Reaction of Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-H) with (Trimethylsilyl)diazomethane and Ethyl Diazoacetate: Facile Hydrogen Transfer Forms the Diazenide Clusters Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-η^1-NNCH$_2$SiMe$_3$) and Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-η^1-NNCH$_2$CO$_2$CH$_2$CH$_3$)

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Introduction

The paramagnetic mono(ethylidyne) monohydride cluster Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-H) (**1**) was isolated as an intermediate in the reaction of Cp*$_3$Co$_3$(μ_2-H)$_3$(μ_3-H) with acetylene[1] and is also formed in the thermolysis of Cp*Co(H$_2$C=CH$_2$)$_2$.[2] Cluster **1** is a paramagnetic, 46-electron compound which reacted rapidly with CO and *tert*-butyl isocyanide to form the 1:1 adducts Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-CO)(μ_2-H) (**2**) and Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-CNCMe$_3$)(μ_2-H) (**3**), respectively.[3] Cluster **1** also reacted rapidly with NO to form the nitrosyl cluster Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-NO) (**4**) (Scheme 1).[3]

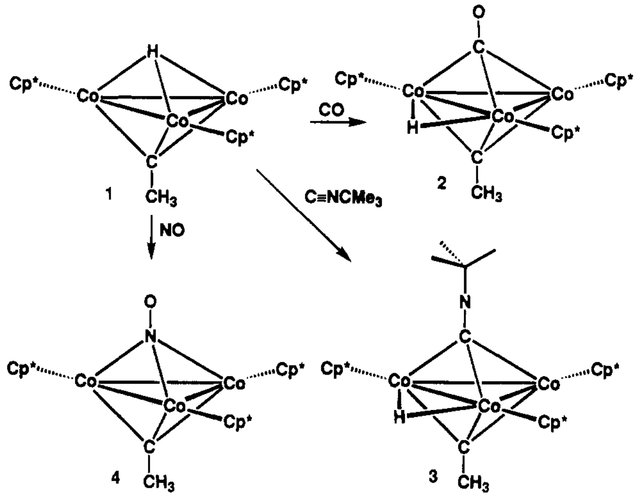
Neutral organic diazo compounds have been shown to behave as two-electron-donor ligands in a variety of polynuclear metal complexes.[4,5] We therefore reacted monohydride cluster **1** with (trimethylsilyl)diazomethane in an effort to prepare a monohydride (trimethylsilyl)diazo cluster analogous to clusters **2** and **3**. Instead, an unusual hydrogen transfer occurred in the reaction of **1** with (trimethylsilyl)diazomethane to form the (trimethylsilyl)diazenide mono(ethylidyne) cluster Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-η^1-NNCH$_2$SiMe$_3$) (**5**). The analogous reaction of **1** with ethyl diazoacetate formed Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-η^1-NNCH$_2$CO$_2$CH$_2$CH$_3$) (**6**). X-ray crystallographic analysis of cluster **5** established the μ_3-η^1-bonding of the (trimethylsilyl)diazenide ligand.

Results

Synthesis of Mono(ethylidyne) Diazenide Clusters 5 and 6.

Reaction of a brown benzene solution of **1** with excess (trimethylsilyl)diazomethane at room temperature gave a black solution from which the mono(ethylidyne) (trimethylsilyl)diazenide cluster Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-η^1-NNCH$_2$SiMe$_3$) (**5**) was isolated in 66% yield as a black microcrystalline solid (Scheme 2). Cluster **5** was characterized by spectroscopy and by X-ray crystallography (see below). In the ^{1}H NMR spectrum, a two-proton singlet at δ 3.80 was assigned to the equivalent diazenide methylene protons; this indicated that hydrogen transfer from cobalt to carbon had occurred. Comparison of this resonance to the ethylidyne methyl resonance at δ 4.66 established the 1:1 ratio of the two ligands.

Scheme 1



The analogous reaction of **1** with ethyl diazoacetate led to the isolation of the diazenide cluster Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-η^1-NNCH$_2$CO$_2$Et) (**6**) in 81% yield as a black powder (Scheme 2). Cluster **6** was characterized by spectroscopy. The spectroscopic properties of **6** were similar to those of **5**. In particular, the ^{1}H NMR spectrum of **6** displayed a 3:2 ratio of the ethylidyne methyl resonance at δ 4.48 to the diazenide methylene resonance at δ 5.04, which established a 1:1 ratio of the ligands.

X-ray Crystal Structure of Cp*$_3$Co$_3$(μ_3-CCH$_3$)(μ_3-η^1-NNCH$_2$SiMe$_3$) (5). The structure of cluster **5** was determined by X-ray crystallography (Figure 1, Tables 1 and 2), which revealed an equilateral triangle of cobalt atoms capped on one face by a μ_3-CCH$_3$ ligand and on the opposite face by a μ_3-η^1-NNCH$_2$SiMe$_3$ ligand. The crystallographic analysis of **5** revealed that the off-axis N(2) and C(3) atoms of the diazenide ligand were necessarily disordered under the crystallographically imposed 3-fold rotation axis. As a result, cluster **5** was refined according to a disordered model which assigned $^1/_3$ occupancy factors to the N(2) and C(3) atoms in each of the three symmetry-equivalent sites. Because of the artificial 3-fold site symmetry of **5**, there are considerable errors in the bond distances and bond angles within the diazenide ligand. The Co–μ_3-C distance [1.875(8) Å] and the μ_3-C–CH$_3$ distance [1.47(2) Å] are similar to the values observed for clusters **2**–**4**; the normal temperature factors of the ethylidyne carbon atoms suggest that their true positions are near the crystal imposed 3-fold axis. The independent Co–Co distance of 2.435(2) Å is similar to the Co–Co distances observed in other 48-electron (Cp*Co)$_3$ clusters.[2,3,6]

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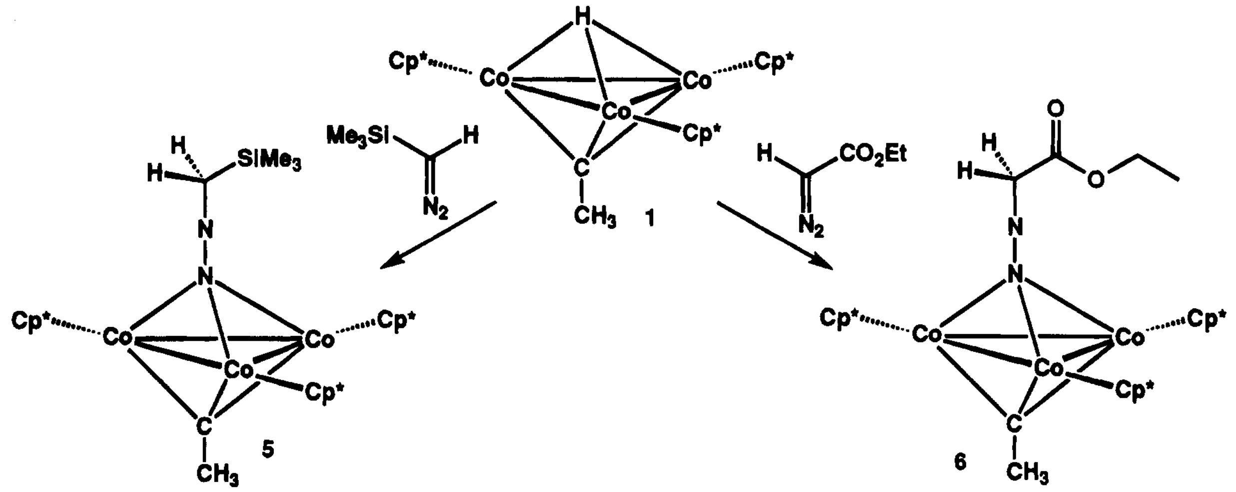
Scheme 2



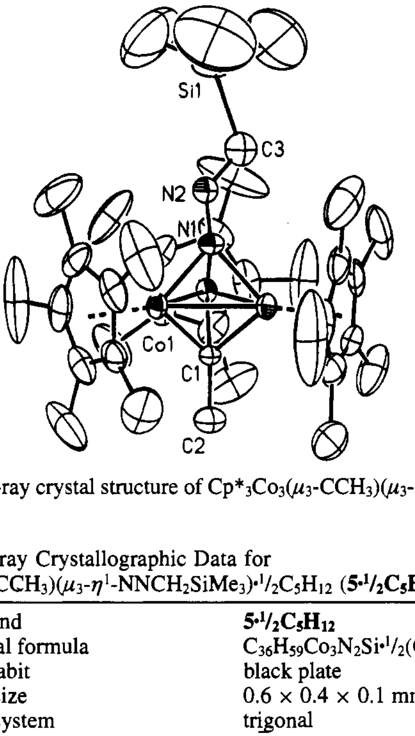


Figure 1. X-ray crystal structure of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2SiMe_3)$ (**5**).

Table 1. X-ray Crystallographic Data for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2SiMe_3)\cdot{}^1/_2C_5H_{12}$ ($\mathbf{5\cdot{}^1/_2C_5H_{12}}$)

compound	$\mathbf{5\cdot{}^1/_2C_5H_{12}}$
empirical formula	$C_{36}H_{59}Co_3N_2Si\cdot{}^1/_2(C_5H_{12})$
color; habit	black plate
crystal size	0.6 x 0.4 x 0.1 mm
crystal system	trigonal
space group	*R*3
unit cell dimens	$a = 10.789(2)$ Å $c = 59.60(2)$ Å
volume	6009(3) Å^3
peaks to determine cell	14
2θ range of cell peaks	45−50°
Z	6
fw	763.8
density (calc)	1.261 g cm^{-3}
abs coeff	10.589 mm^{-1}
F(000)	2430
$R(F)^a$	7.41%
$R_w(F)^b$	8.65%

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

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2SiMe_3)$ (**5**)

Co(1)−Co(1a)	2.435(2)	Co(1)−C(1)−C(2)	131.4(3)
Co(1)−C(1)	1.875(8)	Co(1)−N(1)−N(2)	148(1)
C(1)−C(2)	1.47(2)	Co(1a)−N(1)−N(2)	116(1)
Co(1)−N(1)	1.889(7)	Co(1b)−N(1)−N(2)	128(1)
N(1)−N(2)	1.31(2)	N(1)−N(2)−C(3)	122(3)
N(2)−C(3)	1.25(5)	N(2)−C(3)−Si(1)	113(3)
C(3)−Si(1)	1.99(3)		
Si(1)−C(4)	1.76(3)		

The μ_3-N atom [N(1)] refined to a position on the 3-fold axis with a Co−μ_3-N distance of 1.889(7) Å, similar to the Co−μ_3-C distance. The disordered N(2) nitrogen atom is positioned 0.41 Å from the 3-fold axis; the N(1)−N(2) distance [1.31(2) Å] is consistent with a N=N double bond and the N(2)−C(3) distance [1.41(5) Å] is consistent with a C−N single bond. The disordered methylene C(3) carbon atom is positioned at 0.76 Å from the 3-fold axis and is only 3.25 Å from the nearest Cp* methyl group [C(11)]. The displacement of N(2) from the 3-fold axis appears to relieve unfavorable steric interactions between the C(3) carbon atom of the diazenide ligand and the proximal Cp* methyl groups without excessive deformation of the bond angles within the diazenide ligand. For example, both the sp^2 N(1)−N(2)−C(3) angle [122(3)°] and the sp^3 N(2)−C(3)−Si(1) angle [113(3)°] are only slightly larger than the expected values. The displacement of the N(2) diazenide atom from the 3-fold axis is similar to the deformation observed in the dinuclear diazenide cation $[Ir_2(\mu_2\text{-}O)(\mu_2\text{-}\eta^1\text{-}NN\{C_6H_4\text{-}o\text{-}C_3H_7\})(NO)_2(PPh_3)_2]^+$ (**7**) (Figure 2) in which one of the Ir−N−N angles is ~20° greater than the other Ir−N−N angle.[7] Likewise, the two equivalent phenyldiazenide ligands in the dimanganese octacarbonyl complex $[Mn(CO)_4(\mu\text{-}NNPh)]_2$ possess a large (134°) and a small (119°) Mn−N−N angle.[8] In each case, the distortion of the diazenide ligand is proposed to result from unfavorable steric interactions of the diazenide aryl group with the ancillary ligands.

Discussion

Formation of Diazenide Clusters 5 and 6. Formation of the diazenide clusters **5** and **6** from the monohydride cluster **1** and the respective organic diazo compound requires the formal 1,3 insertion of the diazo compound into the Co−H bond of **1**. The net transfer of a metal hydride to the α-carbon atom of a diazo ligand to form a diazenide ligand is unusual but has been observed in several instances. For example, the reaction of the tungsten tricarbonyl hydride complex $CpW(CO)_3H$ with diazomethane formed the methyldiazenide complex $CpW(CO)_2$-

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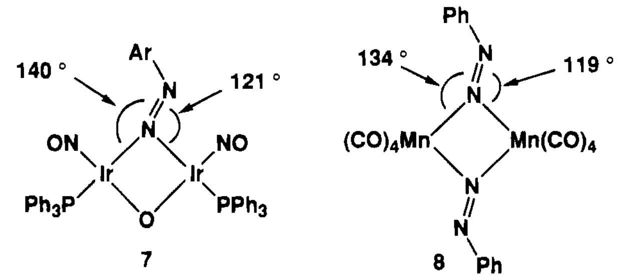
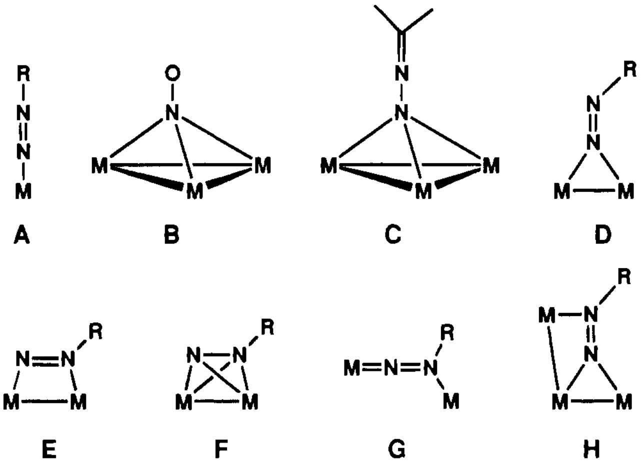


Figure 2. Deformation of the N−N−R angle in the diazenide clusters $[Ir_2(\mu_2\text{-}O)(\mu_2\text{-}\eta^1\text{-}NN\{C_6H_4\text{-}o\text{-}C_3H_7\})(NO)_2(PPh_3)_2]^+$ (**7**) and $[Mn(CO)_4(\mu\text{-}NNPh)]_2$ (**8**).

$NNCH_3$,[9] and the reaction of $HMn(CO)_5$ with diazomethane formed the unusual trinuclear methyldiazenide cluster $[Mn(CO)_4]_3(\mu_3\text{-}\eta^2\text{-}NNCH_3)$.[10]

Several possible pathways for formation of diazenide clusters **5** and **6** are suggested in Scheme 3. Coordination of the organic diazo compound to the 46 electron mono(ethylidyne) cluster **1** would form the 48-electron diazo mono(ethylidyne) intermediate **I**. Transfer of the hydride ligand of **I** to the α-carbon of the diazo ligand would then form diazenide cluster **5** or **6** directly. Alternatively, hydride transfer to the α-nitrogen could form the hydrazide intermediate **II**, which could then undergo a [1,3] sigmatropic hydrogen shift to produce the diazenide clusters. Related 1,1 insertions of diazo compounds into M−H bonds are well documented.[11] A third possibility involves hydride transfer to the β-nitrogen to give intermediate **III** followed by hydrogen migration to carbon.

Bonding of the Diazenide Ligand in Clusters 5 and 6. There are many examples of metal complexes with terminal diazenide (**A**),[11,12] μ_3-nitrosyl (**B**),[13] and μ_3-diazo (**C**)[5] ligands.



However, metal complexes which possess any type of bridging diazenide ligand are rare[12] and complexes **5** and **6** constitute a new structural type. Bridging diazenide ligands display an interesting variety of bonding modes. For example, μ_2-η^1-diazenide ligands (**D**) have been observed in dinuclear compounds[14] such as complexes **7**[7] and **8**[8] and also in trimetallic clusters such as $Os_3(\mu_2\text{-}H)(CO)_{10}(\mu_2\text{-}\eta^1\text{-}NN\text{-}p\text{-}C_6H_4CH_3)$[15] (**9**) and $Ru_3(CO)_9(\mu_2\text{-}\eta^1\text{-}NNC_6H_4)(\mu_3\text{-}PhPCH_2PPh)$ (**10**).[16] It is noteworthy that the trimetallic clusters **9** and **10** possess μ_2-diazenide ligands even though a third metal atom is available for μ_3-bridging. Other types of μ_2-η^2-diazenide complexes include structures of types **E**,[15a,17] **F**,[18] and **G**.[19] For example, the diiridium cation $[Cp^*{}_2Ir_2(CO)_2(\mu_2\text{-}\eta^2\text{-}NNC_6H_4OMe)]^+$ adopts structure **E**,[17] the dicobalt tetracarbonyl complex $[Co_2(CO)_4(\mu_2\text{-}\eta^2\text{-}N_2C_6H_4\text{-}4\text{-}CH_3)(\mu\text{-}Ph_2PCH_2PPh_2)][SbF_6]$ has structure **F**,[18a] and the heterobimetallic tungsten−chromium complex $Cp(CO)_2W(\mu_2\text{-}\eta^2\text{-}NNCH_3)Cr(CO)_5$ possesses structure **G**.[19a] A μ_3-η^2-diazenide ligand of type **H** has been observed in the trimanganese cluster $[Mn(CO)_4]_3(\mu_3\text{-}\eta^2\text{-}NNCH_3)$.[10]

Experimental Section

General Methods. All manipulations were performed under a nitrogen atmosphere in an inert-atmosphere glovebox or by standard high-vacuum techniques. ^1H NMR spectra were obtained on a Bruker WP200 or AM500 spectrometer, and ^{13}C NMR spectra were obtained on a Bruker AM500 (126 MHz) spectrometer. Infrared spectra were recorded on a Mattson Genesis FT-IR spectrometer. Mass spectra were determined on a Kratos MS-80 spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Hexane, pentane, and benzene were distilled from sodium and benzophenone. Benzene-d_6 was distilled from sodium and benzophenone or from sodium−potassium alloy. Ethyl diazoacetate (Aldrich) and (trimethylsilyl)diazomethane (Aldrich, 2 M in hexanes) were used as received.

$Cp^*{}_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2SiMe_3)$ (5). A 2.0 M solution of (trimethylsilyl)diazomethane in hexane (0.3 mL, 0.6 mmol) was added to a solution of **1** (56 mg, 0.1 mmol) in benzene (8 mL), and the mixture was stirred at room temperature for 4 h. Benzene and unreacted $N_2CHSiMe_3$ were evaporated under vacuum to give $Cp^*{}_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2SiMe_3)$ (**5**) (26 mg, 66%) as black powder which was ~98% pure by ^1H NMR. **5** was purified further by crystallization from hexane at −20 °C: ^1H NMR (C_6D_6, 200 MHz) δ 4.66 ($\mu_3\text{-}CCH_3$), 3.80 ($NNCH_2SiMe_3$), 1.52 (Cp*), 0.71 ($NNCH_2SiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ 92.4 (C_5Me_5), 62.6 ($NNCH_2SiMe_3$), 45.7 ($\mu_3\text{-}CCH_3$), 10.8 (C_5Me_5), 0.7 ($NNCH_2SiMe_3$), $\mu_3\text{-}CCH_3$ carbon not observed; IR (KBr) 2943 (s), 2887 (vs), 2840 (s), 1462 (w), 1455 (w), 1369 (m), 1320 (s), 1244 (m), 1195 (m), 1172 (sh), 1158 (sh), 1022 (m), 992 (m), 864 (s), 834 (s) cm^{-1}; HRMS (EI) calcd (found) for $C_{36}H_{59}N_2SiCo_3$ 724.2440 (724.2461). Both amorphous and crystalline samples of **5** were homogeneous and ≥ 98% pure by ^1H NMR.

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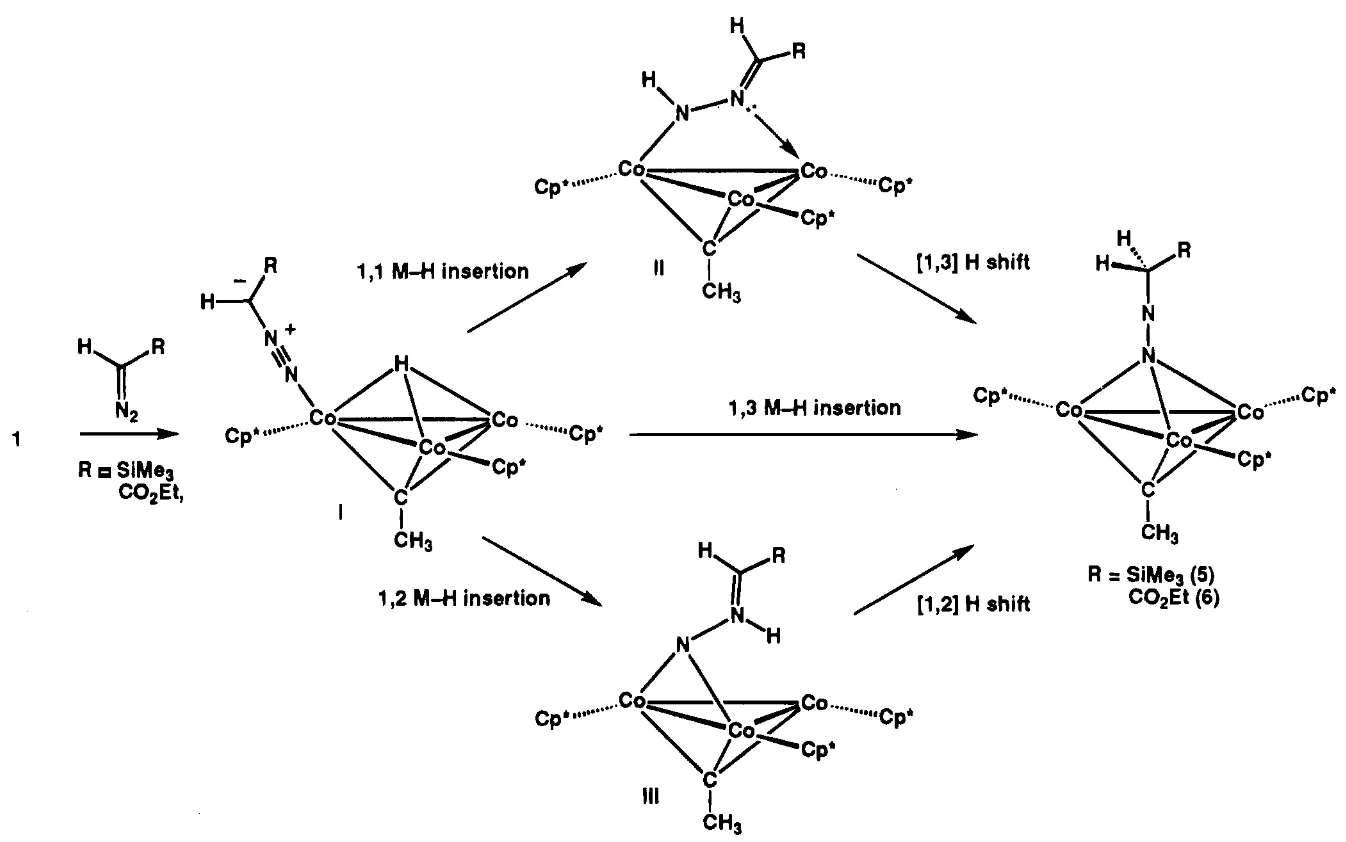
Scheme 3



However, the presence of solvent molecules of crystallization interfered with obtaining satisfactory elemental analysis data for **5**, in which the percent C was consistently high. Slow loss of solvent at room temperature from $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2SiMe_3)\cdot{}^1/_2C_5H_{12}$ (**$5\cdot{}^1/_2C_5H_{12}$**) caused problems with X-ray crystallographic data collection as noted below.

$Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2CO_2CH_2CH_3)$ (6). Ethyl diazoacetate (100 mg, 0.9 mmol) was added to a solution of **1** (56 mg, 0.1 mmol) in benzene (10 mL), and the mixture was stirred at room temperature for 30 min. Benzene and unreacted N_2CHCO_2Et were evaporated under vacuum to give $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2\text{-}CO_2CH_2CH_3)$ (**6**) (54 mg, 81%) as a black powder which was ~98% pure by ^{1}H NMR. **6** was purified further by crystallization from pentane at −20 °C: ^{1}H NMR (C_6D_6, 200 MHz) δ 5.04 ($\mu_3\text{-NNC}\mathit{H}_2\text{CO}_2\text{CH}_2\text{CH}_3$), 4.58 ($\mu_3\text{-CCH}_3$), 4.40 (q, J = 7.2 Hz, $\text{NNCH}_2\text{CO}_2\text{C}\mathit{H}_2\text{CH}_3$), 1.53 ($\text{C}_5\mathit{Me}_5$), 1.25 (t, J = 7.2 Hz; $\text{NNCH}_2\text{CO}_2\text{CH}_2\text{C}\mathit{H}_3$); ^{13}C {^{1}H} NMR ($C_6D_6$, 126 MHz) δ 172.2 ($\text{NNCH}_2\mathit{C}\text{O}_2\text{CH}_2\text{CH}_3$), 92.8 ($\mathit{C}_5\text{Me}_5$), 71.7 ($\text{NN}\mathit{C}\text{H}_2\text{CO}_2\text{CH}_2\text{CH}_3$), 60.2 ($\text{NNCH}_2\text{CO}_2\mathit{C}\text{H}_2\text{CH}_3$), 45.7 ($\mu_3\text{-C}\mathit{C}\text{H}_3$), 14.8 ($\text{NNCH}_2\text{CO}_2\text{CH}_2\mathit{C}\text{H}_3$) 10.6 ($\text{C}_5\mathit{Me}_5$), $\mu_3\text{-}\mathit{C}\text{CH}_3$ carbon not observed; IR (KBr) 2880 (s), 2952 (s), 2905 (vs), 2855 (s), 1724 (s), 1481 (w), 1459 (sh), 1447 (m), 1435 (sh), 1370 (s), 1345 (m), 1306 (w), 1288 (w), 1249 (m), 1153 (s), 1022 (m), 992 (m) cm^{-1}; HRMS (EI) calcd (found) for $C_{36}H_{53}N_2O_2Co_3$(M^+ − 2H) 722.2100 (722.2101). Anal. Calcd (found) for $C_{36}H_{55}N_2O_2Co_3$: C, 59.67 (59.45); H, 7.65 (7.63); N, 3.87 (3.84).

X-ray Crystallography of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2\text{-}SiMe_3)\cdot{}^1/_2C_5H_{12}$ ($5\cdot{}^1/_2C_5H_{12}$). A pentane solution of **5** which contained small seed crystals was slowly cooled to −20 °C to give black crystals of **5** suitable for X-ray analysis. A platelike crystal was coated in epoxy and mounted on the tip of a thin glass fiber. Although large, this crystal was found to be weakly diffracting such that an inadequate data set for a structural determination was originally obtained at low temperature via a Siemens P4 diffractometer/sealed tube generator system (Mo Kα radiation: 55 kV, 40 mA). A subsequent data set obtained with a P4 diffractometer/rotating anode generator system (Cu Kα radiation) at 23(2) °C (i.e., a low-temperature liquid N_2 setup was not available at that time) provided sufficient observed data to elucidate the crystal structure. An empirical ψ-scan absorption correction was applied to the intensities. The 2004 independent reflections collected under trigonal C_{3i}-$\bar{3}$ Laue symmetry (corresponding to the $\bar{h}kl$ octant) produced 1301 independent, observed reflections ($|F| > 4.0\sigma(F)$).

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}\eta^1\text{-}NNCH_2SiMe_3)\cdot{}^1/_2C_5H_{12}$ (**$5\cdot{}^1/_2C_5H_{12}$**)

	x	*y*	*z*	*U*(eq)
Co(1)	5236(1)	2214(1)	652(1)	36(1)
C(1)	6667	3333	444(2)	35(4)
C(2)	6667	3333	197(2)	71(6)
N(1)	6667	3333	864(2)	44(4)
N(2)	6400(35)	2899(21)	1071(3)	48(7)
C(3)	6079(36)	3524(38)	1215(5)	81(10)
Si(1)	6667	3333	1526(1)	104(3)
C(4)	5410(20)	3781(24)	1626(3)	315(30)
C(5)	3025(10)	1557(11)	642(3)	86(6)
C(6)	3268(10)	987(12)	835(2)	78(5)
C(7)	3849(9)	118(9)	756(2)	72(5)
C(8)	3881(9)	183(9)	524(2)	55(4)
C(9)	3397(10)	1054(11)	453(2)	74(5)
C(10)	2204(13)	2354(13)	641(3)	232(15)
C(11)	2888(14)	1097(18)	1062(2)	233(12)
C(12)	4192(13)	−810(11)	902(3)	161(9)
C(13)	4226(13)	−727(12)	375(2)	132(8)
C(14)	3101(13)	1276(14)	216(2)	157(9)
C(1S)	3333	6667	1449(12)	333(37)
C(2S)	4540(80)	7450(80)	1500(12)	191(25)
C(3S)	3730(120)	7980(90)	1603(14)	112(27)

The crystallographic analysis revealed that six molecules of cluster **5** and three molecules of pentane crystallize in a hexagonal unit cell of $R\bar{3}$ space group symmetry. Initial coordinates for the one independent Co atom were found by direct methods, and all other non-hydrogen atoms were located from successive difference Fourier maps. Each tricobalt cluster **5** was found to lie on a crystallographic 3-fold axis which thereby produces an "averaged" composite structure. The pseudo-3-fold axis passes through the C(1) and C(2) atoms of the μ_3-CCH_3 ligand and the N(1) and Si(1) atoms of the μ_3-$NNCH_2SiMe_3$ ligand. The off-axis N(2) and methylene C(2) atoms are crystallographically disordered over three symmetry-equivalent positions and hence were refined with unit occupancy factors of $^1/_3$. The fact that each pentane molecule has crystallographic $\bar{3}$ site symmetry gives rise to a badly disordered solvent molecule which could not be reliably modeled; the resulting large atomic esd's indicate that its molecular parameters are not physically meaningful.

All non-hydrogen atoms were refined anisotropically along with fixed contributions from the hydrogen atoms located at idealized positions with isotropic thermal parameters of $U = 0.08$ Å^2. Crystallographic computations were performed with SHELXTL-PLUS[20] software. The largest residual on the final difference map was only -0.54 e Å^{-3}. Crystallographic data (Table 1), selected bond lengths and bond angles (Table 2), and atomic coordinates (Table 3) are presented.

It is apparent that the crystal packing is determined by the sterically demanding clusters, with the solvent molecules occupying the voids. Although a non-disordered crystal structure would have been highly desirable, crystals could not be obtained despite great effort. Of prime importance, however, is that the structural determination unequivocally established the connectivities of all non-hydrogen atoms in **5**.

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Supplementary Material Available: Tables of structure determination data, anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, and idealized atomic parameters of hydrogen atoms for compound **5** (8 pages). Ordering information is given on any current masthead page.

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

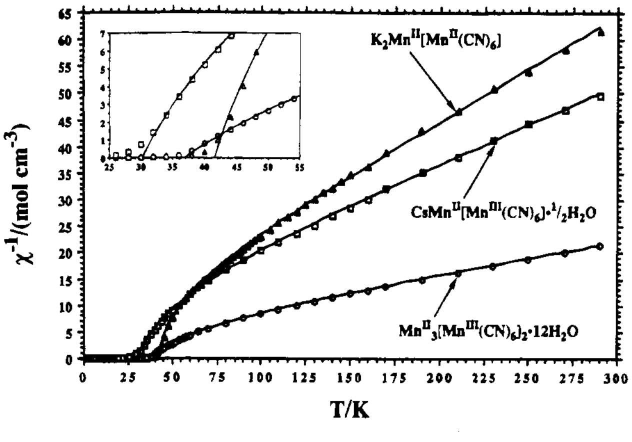
Additions and Corrections

1994, Volume 33

William R. Entley and Gregory S. Girolami*: New Three-Dimensional Ferrimagnetic Materials: $K_2Mn[Mn(CN)_6]$, $Mn_3[Mn(CN)_6]_2 \cdot 12H_2O$, and $CsMn[Mn(CN)_6] \cdot {}^1/_2H_2O$.

Page 5165. In Table 1, the oxidation states for the metal centers in compound **2** were incorrect; the correct formulation is $Mn^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$.

Page 5166. The degrees of hydration of compounds **2** and **3** in Figure 2 were incorrect. A revised version of Figure 2 is shown below.



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