, it was presumed that (mixed ligand)-capped $M_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NR)$ The fact that no electrochemical measurements had been performed on RN-capped molecules provided a special incentive to explore their electrochemical reactivity, with one major goal being the isolation of oxidized and/or reduced species for comparative structural-bonding analysis. Our initial observation that cyclic voltammetric measurements of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ (Ia) exhibited one reversible oxidation (as well as one reversible reduction) led to attempts to oxidize this cluster by chemical means. However, when $NOBF_4$ was used as an oxidant, Ia was not oxidized but instead underwent a remarkable reaction to form a new bicapped triangular metal cluster, the 48-electron $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (IIIa), which was isolated in essentially quantitative yield. Our belief that the simple replacement of a μ_3-CO ligand by an isoelectronic μ_3-NO^+ ligand would be independent of the concomitant transformation of the μ_3-$NSiMe_3$ ligand into a μ_3-NH ligand by its reaction with the tetrafluoroborate anion was substantiated by the subsequent quantitative preparation of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIa) by reaction of Ia with the fluoride anion. In turn, IIa was quantitatively converted into the desired nitrosyl-substituted monocation (IIIa) by reaction with $NOBF_4$.

Since a preliminary X-ray crystallographic investigation of the C_5H_5-containing monocation IIIa indicated hexagonal C_{3h}—$3/m$ crystallographic site symmetry which necessitates a crystal disorder of the ON- and HN-capped ligands, our efforts then turned to extending this chemistry to the C_5H_4Me- and C_5Me_5-containing analogues with the hope that subsequent crystallization would lead to ordered crystal structures. The resulting new clusters created opportunities for further electrochemical and structural-bonding studies.

All of our original goals have been accomplished except for the isolation of a cluster containing a "bare" trimetal-coordinated, pyramidal-like nitride ligand. Here we report the results of our systematic explorations involving the reactions of the $Co(\eta^5\text{-}C_5H_{5-x}Me_x)(CO)_2$ monomers (x = 0, 1, 5) with $SiMe_3N_3$, from which $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ (x = 0, Ia; x = 1, Ib), $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV), and $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc) were isolated. Subsequent syntheses of the $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (x = 0, IIa; x = 1, IIb) from the reactions of Ia and Ib with $[(n\text{-}Bu)_4N]^+[F]^-$ and of 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) from the reactions of Ia and Ib with $NOBF_4$ are likewise described. Characterization of these (mixed-ligand)-capped, 48-electron clusters was achieved by infrared, ^1H NMR, and electrochemical measurements coupled with mass spectral and X-ray diffraction analysis of selected compounds. The possible reactivity of the HN-capped nitrene ligand in IIa and IIb with certain reagents including hydrogen atom and proton extractors was examined. Also presented are the details of X-ray diffraction studies of three selected crystal-ordered clusters, viz., $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc), the $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (IIIb) as the tetraphenylborate salt, and the novel formamidonitrene-capped $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV). Of prime importance is that a comparative analysis of these three 48-electron species with one another and with several other related complexes has allowed an assessment of the relative steric-bonding effects of the terminal and trimetal-capped ligands on the structural parameters. Details of a systematic electrochemical investigation of these (mixed ligand)-capped $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]^n$ clusters (x = 0, 1 for X = CO, Y = $NSiMe_3$, n = 0; x = 0, 1, 5 for X = CO, Y = NH, n = 0; x = 0, 1 for X = NO, Y = NH, n = 1+), which exhibit marked redox variations as a function of coordinating ligands, are given in the following paper.[12] Chemical syntheses of the neutral 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) by one-electron reductions of the corresponding monocations IIIa and IIIb with cobaltocene are reported elsewhere[13] together with an X-ray diffraction study of the crystal-ordered C_5H_4Me derivative Vb. The resulting differences found between its redox-generated geometry and that previously determined (and reported herein) for the 48-electron parent (monocation) have allowed an unequivocal assignment (by an experimental differentiation between two possible theoretical choices) of the nature of the HOMO occupied by the unpaired electron for a 49-electron, mixed-ligand system containing both a π-acidic ON-capped and a π-donor HN-capped ligand.

During the period in which this work was in progress, Gladfelter and co-workers reported the syntheses of two trimetal carbonyl nitrene species, $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (in 50% yield) and $FeRu_2(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NH)$, via an entirely different synthetic approach involving protonation reactions of the 62-electron $[Ru_4(CO)_{12}(\mu_4\text{-}N)]^-$ and $[FeRu_3(CO)_{12}(\mu_4\text{-}N)]^-$ monoanions which contain a butterfly-like M_4N core with a five-electron-donating, tetrametal-bridged nitrogen atom.

Experimental Section

General. All manipulations were carried out under dry nitrogen in Schlenk-type glassware with stainless steel cannulas used for transferring solutions and/or in a Vacuum Atmospheres drybox. Reaction solvents were dried over appropriate agents and distilled immediately before use. The $Co(\eta^5\text{-}C_5H_{5-x}Me_x)(CO)_2$ monomers (x = 0, 1, 5) were made by the method of Rausch and Genetti;[15] the C_5Me_5 complex was purified by silica gel chromatography. The reagents $SiMe_3N_3$, $NOBF_4$, CPh_3Br, n-BuLi (1.6 M hexane), $[(n\text{-}Bu)_4N]^+[F]^- 3H_2O$ (Aldrich) and $NaBPh_4$ (Alfa) were used as received. Trityl radical was prepared by the stirring of CPh_3Br with zinc powder in toluene. The $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ (Ia) was made in yields of about 60% by the method of Abel et al.[4] with the modification that the reaction was carried out in hexane within a medium-pressure, thick-walled, glass "pop-bottle". IR spectra were recorded on a Beckman IR-4240 spectrometer, while ^1H FT-NMR spectra were recorded on a Bruker WP-200 spectrometer.

Reaction of $Co(\eta^5\text{-}C_5H_4Me)(CO)_2$ with $SiMe_3N_3$. Isolation and Characterization of $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ (Ib), $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIb), and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV). In a typical reaction $Co(\eta^5\text{-}C_5H_4Me)(CO)_2$ (1.7 mL; 11 mmol) and $SiMe_3N_3$ (1.3 g; 11.3 mmol) were dissolved in

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20 mL of hexane and placed in a glass "pop-bottle" reactor which was then sealed with a rubber-lined steel bottle cap. The bottle was immersed (1 in.) into an oil bath (at 120 °C) for 48 h, after which the solution was transferred to a Schlenk tube. Left behind was a bright green, hexane-insoluble oily residue which was soluble in dichloromethane and acetone. An IR spectrum of this residue exhibited a strong band at 2200 cm^{-1} characteristic of azide or isocyanate ligands, while a ^1H NMR spectrum displayed broad resonances indicative of possible paramagnetism. Attempts to crystallize this green material were unsuccessful.

Purification of the hexane solution, which was reduced in volume and then slowly chromatographed on a SiO_2 column with hexane–toluene mixtures, yielded several products. The first band eluted was unreacted brown $Co(\eta^5-C_5H_4Me)(CO)_2$ (about 0.5 mL), while the second band was the sought-after $Co_3(\eta^5-C_5H_4Me)_3(\mu_3-CO)(\mu_3-NSiMe_3)$ (Ib), isolated in ca. 24% yield. A trace green third band, sometimes isolated after short reaction times, was determined to be $Co_3(\eta^5-C_5H_4Me)_3(\mu_3-CO)(\mu_3-NH)$ (IIb). A fourth band obtained in approximately 5% yield was identified as $Co_3(\eta^5-C_5H_4Me)_3(\mu_3-CO)(\mu_3-NC(O)NH_2)$ (IV).

$Co_3(\eta^5-C_5H_4Me)_3(\mu_3-CO)(\mu_3-NSiMe_3)$ (Ib) was characterized by spectral analysis and by cyclic voltammetry. An IR spectrum (KBr pellet) exhibited a triply bridging carbonyl frequency at 1670 cm^{-1}. A ^1H NMR spectrum ($CDCl_3$) displayed three resonances at δ 4.36 (s, 4 H), δ 1.87 (s, 3 H), and δ 0.77 (s, 3 H) which were readily assigned to 12 ring hydrogens of the three C_5H_4Me rings, the 9 methyl-ring hydrogens, and the 9 methyl-silyl hydrogens, respectively.

$Co_3(\eta^5-C_5H_4Me)_3(\mu_3-CO)(\mu_3-NH)$ (IIb) was likewise analyzed by spectroscopic and electrochemical measurements. An IR spectrum (KBr pellet) gave a strong carbonyl band at 1676 cm^{-1} and a sharp but weak N–H stretching frequency at 3325 cm^{-1}. A ^1H NMR spectrum ($CDCl_3$) exhibited an AA′BB′ pattern at δ 4.41 (m, 2 H) and δ 4.38 (m, 2 H) as well as a methyl ring signal at δ 1.89 (s, 3 H).

The composition of $Co_3(\eta^5-C_5H_4Me)_3(\mu_3-CO)(\mu_3-NC(O)NH_2)$ (IV) was ascertained from an X-ray structural determination (vide infra). An IR spectrum (KBr pellet) gave two strong carbonyl bands at 1687 and 1650 cm^{-1} along with a weak, sharp N–H stretching band at 3480 cm^{-1}. A ^1H NMR spectrum ($CDCl_3$) showed an AA′BB′ pattern at δ 4.49 (m, 2 H) and δ 4.30 (m, 2 H) together wwith a methyl ring resonance at δ 1.87 (s, 3 H); NH_2 proton resonances were not observed.

Reaction of $Co(\eta^5-C_5Me_5)(CO)_2$ with $SiMe_3N_3$: Isolation and Characterization of $Co_3(\eta^5-C_5Me_5)_3(\mu_3-CO)(\mu_3-NH)$ (IIc). In a typical reaction $Co(\eta^5-C_5Me_5)(CO)_2$ (1.18 g; 4.7 mmol) and $SiMe_3N_3$ (0.45 g; 14.1 mmol) were dissolved in 20 mL of hexane and sealed under vacuum in a thick-walled Vycor Carius tube. The tube was placed in a 115 °C oven for 24 h during which time the color of the solution changed from brown to green. The tube was cooled and broken open in a drybox, and the solution was placed into a Schlenk tube. The volume of solution was reduced, and the products were chromatographed on Al_2O_3 with hexane–toluene mixtures. Three bands were eluted, the first being a brown band which was identified as $Co(\eta^5-C_5Me_5)(CO)_2$, the second and major band being the dark green $Co_2(\eta^5-C_5Me_5)_2(\mu_2-CO)_2$, and the third band being the brown $Co_3(\eta^5-C_5Me_5)_3(\mu_3-CO)(\mu_3-NH)$ (IIc).

The composition of $Co_3(\eta^5-C_5Me_5)_3(\mu_3-CO)(\mu_3-NH)$ (IIc), which was obtained in 5–10% yield, was established from spectral and CV measurements coupled with a single-crystal X-ray diffraction study. An IR spectrum (KBr pellet) displayed a strong carbonyl stretching band at 1665 cm^{-1} and a weak, sharp NH stretching band at 3400 cm^{-1}. A ^1H NMR spectrum (benzene-d_6) possessed one resonance at δ 1.67(s) indicative of equivalent C_5Me_5 rings.

Reactions of $Co_3(\eta^5-C_5H_{5-x}Me_x)_3(\mu_3-CO)(\mu_3-NSiMe_3)$ ($x = 0$, Ia; $x = 1$, Ib) with $[(n-Bu)_4N]^+[F]^-\cdot 3H_2O$: Isolation and Characterization of $Co_3(\eta^5-C_5H_{5-x}Me_x)_3(\mu_3-CO)(\mu_3-NH)$ ($x = 0$, IIa; $x = 1$, IIb). Due to the similarity of the reactions by which IIa was obtained from Ia and IIb from Ib, a description of only the former reaction is given. Ia (153 mg; 0.31 mmol) and $[(n-Bu)_4N]^+[F]^-\cdot 3H_2O$ (100 mg; 0.31 mmol) were stirred at room temperature in 50 mL of THF for 12 h. During stirring the color of the solution changed from green-brown to green. After removal of the solvent under vacuum and washing of the residue with toluene, the product was recrystallized from a dichloromethane–diisopropyl ether mixture and isolated in greater than 90% yield. IR, ^1H NMR, and mass spectral data established that this compound was $Co_3(\eta^5-C_5H_5)_3(\mu_3-CO)(\mu_3-NH)$ (IIa). The C_5H_4Me analogue, IIb, was prepared in a similar fashion except that a washing of the crude product was performed with pentane instead of toluene to prevent loss of compound because of its enhanced solubility due to the C_5H_4Me ligands.

An IR spectrum (KBr pellet) of IIa (shown in a figure available as supplementary material) exhibited a strong carbonyl stretching band at 1692 cm^{-1} along with a weak but sharp NH stretching band at 3324 cm^{-1}. An EI mass spectrum, recorded on a Kratos MS-80 spectrometer at low voltage (30 eV), showed a molecular ion peak at m/e 415 together with prominent fragment ion peaks corresponding to the loss of C_5H_5 and/or CO ligands. A ^1H NMR spectrum ($CDCl_3$) displayed one resonance at δ 4.61 (s) indicative of equivalent C_5H_5 rings. Spectral data for IIb are given in a previous section.

Reaction of $Co_3(\eta^5-C_5H_5)_3(\mu_3-CO)(\mu_3-NSiMe_3)$ (Ia) with CsF. Cesium fluoride was thoroughly dehydrated by repeated heating with a heat gun while under high vacuum. The dimethoxyethane solvent was carefully dried by initial treatment with sodium metal followed by treatment with activated molecular sieves (3A) for 12 h, after which it was vacuum-transferred into a dry Schlenk tube. Ia (99 mg; 0.20 mmol) and CsF (30.9 mg; 0.20 mmol) were then added to dimethoxyethane in the drybox, and the resulting solution was stirred for 20 h at 55 °C. A cooling of the solution gave a green crystalline precipitate. A spectral examination of this product, isolated in essentially quantitative yield, clearly identified it as IIa (vide supra).

Attempted Reaction of $Co_3(\eta^5-C_5H_5)_3(\mu_3-CO)(\mu_3-NH)$ (IIa) with Trityl Radical. A treatment of IIa (40 mg; 0.096 mmol) was a stoichiometric quantity of trityl radical (23.4 mg of dimer; 0.096 mmol) in THF at room temperature for 12 h followed by solvent removal and washing with toluene gave a green residue. The fact that IR and ^1H NMR measurements of this residue detected only starting material (IIa) indicated that no reaction had taken place.

Attempted Reactions of $Co_3(\eta^5-C_5H_5)_3(\mu_3-CO)(\mu_3-NH)$ (IIa) with *n*-Butyllithium and Methyl Iodide. IIa (76 mg; 0.18 mmol) was treated with *n*-BuLi (0.114 mL; 0.18 mmol) at −78 °C in THF; no color change occurred when the solution was warmed to room temperature. A spectral analysis of the resulting solid material indicated only the starting cluster (IIa).

An attempt to form the N-methylated $Co_3(\eta^5-C_5H_5)_3(\mu_3-CO)(\mu_3-NMe)$ from IIa by initial treatment of IIa with *n*-BuLi in THF at −78 °C followed by the addition of a stoichiometric amount of MeI was also unsuccessful; the only cluster detected by IR and ^1H NMR spectra was IIa.

Reactions of Ia and Ib with $NOBF_4$: Isolation and Characterization of the $[Co_3(\eta^5-C_5H_{5-x}Me_x)_3(\mu_3-NO)(\mu_3-NH)]^+$ Monocations ($x = 0$, IIIa; $x = 1$, IIIb). Because of the similar reactions by which Ia was converted to IIIa and Ib to IIIb, a description of only the former reaction is given. In a typical reaction Ia (163 mg; 0.34 mmol) and $NOBF_4$ (39 mg; 0.33 mmol) were stirred for 10–12 h at room temperature in 100 mL of dichloromethane. The solution changed color from brown-green to red-brown with concurrent gas evolution during the first 2 to 3 h of the reaction. At the end of the reaction period, the solvent was removed under vacuum and the product washed with toluene to remove a small amount of unreacted starting material (Ia). The product was then extracted with dichloromethane to give a dark red-brown solution. This treatment left a small quantity of a red-brown solid which dissolved in a few milliliters of acetone.

Infrared spectra (KBr pellets) of both the dichloromethane and acetone extracts gave essentially identical absorption bands in the regions of interest (viz., the 1300–1500 and 3300–3400-cm^{-1} ranges). These data combined with ^1H NMR and mass spectral data established the reddish browwn species to be the $[Co_3(\eta^5-C_5H_5)_3(\mu_3-NO)(\mu_3-NH)]^+$ monocation (IIIa) with an unknown anion. It is presumed that the counterion is probably a mixture of at least two anions (e.g., $[BF_4]^-$, F^-, and/or $[HF_2]^-$) because the dichloromethane and acetone extracts possess different solubilities but analogous IR spectra in the triply bridging NO and NH stretching regions.

An IR spectrum (KBr pellet) of IIIa (shown in a figure available as supplementary material) exhibited a sharp NH stretching band at 3310 (w) cm^{-1} and two nitrosyl frequencies at 1452 (vs) and 1410 (m) cm^{-1}; this reproducible two-band nitrosyl pattern is attributed to solid-state interactions which give rise to nonequivalent monocations (due presumably to ion-pair effects involving the nitrosyl ligand). A ^1H NMR spectrum (acetone-d_6) displayed a single resonance at δ 5.23 thereby indicating three equivalent C_5H_5 rings. Infrared laser excited negative and positive ion mass spectra were obtained on a Nicolet FT MS-1000 mass spectrometer for IIIa. The spectra displayed a parent ion peak for IIIa at m/e 417 as well as a fragment ion peak at m/e 387 corresponding to the loss of an NO ligand.

An infrared spectrum (KBr pellet) of the methylcyclopentadienyl analogue (IIIb), which was similarly synthesized, revealed a somewhat different nitrosyl pattern with a sharp band at 1482 (m) cm^{-1} and a broad band at 1445 (vs) cm^{-1} as well as a sharp, clearly identifiable NH stretching band at 3280 (w) cm^{-1}. A ^1H NMR spectrum of IIIb in $CDCl_3$ displayed an AA′BB′ pattern for the C_5H_4Me ring protons at δ 5.17 (m, 2 H) and δ 4.79 (m, 2 H) along with a methyl proton resonance at δ 1.86 (s, 3 H). The identity of IIIb (and thus that of IIIa) was ascertained by a single-crystal X-ray diffraction study (vide infra) of the tetraphenylborate salt of IIIb.

Isolation of the Tetraphenylborate Salt of the $[Co_3(\eta^5-C_5H_4Me)_3(\mu_3-NO)(\mu_3-NH)]^+$ Monocation (IIIb) by Anion Metathesis. In order to

Table I. Crystal and Data-Collection Parameters for $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (**IIc**), $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+[BPh_4]^-$ ($[IIIb]^+[BPh_4]^-$), and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV)

	A. Crystal Parameters		
compound	IIc	$[IIIb]^+[BPh_4]^-$	IV
formula	$C_{31}H_{46}NOCo_3$	$C_{42}H_{42}BN_2OCo_3$	$C_{20}H_{23}N_2O_2Co_3$
a, Å	10.516 (5)	11.092 (3)	9.204 (4)
b, Å	17.859 (9)	10.666 (5)	15.165 (4)
c, Å	8.443 (4)	30.022 (12)	14.267 (5)
α, deg	90.00	90.00	90.00
β, deg	111.76 (5)	94.70 (3)	98.87 (3)
γ, deg	90.00	90.00	90.00
V, $Å^3$	1473 (1)	3540 (2)	1968 (1)
space group	$P2_1/m$	$P2_1/c$	$P2_1/c$
crystallographic site symmetry	C_s—*m*	C_1—1	C_1—1
mol wt	625.57	764.45	500.24
Z	2	4	4
d(calcd), g cm^{-3}	1.39	1.44	1.66
μ(calcd), cm^{-1}	15.37	12.88	22.92
crystal face indices	$(\bar{1},0,1)$; $(0,1,\bar{2})$; $(1,0,\bar{1})$; $(0,1,0)$; $(0,1,\bar{2})$; $(0,\bar{1},0)$	$(0,1,\bar{1})$; $(1,0,0)$; $(0,\bar{1},1)$; $(\bar{1},0,0)$; $(1,1,\bar{1})$; $(\bar{1},0,2)$; $(\bar{1},\bar{1},1)$; $(1,0,\bar{2})$	$(0,1,1)$; $(0,1,\bar{1})$; $(0,\bar{1},\bar{1})$; $(1,0,0)$; $(0,\bar{1},1)$; $(1,0,0)$
	B. Data Measurement Parameters		
data collection temp, °C	22	−30	−50
scan mode	θ–2θ	θ–2θ	θ–2θ
scan speed, deg/min	variable (2–24)	variable (4–24)	variable (4–24)
scan range, deg above $K\alpha_1$/below $K\alpha_2$	0.8/0.8	1.0/1.0	1.0/1.0
2θ limits, deg	3–50	3–50	3–55
std reflctns	$(1,1,\bar{2})$; $(1,1,1)$	$(0,2,\bar{3})$; $(0,\bar{3},\bar{1})$; $(\bar{1},0,2)$; $(\bar{1},2,14)$; $(2,1,\bar{1})$	$(2,7,\bar{3})$; $(\bar{2},\bar{8},\bar{3})$; $(\bar{3},1,1)$; $(2,3,\bar{2})$
frequency of stds.	2 per 48	5 per 45	4 per 46
reflctns measured	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$
no. of unique reflctns	1346	3354	4685
cutoff for obsd data	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
no. of obsd reflctns	772	2239	3392
data/parameter ratio	10.3	8.2	13.9
anisotropic convergence, %	$R_1 = 6.50$; $R_2 = 8.03$	$R_1 = 6.73$; $R_2 = 6.98$	$R_1 = 3.24$; $R_2 = 4.09$
goodness-of-fit	2.02	2.15	1.64

isolate diffraction-quality crystals of a salt of IIIb, the cationic cluster IIIb with its mixed counterions was stirred in a saturated acetone solution of sodium tetraphenylborate. After removal of solvent, extraction of the residue with chloroform yielded a red-brown solution of $[IIIb]^+[BPh_4]^-$. The composition of this salt was confirmed from a subsequent examination by X-ray diffraction (vide infra). An IR spectrum of this material in the nitrosyl stretching region (1600–1350 cm^{-1}) was complicated by the phenyl ring stretching modes of the $[BPh_4]^-$ anion.

Reaction of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIa) with $NOBF_4$: Isolation of the $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ Monocation (IIIa) from IIa. In this reaction IIa (70 mg; 0.17 mmol) and $NOBF_4$ (19.7 mg; 0.17 mmol) were stirred at room temperature in 50 mL of dichloromethane. Gas evolution was immediately discernible, and within 5 min the color of the solution turned from green to red-brown. The $[IIIa]^+[BF_4]^-$ salt was obtained in quantitative yield. The monocation IIIa was readily identified from its IR and ^1H NMR spectra.

Structural Determinations of $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc), $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+[BPh_4]^-$ ($[IIIb]^+[BPh_4]^-$), and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV). (a) General. A Syntex (Nicolet) $P\bar{1}$ diffractometer with graphite-monochromatized Mo Kα radiation was used to obtain intensity data for each of the three structures. Details of crystal alignment, data collection, and a listing of crystallographic programs (other than those mentioned specifically) are given elsewhere.[16] Data-collection parameters and crystal data for each structure are given in Table I. The quoted cell dimensions and esd's were derived from least-squares analysis of setting angles for 15 well-centered reflections with $25° \leq 2\theta \leq 30°$ for each crystal. The intensities of the chosen standard reflections for each crystal (Table I) did not vary significantly during data collection. Analytical absorption corrections[17] were applied to each data set based upon an indexing of the crystal faces (Table I). Atomic scattering factors for neutral atoms were used together with anomolous dispersion corrections[18] for all non-hydrogen atoms.

(b) $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc). Crystals of this compound were obtained by slow evaporation of a concentrated benzene solution. A black parallelopiped-shaped crystal of dimensions 0.16 × 0.21 × 0.04 mm was mounted under argon into a thin-walled, Lindemann glass capillary, which was then hermetically sealed.

The observed systematic absences of $\{0k0\}$ for *k* odd indicated that the probable space groups were $P2_1$ and $P2_1/m$. The crystal structure was solved via the application of MULTAN[19] under $P2_1/m$ symmetry which imposes crystallographic C_s—*m* site symmetry on the IIc molecule with the vertical mirror plane passing through one cobalt atom, Co1, and the bicapped NH and CO ligands and bisecting the C_5Me_5 ligand coordinated to Co1. Full-matrix isotropic least-squares refinement of all non-hydrogen atoms was performed with RAELS;[20a] in this and subsequent refinements each C_5Me_5 ligand was constrained as a rigid group of C_{5v} symmetry with the methyl hydrogen atoms idealized at tetrahedral bond angles with a C–H length of 0.96 Å. A subsequent difference electron-density map indicated that the Co1-coordinated C_5Me_5 ligand was not per se bisected by the crystallographic mirror plane but rotated off the mirror. This presumed static crystal disorder gives rise to two mirror-related, half-weighted orientations for this C_5Me_5 ligand. Full-matrix least-squares refinement was then carried out with RAELS[20a] in which anisotropic thermal parameters were utilized for all non-hydrogen atoms, and the thermal motion of each of the full-weighted and half-weighted C_5Me_5 ligands was treated by use of a TLX model (with 15 librational thermal parameters) as described by Rae.[20b] A final difference electron-density synthesis, which exhibited no further abnormal residual density, revealed a distinct positive peak at the expected position for the imido (NH) hydrogen atom.

Positional and thermal parameters obtained from the output of the last least-squares cycle are available as supplementary material along with "best" least-squares planes and perpendicular distances of selected atoms from these planes. Interatomic distances and bond angles are presented in Table II. Observed and calculated structure factor amplitudes are available as supplementary material.

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Table II. Interatomic Distances and Bond Angles in $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc)

A. Distances (Å)			
Co1–Co2	2.432 (3)	Co2–C21	2.032 (13)
Co2–Co2′	2.419 (4)	Co2–C22	2.047 (13)
Co1–C1	1.921 (22)	Co2–C23	2.083 (13)
Co2–C1	1.935 (16)	Co2–C24	2.090 (13)
Co1–N1	1.825 (14)	Co2–C25	2.059 (12)
Co2–N1	1.837 (13)	Co1–C11	2.066 (16)
C1–O1	1.232 (21)	Co1–C12	2.100 (10)
Co1–Cp*1[a]	1.72	Co1–C13	2.089 (13)
Co2–Cp*2	1.72	Co1–C14	2.048 (13)
		Co1–C15	2.033 (10)
		C17···C29[b]	3.220 (13)
		C110···C29′[b]	3.505 (13)
		C27···C27′[b]	3.203 (13)
B. Bond Angles (deg)			
Co1–C1–O1	134.2 (16)	C1–Co1–N1	84.0 (8)
Co2–C1–O1	133.0 (10)	C1–Co2–N1	83.4 (6)
Co1–C1–Co2	78.2 (8)	Co1–Co2–Cp*2	149.9
Co2–C1–Co2′	77.4 (6)	Co2–Co1–Cp*1	152.1
Co1–N1–Co2	83.2 (6)	Co2′–Co2–Cp*2	149.9
Co2–N1–Co2′	82.3 (5)		

[a] Cp*n denotes the centroid of the C_5Me_5 ligand coordinated to the Co*n* atom. [b] Distances denote closest intramolecular contacts between Me groups on adjacent C_5Me_5 ligands.

(c) $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+[BPh_4]^-$ ($[IIIb]^+[BPh_4]^-$). Crystals of this compound were obtained by slow diffusion of cyclohexane into a saturated chloroform solution. A hexagonal-shaped crystal of horizontal dimensions 0.41 × 0.41 × 0.33 mm and thickness 0.11 mm was mounted under argon into a Lindemann glass capillary which subsequently was hermetically sealed.

The observed systematic absences of $\{h0l\}$ for l odd and $\{0k0\}$ for k odd uniquely define the probable space group to be $P2_1/c$; thus, the crystallographically independent unit consists of one monocation (IIIb) and one tetraphenylborate monoanion.

Initial coordinates for the three cobalt atoms were obtained by the use of MULTAN,[19] and the remaining non-hydrogen atoms were located from successive electron-density maps. Least-squares refinement of the crystal structure with RAELS[20a] was based upon the following: (1) anisotropic thermal atomic parameters being used for all non-ring, non-hydrogen atoms and for the carbon atoms in two well-behaved C_5H_4Me rings; (2) the one C_5H_4Me ligand (which appeared to possess considerable librational motion) and the four C_6H_5 rings each being constrained to a rigid group of C_{2v} symmetry with the hydrogen atoms idealized at trigonal or tetrahedral bond angles with a C–H distance of 0.96 Å; and (3) the thermal motion of the C_5H_4Me ring being described by a TLX model[20b] (with 15 thermal parameters) and that of each C_6H_5 ring being approximated by a TL model[20b] (with 12 thermal parameters). A final difference synthesis, which showed a residual positive peak at the expected position for the imido hydrogen atom, did not display any anomalous features.

The positional and thermal parameters obtained from the output of the last least-squares cycle are available as supplementary material together with appropriate least-squares planes and perpendicular displacements of atoms from these planes. Selected interatomic distances and bond angles are listed in Table III. A listing of observed and calculated structure factor amplitudes is available as supplementary material.

(d) $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV). Crystals of this compound were isolated by slow evaporation of a concentrated toluene solution. An approximately cubic-shaped crystal of dimensions 0.40 × 0.38 × 0.35 mm was inserted into an argon-filled Lindemann glass capillary.

The space group $P2_1/c$, uniquely determined from the observed systematic absences, results in the crystallographically independent unit being composed of one entire molecule.

Table III. Interatomic Distances and Bond Angles in the $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ Monocation (IIIb)

A. Distances (Å)			
Co1–Co2	2.428 (3)	Co1–C11	2.038 (16)
Co1–Co3	2.391 (2)	Co1–C12	2.076 (13)
Co2–Co3	2.399 (3)	Co1–C13	2.081 (13)
Co1–N1	1.866 (10)	Co1–C14	2.025 (16)
Co2–N1	1.849 (11)	Co1–C15	2.031 (16)
Co3–N1	1.892 (11)	Co2–C21	2.007 (16)
Co1–N2	1.849 (9)	Co2–C22	2.080 (17)
Co2–N2	1.818 (10)	Co2–C23	2.023 (15)
Co3–N2	1.838 (9)	Co2–C24	2.068 (16)
N1–O1	1.249 (11)	Co2–C25	2.076 (14)
Co1–Cp′1[a]	1.68	Co3–C31	1.955 (14)
Co2–Cp′2	1.67	Co3–C32	2.101 (12)
Co3–Cp′3	1.71	Co3–C33	2.134 (12)
		Co3–C34	2.112 (12)
		Co3–C35	2.052 (12)
B. Bond Angles (deg)			
Co1–N1–O1	132.4 (8)	N1–Co1–N2	82.4 (4)
Co2–N1–O1	133.6 (9)	N1–Co2–N2	83.8 (5)
Co3–N1–O1	129.7 (8)	N1–Co3–N2	82.0 (4)
Co1–N1–Co2	81.6 (4)	Co1–Co2–Cp′2	153.5
Co1–N1–Co3	79.0 (4)	Co2–Co1–Cp′1	152.6
Co2–N1–Co3	79.8 (4)	Co1–Co3–Cp′3	141.5
Co1–N2–Co2	82.9 (4)	Co3–Co1–Cp′1	147.7
Co1–N2–Co3	80.9 (4)	Co2–Co3–Cp′3	157.6
Co2–N2–Co3	82.0 (4)	Co3–Co2–Cp′2	147.1

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

Table IV. Interatomic Distances and Bond Angles in $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV)

A. Distances (Å)			
Co1–Co2	2.404 (1)	Co1–C11	2.115 (3)
Co1–Co3	2.414 (1)	Co1–C12	2.085 (3)
Co2–Co3	2.382 (1)	Co1–C13	2.099 (3)
Co1–C1	1.947 (3)	Co1–C14	2.053 (3)
Co2–C1	1.967 (3)	Co1–C15	2.086 (4)
Co3–C1	1.945 (3)	Co2–C21	2.086 (3)
C1–O1	1.198 (3)	Co2–C22	2.063 (3)
Co1–N1	1.838 (3)	Co2–C23	2.076 (3)
Co2–N1	1.840 (2)	Co2–C24	2.095 (3)
Co3–N1	1.828 (2)	Co2–C25	2.085 (3)
N1–C2	1.419 (4)	Co3–C31	2.078 (3)
C2–O2	1.234 (4)	Co3–C32	2.066 (3)
C2–N2	1.340 (4)	Co3–C33	2.080 (3)
N2–H1	0.96	Co3–C34	2.075 (3)
N2–H2	0.88	Co3–C35	2.078 (4)
Co1···C2	2.893 (4)	CMe1–C11	1.497 (5)
Co2···C2	3.038 (4)	CMe2–C21	1.498 (4)
Co3···C2	2.955 (4)	CMe3–C31	1.492 (5)
O2···N2′[a]	2.90	Co1–Cp′1[b]	1.691
O2···H1′[a]	2.0	Co2–Cp′2	1.696
		Co3–Cp′3	1.686
B. Bond Angles (deg)			
Co1–C1–O1	133.6 (3)	N1–C2–O2	121.1 (3)
Co2–C1–O1	134.8 (2)	N1–C2–N2	115.6 (3)
Co3–C1–O1	136.0 (2)	O2–C2–N2	123.2 (3)
Co1–C1–Co2	75.8 (1)	H1–N2–H2	115
Co1–C1–Co3	76.7 (1)	C1–Co1–N1	85.8 (1)
Co2–C1–Co3	75.0 (1)	C1–Co2–N1	85.2 (1)
Co1–N1–C2	124.7 (2)	C1–Co3–N1	86.2 (1)
Co2–N1–C2	137.2 (2)	Co1–Co2–Cp′2	151.4
Co3–N1–C2	130.6 (2)	Co2–Co1–Cp′1	148.8
Co1–N1–Co2	81.6 (1)	Co1–Co3–Cp′3	153.7
Co1–N1–Co3	82.4 (1)	Co3–Co1–Cp′1	151.1
Co2–N1–Co3	81.0 (1)	Co2–Co3–Cp′3	145.9
		Co3–Co2–Cp′2	147.0

[a] These distances correspond to intermolecular H-bonding distances. [b] Cp′*n* denotes the centroid of the C_5H_4Me ligand attached to the Co*n* atom.

The crystal structure was determined by the application of MULTAN[19] which provided initial coordinates for the three cobalt atoms. The other non-hydrogen atoms were resolved from successive Fourier syntheses, and the two amido hydrogen atoms were readily located from a difference map. Full-matrix least-squares refinement was carried out with ORFLS[20c] in which anisotropic thermal parameters were utilized for all non-hydrogen atoms. The determined hydrogen atoms of the formamidonitrene ligand and those of the three C_5H_4Me ligands (whose idealized positions at regular trigonal or tetrahedral bond angles with C–H distances of 0.96 Å were reset after each least-squares cycle) were included in the least-squares refinement as fixed-atom contributions. A final difference map displayed no unusual features. The positional and thermal parameters from the output of the last least-squares cycle are available as supplementary material along with certain least-square planes and perpendicular distances of atoms from these planes. Interatomic distances and

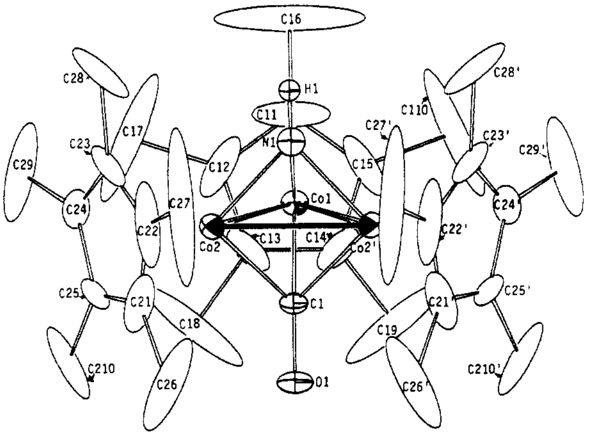

Figure 1. A view of the 48-electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc) which has crystallographic C_s—*m* site symmetry. The abnormally elongated thermal ellipsoids (characteristic of unusually large thermal ring libration) for the "sterically crowded" pentamethylcyclopentadienyl carbon atoms are presumed to reflect a mirror-plane "averaged" structure resulting from a "static" crystal disorder of each C_5Me_5 ring in at least two orientations.

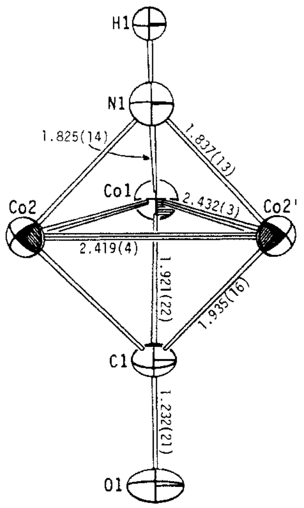

Figure 2. The bicapped tricobalt $Co_3(CO)(NH)$ core of $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc) with its independent interatomic distances under crystallographic C_s—*m* site symmetry. The position of the nitrene hydrogen atom was located from an electron-density difference synthesis.

bond angles are given in Table IV. A listing of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

Structural Features. (a) $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc). There is not any evidence for the existence of any unusual packing interactions in that all intermolecular contacts are greater than the sum of van der Waals radii for the nearest atoms.

The overall molecular configuration of IIc, shown in Figure 1, conforms to crystallographic C_s—*m* site symmetry. The striking fact that all of the atomic thermal ellipsoids of both the ordered C_5Me_5 ligand and mirror-disordered C_5Me_5 ligand (of which only one half-weighted orientation is shown) are similarly elongated (in a librational-like manner within the mean plane of each C_5Me_5 ring) provides prime evidence for a crystal disordering of each C_5Me_5 ligand among at least two orientations about the central $Co_3(CO)(NH)$ core.

Such a crystal disorder of these C_5Me_5 rings is a likely consequence of "steric" overcrowding within the molecule. The closest interring $H_3C\cdots CH_3$ contacts of 3.20 (1) Å between the C27, C27′ pair, 3.22 (1) Å between the C17, C29 pair, and 3.50 (1) Å between the C110, C29′ pair are all shorter than twice the van der Waals "effective" radius of 1.8 Å for a methyl group. Calculations reveal that these particular methyl carbon atoms with the greatest intramolecular "steric" interactions also have the largest perpendicular displacements from the mean plane of their five ring carbon atoms, viz., 0.16 Å for C27 and C27′, 0.09 Å for C17, 0.14 Å for C29 and C29′, and 0.35 Å for C110. For the other methyl substituents, only C19 (with 0.16 Å) has an out-of-plane displacement greater than 0.10 Å. The effect of these steric interactions on the Co–Co′ distances is examined later.

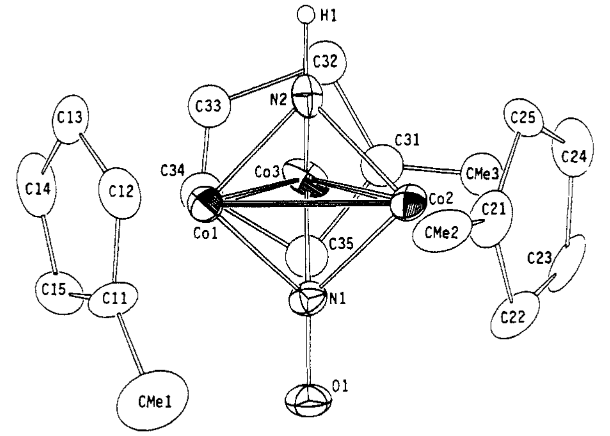

Figure 3. A view of the 48-electron $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (IIIb) which has no crystallographically required symmetry. The atomic thermal ellipsoids for the C_5H_4Me ring attached to Co_3 have been idealized for the sake of clarity because of a crystal disorder which results in this ligand having unusually large anisotropic thermal parameters.

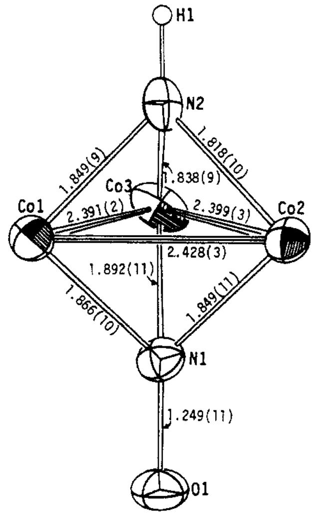

Figure 4. The bicapped tricobalt $Co_3(NO)(NH)$ core of the $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (IIIb) with its independent interatomic distances under crystallographic C_1—1 site symmetry. The position of the nitrene hydrogen atom was located from an electron-density difference synthesis.

Despite these abnormal cigar-shaped thermal ellipsoids for the pentamethylcyclopentadienyl carbon atoms, the atomic thermal ellipsoids for the $Co_3(CO)(NH)$ core are normal. Furthermore, the selected bond distances shown in Figure 2 for the $Co_3(CO)(NH)$ core not only correspond to reasonable values (vide infra) but also are consistent with this core possessing an idealized C_{3v} geometry.

(b) $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]^+[BPh_4]^-$ ($[IIIb]^+[BPh_4]^-$). The monocations and monoanions are well separated in the unit cell with no interionic non-hydrogen contacts less than 3.5 Å. Hence, there is not any evidence of unusual packing interactions which would produce marked distortions of the independent monocation.

The overall configuration (Figure 3) of the monocation (IIIb) roughly conforms to C_3—3 symmetry except for the Co1-coordinated C_5H_4Me ring, whose methyl substituent is drastically offset from the threefold-related orientation by a counterclockwise ring rotation of ca. 144° (corresponding to its being attached to C11

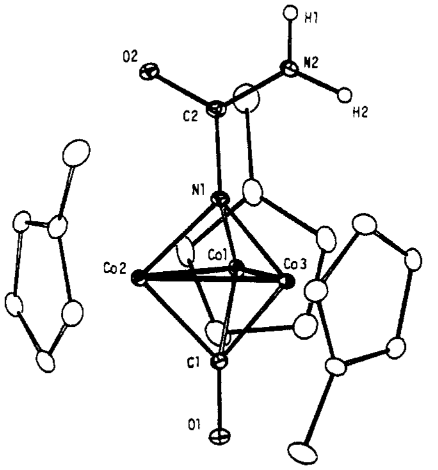

Figure 5. A view of the 48-electron $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ molecule (IV) which has no crystallographically imposed symmetry. The atomic thermal ellipsoids for all atoms are well-behaved.

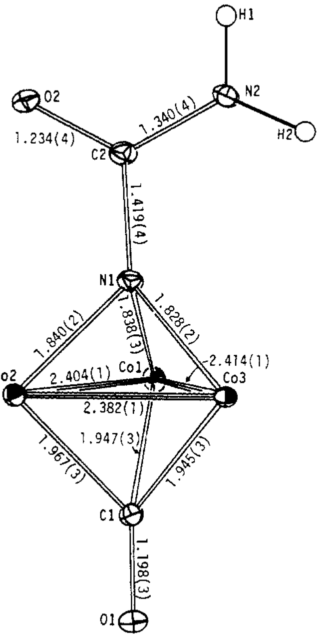

Figure 6. The bicapped tricobalt $Co_3(CO)(NC(O)NH_2)$ core of the $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ molecule (IV) with its independent interatomic distances under crystallographic C_1—1 site symmetry. The two amide hydrogen atoms of the planar formamidonitrene ligand were located from an electron-density difference map.

instead of C14). Figure 4 shows that the solid-state geometry of the $Co_3(NO)(NH)$ core appears to be slightly distorted from regular C_{3v} symmetry. Because the observed variations are not large, one can assume a mean C_{3v} geometry for IIIb in order to simplify a comparative analysis with the other two related clusters (vide infra).

(c) $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV). The molecular architecture of IV shown in Figure 5 lacks crystallographically imposed site symmetry. The entire molecule has well-behaved atomic thermal ellipsoids. If the formamidonitrene substituent (viz., $C(O)NH_2$) is neglected, the remaining part of the molecule viewed in Figure 5 approximates C_3—3 symmetry except for the Co3-coordinated C_5H_4Me ring whose methyl substituent is oriented in the opposite direction (corresponding to a 180° ring rotation) from the threefold-related position. The geometry of the $Co_3(CO)(NC(O)NH_2)$ fragment is presented in Figure 6; the corresponding distances show that the $Co_3(CO)(N)$ fragment ideally possesses a C_{3v} geometry.

A salient structural feature (displayed in Figure 7) is the dimerization of two centrosymmetrically related clusters via hydrogen bonding involving the formamidonitrene-capped ligand.

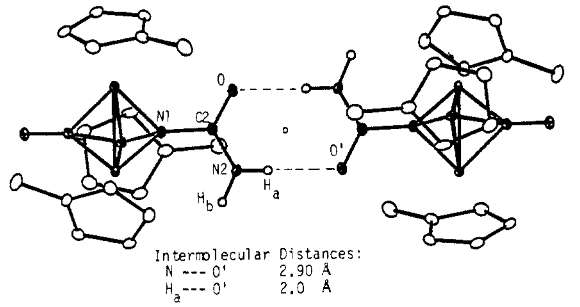

Figure 7. Dimerization of two crystallographically equivalent $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ molecules (IV) via hydrogen bonding of their formamidonitrene ligands. The two identical N—H···OC interactions for the coplanar $\mu_3\text{-}NC(O)NH_2$ ligands of the two clusters are related by a crystallographic center of symmetry.

Table V. Comparison of Mean Distances (Å) and Bond Angles (deg) Under C_{3v} Symmetry for $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc), $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ (IIIb), and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV)

	IIc	IIb	IV
Co–Co′	2.428	2.406	2.400
Co–XO[a]	1.930	1.869	1.953
Co–NR	1.833	1.835	1.835
Co–Cp*[b]	1.72	1.69	1.69
X–O[a]	1.232	1.249	1.198
Co–XO–Co′[a]	77.9	80.1	75.8
Co–NR–Co′	82.9	81.9	81.7
NR–Co–XO[a]	83.6	82.7	85.7

[a] X = C in IIc and IV, X = N in IIIb. [b] Cp* denotes the centroid of the C_5R_5 ligand.

The observed N···O and H···O distances (Figure 7) for each of the two identical N—H···O interactions are within the range of values observed for analogous N—H···O hydrogen-bonded systems in urea (viz., $NH_2C(O)NH_2$)[21] and in other amides and peptides.[22]

As expected for an amido group, the formamidonitrene ligand is coplanar, i.e., the non-hydrogen atoms are within 0.007 Å of their mean plane and both hydrogen atoms are within 0.14 Å. This planar $NC(O)NH_2$ ligand is oriented parallel to the bond vector betwween Co2 and Co3.

One steric consequence of the molecular dimerization is that the methyl substituents of the Co1- and Co2-coordinated C_5H_4Me ligands are oriented toward the formamidonitrene ligand, whereas the methyl substituent of the Co3-coordinated C_5H_4Me ligand is oriented away from this ligand toward the OC-capped ligand. Least-squares plane calculations show that the dispositions of these C_5H_4Me ligands result in the Co1- and Co2-bonded C_5H_4Me rings being similarly canted by 6.8° (av) and the Co3-bonded C_5H_4Me ring by only 2.6° from their expected perpendicular orientations with the tricobalt plane toward the OC-capped ligand.

Structural Comparison and Resulting Bonding Implications. In order to facilitate a comparative structural-bonding analysis of these three 48-electron clusters containing a central $Co_3(XO)(NR)$ core with a π-acidic CO or NO ligand and a π-donor ligand, mean distances and bond angles are presented in Table V.

(a) Co–Co′ Distances: Steric Influence of the C_5Me_5 Ligands on the Metal–Metal Bonding in These Clusters and in the Related 49-Electron $Ni_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)_2$ Clusters (x = 0, 1, 5). Both IIIb and IV, which possess sterically innocent C_5H_4Me ligands, have virtually identical mean Co–Co′ distances of 2.406 and 2.400 Å, respectively, while IIc, which has sterically crowded C_5Me_5 ligands, has a 0.025 Å longer mean Co–Co′ distance of 2.428 Å. This relatively small steric influence of the C_5Me_5 ligands on the Co–Co′ bond lengths is attributed to the relative strength

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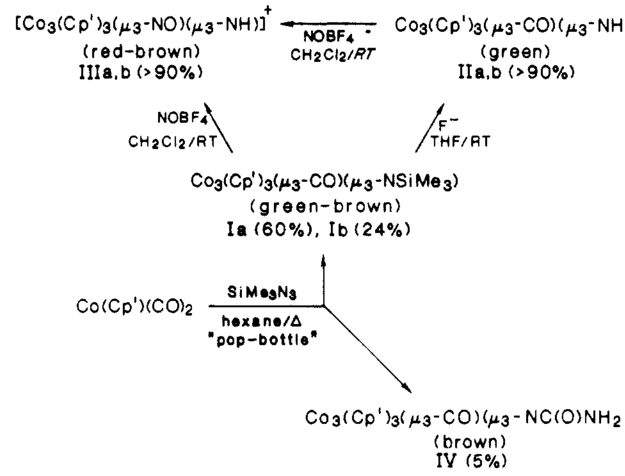
Scheme I



of the combined metal–metal and metal–ligand bonding interactions which are strongly intermixed in low-energy MOs in these ligand-bicapped, triangular metal cores. It is noteworthy (Table V) that the Co–Cp(centroid) distance for the C_5Me_5-containing molecule (IIc) is 0.03 Å larger than those for the two C_5H_4Me-containing complexes (IIIb and IV).

In marked contrast, a comparison of the Ni–Ni′ distances for the 49-electron $Ni_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)_2$ clusters (x = 0,[8,23] 1,[24] 5[9b]) shows that the bulky C_5Me_5 ligands cause a pronounced increase in the Ni–Ni′ distances. The mean Ni–Ni′ distance of 2.530 (3) Å in the pentamethylcyclopentadienyl analogue (x = 5) is 0.14 Å longer than the identical Ni–Ni bond lengths of 2.389 (2) Å in the Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule of crystallographic C_{3h}—$3/m$ site symmetry and 2.389 (3) Å in the methylcyclopentadienyl analogue (x = 1) of crystallographic C_1—1 site symmetry.[24] The comparatively drastic steric effect of the C_5Me_5 ligands in the trinickel cluster is presumed to be due to the inherently weaker Ni–Ni′ bonding, which partly arises from the unpaired electron in this 49-electron system occupying an a_2' MO (under assumed D_{3h} symmetry) which is primarily of trimetal antibonding character.

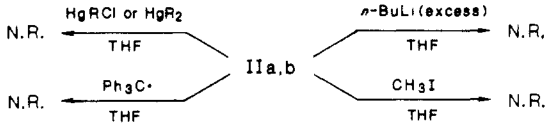
(b) Co–CO and Co–NO Bond Lengths. Table V reveals that the mean Co–NO bond length of 1.869 Å for the ON-capped ligand in IIIb is considerably smaller by 0.07 Å (av) than the mean Co–CO bond length for the OC-capped ligand in both IIc (1.930 Å) and IV (1.953 Å). The shorter Co–NO bond lengths are readily rationalized on the basis of the relatively greater electron-acceptor ability of the nitrosyl ligand in these tricobalt clusters. A similarly shorter mean Co–NO bond length of 1.843 (9) Å was found[25] in the 48-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$.

(c) Co–NR Bond Lengths. The average distance between the three cobalt atoms and the RN-capped ligand is remarkably constant in IIc (1.833 Å), IIIb (1.835 Å), and IV (1.835 Å). That these mean Co–NR bond lengths are 0.034 Å shorter than the mean Co–NO bond length in IIIb is presumed to reflect the relatively stronger linkage of the four-electron donating NR ligand.

A somewhat greater shortening of 0.056 Å (av) in the mean Co–NR bond lengths for the HON-capped ligand in the 48-electron $[Mn_3(\eta^5\text{-}C_5H_4Me)_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NOH)]^+$ monocation (1.873 Å)[6] and for the HN-capped ligand in the 48-electron $[Mn_3(\eta^5\text{-}C_5H_4Me)_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NH)]^+$ monocation (1.872 Å)[6] compared to the ON-capped ligand in the 48-electron $Mn_3(\eta^5\text{-}C_5H_5)_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NO)$ (1.929 Å)[26] was previously pointed out by Legzdins and co-workers.[6] The constancy of the mean Mn–Mn′ bond lengths (*viz.*, 2.508, 2.503, and 2.506 Å) in these three triangular manganese clusters is another conspicuous structural feature which lends support to this comparative bond-length analysis of the different triply bridging ligands.

Scheme II

Nonreactivity of $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIa, x = 0; IIb, x = 1)



Synthesis and Chemistry of the Triangular Tricobalt Clusters with HN- or RN-Capped Ligands. Scheme I outlines the important trimeric products arising from the reactions of the $Co(\eta^5\text{-}C_5H_{5-x}Me_x)(CO)_2$ monomers (x = 0, 1) with $SiMe_3N_3$ as well as the interconversions involving the bicapped ligands of the triangular metal species.

(a) The Reaction of $Co(\eta^5\text{-}C_5H_4Me)(CO)_2$ with $SiMe_3N_3$. This reaction, which yielded a more varied array of products than the analogous reaction of $Co(\eta^5\text{-}C_5H_5)(CO)_2$, produced, in addition to the expected $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ (Ib), the new clusters $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIb) and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (IV).

Although the formamidonitrene cluster (IV) was isolated in only 5% yield, its possible mode of formation is intriguing. The (μ_3-NC(O)NH$_2$) ligand may be formed via a reaction involving an isocyanate intermediate. Reactions of carbon monoxide with a variety of azido-transition-metal compounds to form isocyanato–metal complexes have been previously observed.[27] An alternative reaction route would be via the initial formation of a dimeric ureylene-bridged intermediate, $Co_2(\eta^5\text{-}C_5H_4Me)_2(\mu_2\text{-}RNC(O)NR)$ (R = Me_3Si or H). Such dimers, $Co_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}t\text{-}BuNC(O)N\text{-}t\text{-}Bu)$[2] and the isolobal $Fe_2(CO)_6(\mu_2\text{-}PhNC(O)NPh)$,[28] have been previously isolated and structurally characterized as low-yield products from reactions of organic azides and diimides with metal carbonyls.[2,28] The proposed formation of IV from the ureylene-bridged intermediate would involve the "net" cycloaddition of a 16-electron $Co(\eta^5\text{-}C_5H_4Me)(CO)$ fragment together with a homolytic replacement of a Me_3Si substituent on each N atom with a H atom. In retrospect, it is evident that the (μ_3-NC(O)N(SiMe$_3$)$_2$) analogue of IV would probably not exist due to steric constraints involving the C_5H_4Me ligands.

(b) The Reaction of $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ with $SiMe_3N_3$. This reaction results in a 10–15% yield of $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIc) with the major product being the Co–Co′ double-bonded $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$.[29] Few reactivity studies were undertaken on IIc due to its availability in only small quantities. This compound is one of a small group of structurally characterized $(\eta^5\text{-}C_5Me_5)_3$ triangular metal clusters, which include the 46-electron $M_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$ (M = Rh;[30] M = Co[31]), the 49-electron $Ni_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$,[9b] and the 48-electron $[Rh_3(\eta^5\text{-}C_5Me_5)_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ monocation.[32]

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The initially expected Me_3SiN-capped product of this reaction was not formed presumably as a consequence of previously discussed steric effects. The isolated nitrene species (IIc) may, therefore, result from an intermediate undergoing a sterically induced N–$SiMe_3$ cleavage reaction with concomitant H-atom abstraction.

(c) Reaction of $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ (Where $x = 0, 1$) with $[NBu_4]^+[F]^-\cdot 3H_2O$. The ($\mu_3$-$NSiMe_3$) clusters Ia and Ib readily react at room temperature in an almost quantitative fashion (>90%) with $[n\text{-}Bu_4N]^+[F]^-\cdot 3H_2O$ to form the new nitrene $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ clusters ($x = 0$, IIa; $x = 1$, IIb). Attempts to isolate a trigonal pyramidal, "bare", nitrido (μ_3-N) monoanion via the N–$SiMe_3$ cleavage reaction of Ia and Ib with cesium fluoride under rigorous dry conditions invariably gave rise instead to quantitative yields of the protonated forms (viz., IIa and IIb). These results indicated that the presumed trigonal pyramidal nitride-capped, anionic intermediates were extremely powerful bases; this hypothesis is supported by the nonreactivity of IIa and IIb with excess n-BuLi.

The apparent inertness of this nitrene ligand in IIa and IIb was further explored by treatment with various reagents (including hydrogen atom extractors), as given in Scheme II.

Organomercurials HgRCl and HgR_2, which have been shown to substitute R for H in (μ_3-CH) clusters,[33] did not react with the nitrene species. Reactions did not occur upon similar treatments of IIa and IIb with trityl radical[34] and with CH_3I. Thus, the triply bridging nitrene moiety in these clusters appears to be quite inert to various reagents. Further electrochemical reactivity studies of these nitrene clusters will be presented in the following paper.[12]

(d) Reactions of $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ ($x = 0$, Ia; $x = 1$, Ib) with $NOBF_4$: Isolation of a New Class of Bicapped Nitrene–Nitrosyl Clusters. Reactions of the olive-green Ia and Ib with $NOBF_4$ resulted in a greater than 90% yield of the reddish-brown ON- and HN-capped $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocations ($x = 0$, IIIa; $x = 1$, IIIb). Reaction of the green $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIa) with $NOBF_4$ also produced a nearly quantitative yield of cationic IIIa with a $[BF_4]^-$ counterion. The much shorter reaction time (as qualitatively observed from the color changes) in forming the reddish-brown IIIa from the preformed green HN-capped IIa than that in forming IIIa from the olive-green Ia, which additionally involves a N–Si bond cleavage via the tetrafluoroborate anion, is consistent with the hypothesis that N–Si bond cleavage occurs prior to the simple substitution of an NO^+ ligand in place of the isoelectronic OC-capped ligand.

Previous studies of reactions of NO^+ with metal cluster compounds have primarily involved a wide variety of polynuclear metal carbonyl anions including the $[Co_6(CO)_{15}]^{2-}$,[35] $[Fe_2(CO)_8]^{2-}$,[36] $[Fe_4N(CO)_{12}]^-$,[5a] $[H_3Os_4(CO)_{12}]^-$,[37] $[H_3Ru_4(CO)_{12}]^-$,[37] $[Os_{10}C(CO)_{24}]^{2-}$,[38] $[Fe_4(CO)_{13}]^{2-}$, $[Fe_3Co(CO)_{13}]^-$, $[FeCo_3(CO)_{12}]^-$, $[CoRu_3(CO)_{13}]^-$, $[H_2CoRu_3(CO)_{12}]^-$, $[H_2CoRu_3(CO)_{13}]^-$, $[HFe_3(CO)_{11}]^-$, and $[HFe_4(CO)_{13}]^-$ anions.[5b] These reactions have given rise to enclosed metal (interstitial), five-metal (square-pyramidal), and four-metal (butterfly-shaped) nitride clusters, to small yields of nitrene (NH) clusters, as well as to terminal and doubly bridging nitrosyl systems. Treatment of neutral metal carbonyl clusters such as $Ru_3(CO)_9(PPh_3)_3$ and $Os_3(CO)_9(PPh_3)_3$ with NO^+ has resulted in oxidation and/or fragmentation.[39]

The unprecedented, quantitative substitution of a μ_3-CO ligand with a μ_3-NO^+ ligand in the initially neutral clusters Ia, Ib, IIIa, and IIb indicates that similar kinds of reactions may provide a useful synthetic route for obtaining ON^+-capped clusters from OC-capped clusters. The possible generality of this simple substitution reaction may be operationally tested by treatment of the known $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$,[9b] $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$,[1,40] $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}O)(\mu_3\text{-}CO)$,[41] $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_2\text{-}CO)_2(\mu_3\text{-}CO)$,[42] $(\eta^5\text{-}C_5H_4Me)MnCo_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_3(\mu_3\text{-}CO)$, and $(\eta^4\text{-}C_4H_4)FeCo_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_3(\mu_3\text{-}CO)$[43] clusters with $NOBF_4$. The latter three clusters will also allow determination of the relative preferences of CO or NO to assume a triply bridged ligation. An extension of this NO^+ reaction to larger OC-capped clusters such as $Fe_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}CO)_4$[44] and $Co_4(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2$[45] may possibly give rise to ON-capped tetranuclear metal clusters.

(e) Reactivity Studies of the Monocations IIIa and IIIb. 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 neutral analogues had taken place. The electrochemical aspects of these clusters will be given in the following paper,[12] and the subsequent isolation and structural-bonding analysis of the 49-electron species will be presented elsewhere.[13]

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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; $[IIIa]^+[BF_4]^-$, 103201-01-0; IIIb, 103190-59-6; $[IIIb]^+[BPh_4]^-$, 103201-00-9; IV, 103148-50-1; $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$, 69657-52-9; $Co(\eta^5\text{-}C_5H_4Me)(CO)_2$, 75297-02-8; $Co(\eta^5\text{-}C_5Me_5)(CO)_2$, 12129-77-0; $SiMe_3N_3$, 4648-54-8; Co, 7440-48-4.

Supplementary Material Available: Two figures displaying solid-state IR spectra (KBr pellet) of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ (IIa) and the $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (IIIa) and tables listing the atomic parameters and selected least-squares planes for $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$, $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+[BPh_4]^-$, and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (15 pages); tables of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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