Contribution No. 3572 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Structures of Metallocarboranes. 7. Preparation of Monocarbon Polymetallocarboranes and the Crystal and Molecular Structure of a Novel Electron-Rich *nido*-Trimetallocarborane[1]

CHRIS G. SALENTINE, CHARLES E. STROUSE,* and M. FREDERICK HAWTHORNE*

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Reaction of *nido*-3-R-2-CB_5H_8 (R = H or CH_3) with nickelocene and sodium amalgam has yielded the first trimetallocarboranes containing nickel, $(C_5H_5Ni)_3CB_5H_5R$, isolated in several isomeric forms. The complexes are formulated as formal mixed-valence Ni(III)–Ni(III)–Ni(IV) systems; the near-infrared spectra support this formulation and indicate substantial mixed-valence charge transfer. Reaction of *closo*-1-$CB_9H_{10}^-$ with cobaltocene and sodium amalgam produced the closo icosahedral bimetallic species $(C_5H_5Co)_2CB_9H_{10}^-$ containing a metal–metal bond. The crystal structure of one isomer of $(C_5H_5Ni)_3CB_5H_6$ was determined from three-dimensional x-ray counter data. The complex crystallizes in the orthorhombic system, space group *Pbnm* (alternate setting of *Pnma*) with $a = 7.518$ (1) Å, $b = 14.740$ (2) Å, $c = 15.711$ (3) Å, and $Z = 4$. Refinement of 1840 independent reflections with $F_o > 3\sigma(F_o)$ led to a final value of $R = 3.16\%$. The electron-rich trimetallocarborane was found to adopt a novel nido geometry best described as a distorted monocapped square antiprism. Three nickel atoms and a boron atom compose the four-membered open face; the two equivalent nickel–nickel distances are 2.404 (1) Å. Nonbonded distances in the open face are Ni–Ni = 3.250 (1) Å and Ni–B = 2.991 (5) Å. The carbon resides in the cap position. The geometry is discussed in relation to electron-counting rules for polyhedral heteroboranes.

Previous work has shown that monocarbon carborane ligands may incorporate formal $\{C_5H_5Co\}^{2+}$ and $\{C_5H_5Ni\}^{3+}$ vertices in stable metallocarborane polyhedra.[2-6] In addition, recent work in these laboratories established the ability of borane ligands to incorporate formal $\{C_5H_5Ni\}^{3+}$ vertices into stable *closo*-heteroborane systems.[7,8] As a continuation of our studies[3-6] of monocarbon metallocarboranes, we have investigated the chemistry of the monocarbon carboranes $CB_9H_{10}^-$ and CB_5H_8R (R = H or CH_3). Reported here are the synthesis of bi- and trimetallocarboranes containing these carborane ligands and the full details of an x-ray crystal structure determination of one of these complexes, $(C_5H_5Ni)_3CB_5H_6$. A preliminary account of a portion of this work has appeared.[9]

Results and Discussion

Cage Opening of $CB_9H_{10}^-$. Recent work[7] has shown that the *closo*-borane anions $B_{10}H_{10}^{2-}$ and $B_{11}H_{11}^{2-}$ react with low-valent nickel reagents to yield the stable, icosahedral *closo*-metalloboranes $(C_5H_5Ni)_2B_{10}H_{10}$ and $C_5H_5NiB_{11}H_{11}^-$, electronic analogues[10] of $C_2B_{10}H_{12}$ and $CB_{11}H_{12}^-$, respectively. This constituted yet another example of direct insertion of transition metal atoms into closo polyhedra,[11,12] involving the use of low-valent metal reagents which are oxidized as they formally reduce the polyhedral heteroborane.

The carborane 1-carba-*closo*-decaborane(10)(1–), 1-$CB_9H_{10}^-$, was found to be inert toward cobaltocene in tetrahydrofuran (THF) at reflux. However, upon addition of sodium amalgam to the mixture, a reaction began immediately and the deep green, diamagnetic complex $[(CH_3)_4N][2,11\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}2,11\text{-}Co_2\text{-}1\text{-}CB_9H_{10}]$, I, could subsequently be isolated. Figure 1 depicts this reaction to form the air-stable icosahedral bimetallocarborane.

The 60-MHz ^1H NMR spectrum of I showed two resonances of equal intensity at τ 5.04 and 5.27, assigned to cyclopentadienyl groups. Also present were cation (τ 6.91) and carborane C–H (τ 7.61) resonances. The four peaks were of relative intensities 5:5:12:1, respectively (Table I). The 80.5-MHz ^{11}B NMR spectrum (Table II) showed nine unique resonances, indicating a lack of symmetry in the molecule. Tables III and IV present the infrared and electronic spectra and electrochemical data for complex I. As with other anionic Co(III) monocarbon metallocarboranes,[3a,4] a reversible oxidation was observed in the cyclic voltammogram. Both the color[13] of the complex and its mode of formation[7] imply the presence of a cobalt–cobalt bond in the polyhedron. With this assumption, the lack of symmetry uniquely defines the structure as that depicted in Figure 1.

Table I. The 60-MHz ^1H NMR Spectral Data

Complex[a]	Resonance, τ[b] (rel area)	Assignment[a]
I,[c] $[(CH_3)_4N][Cp_2Co_2CB_9H_{10}]$	6.91 (12) s 5.04 (5) s, 5.27 (5) s 7.61 (1) br	$(CH_3)_4N^+$ Cp C–H
II,[d] $Cp_3Ni_3CB_5H_6$	4.46 (1) s, 4.83 (2) s	Cp
III,[d] $Cp_3Ni_3CB_5H_6$	4.85 (2) s, 5.07 (1) s	Cp
V,[e] $Cp_3Ni_3CB_5H_5CH_3$	4.58 (1) s, 4.67 (1) s 4.76 (1) s	Cp Cp
VI,[d] $Cp_3Ni_3CB_5H_5CH_3$	4.62 (5) s, 4.82 (5) s 4.99 (5) s 9.06 (3) s 7.28 (1) br	Cp Cp CH_3 C–H

[a] Cp = cyclopentadienyl; C–H = carborane C–H. [b] Chemical shifts are relative to TMS = τ 10.00; s = singlet, d = doublet, br = broad. [c] Measured in CD_3CN. [d] Measured in benzene-d_6. [e] Measured in CCl_4.

Table II. The 80.5-MHz ^{11}B NMR Data

Complex	Rel areas	Chem shift[a] (J_{B-H}, Hz)
I[b]	1:1:1:1:1:1:1:1:1	–28.4 (135), –14.0 (135), –3.8 (130), –5.3 (130), +1.2, +2.1, +3.7 (150), +9.9 (130), +18.3 (135)
II[c]	1:2:2	–43.3, –31.6, –28.6
III[c]	1:2:2	–78.5, –26.2, +9.5
V[d]	1:1:1:1:1	–47.6 (155), –39.9,[e] –30.4 (140), +6.9 (140), +10.8 (150)
VI[c]	1:1:1:1:1	–72.3 (145), –33.5,[e] –14.9, –14.1, –3.0 (145)

[a] Relative to $Et_2O{\cdot}BF_3 = 0$. [b] Measured in acetone. [c] Measured in benzene. [d] Measured in CCl_4. [e] Singlet, confirmed from proton-decoupled spectrum.

The proposed structure of I contains some interesting implications regarding the mechanism of the cage-opening process. The cage opening of *closo*-$B_{10}H_{10}^{2-}$ to *nido*-$B_{10}H_{12}L_2$ (L = ligand) species has been reported,[14] and the proposed mechanism was essentially the reverse of the cage-closing process[15] observed for the reaction $B_{10}H_{12}L_2 \rightarrow B_{10}H_{10}^{2-}$. If 1-$CB_9H_{10}^-$ opens to a decaborane(14)-like intermediate by the proposed mechanism, the apex carbon may occupy any of the positions numbered 1, 3, 10, or 12 in Figure 1. Since

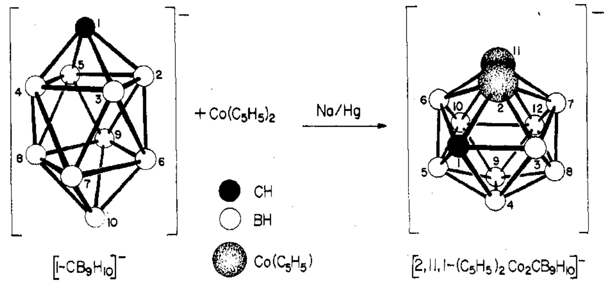

Figure 1. Cage-opening reaction of $CB_9H_{10}^-$ to the icosahedral bimetallic anion $(C_5H_5Co)_2CB_9H_{10}^-$.

Table III. Infrared Spectra

Complex	Freq, cm^{-1} (Nujol mull)
I	3050 w, 2450 vs, 1480 s, 1420 w, 1120 w, 1105 w, 1040 w, 1010 m, 955 m, 905 w, 885 w, 825 s, 805 m
III^a	2920 m, 2960 m, 2860 w, 2500 s, 1715 s, 1460 m, 1410 m, 1370 w, 1340 w, 1280 m, 1255 s, 1200 m, 1090 m, 1070 m, 1007 m, 865 m, 830 m, 800 s
V	3060 w, 2500 s, 2450 m, 1600 w, 1410 m, 1330 m, 1295 m, 1140 m, 1065 m, 1040 s, 1020 m, 1000 w, 905 w, 855 m, 805 vs, 780 m, 740 m
VI	3060 w, 2500 s, 2420 m, 1790 w, 1620 w, 1400 m, 1330 m, 1285 m, 1120 w, 1085 w, 1050 w, 1030 w, 1020 m, 1005 m, 885 s, 835 s, 803 vs, 794 vs, 743 w, 698 w

[a] Obtained with a Perkin-Elmer Model 421 spectrophotometer in $CHCl_3$ solution vs. a $CHCl_3$ standard.

Table IV. Electronic Spectra and Electrochemical Data

Complex	λ_{max}, nm (log ϵ)^a	$E_{p/2}$, V, vs. SCE^b
I	606 (2.91), 427 sh (2.87), 305 (4.52)	+0.20 ox.
III^c	850 (2.845),^{d} 630 (3.175), 318 (4.30), 285 (4.46)	
V^c	890 (2.30),^{d} 625 (3.36), 320 sh (4.43), 277 (4.57)	
VI	875 (2.66),^{d} 630 (3.36), 318 (4.45), 275 (4.53)	−0.95 red. +0.49 ox.^{e}

[a] Measured in Spectroquality CH_3CN, except where noted; sh = shoulder. [b] Cyclic voltammetry in CH_3CN with 0.1 M $R_4N^+PF_6^-$ ($R = C_2H_5$ or C_4H_9) supporting electrolyte, platinum button electrode; reversible waves except where noted; red. = reduction, ox. = oxidation. [c] Electronic spectrum measured in Spectroquality CH_2Cl_2. [d] Near-infrared band was broad and stretched to 1500 nm. [e] Irreversible wave.

these positions are all equivalent, even after metal complexation, only one isomer of I could be formed by this mechanism, the isomer with no plane of symmetry. With carbon at any other of the six possible positions, a plane of symmetry would exist. Thus the production of I may be seen as further supporting evidence for both the proposed[14] cage-opening mechanism and the use of this mechanism in the analogous synthesis of $(C_5H_5Ni)_2B_{10}H_{10}$ from $B_{10}H_{10}^{2-}$. Whether this cage opening occurs prior to or during reaction with the metal species is uncertain.

It is curious that no monometallic products are observed in the cage-opening reactions of $B_{10}H_{10}^{2-}$ or $CB_9H_{10}^-$; this may indicate that the overall mechanism does not involve a monometallic intermediate.

Synthesis of Electron-Rich Trimetallocarboranes. The reaction of 2-carba-*nido*-hexaborane(9), CB_5H_9, with nickelocene and sodium amalgam in THF afforded a mixture of

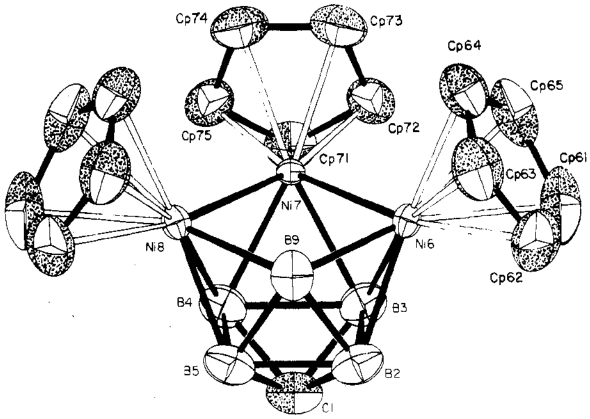

Figure 2. ORTEP drawing of *nido*-$(C_5H_5Ni)_3CB_5H_6$, III. Atoms are shown as 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

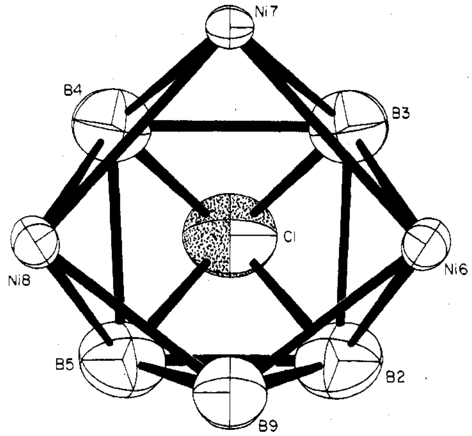

Figure 3. View of the $(C_5H_5Ni)_3CB_5H_6$ polyhedron approximately normal to the nido face. Cyclopentadienyl groups and hydrogen atoms have been omitted.

products. Two isomers of green, diamagnetic, air-stable $(C_5H_5Ni)_3CB_5H_6$, II and III, were isolated in low yield by column chromatography on silica gel. The mass spectra of II and III were identical, showing cutoffs at *m/e* 448 corresponding to the $^{12}C_{16}{}^1H_{21}{}^{11}B_5{}^{60}Ni_3{}^+$ ion.

The 60-MHz ^1H NMR spectra of both II and III (Table I) contained sharp singlets of relative area 2:1 which were assigned to the cyclopentadienyl moieties. The 80.5-MHz ^{11}B NMR spectra (Table II) were also similar and showed resonances of relative area 1:2:2. These data are consistent with a molecular plane of symmetry for both II and III.

Because $\{C_5H_5Ni\}$ is isoelectronic with $\{CH\}$ (with respect to the number of electrons donated to polyhedral bonding[10]), metallocarboranes II and III are analogous to the hypothetical species $C_4B_5H_9$. Thus these trimetallocarboranes possess two more electrons than required for a closo geometry and are predicted[16,17] to have nido structures. The types of polyhedral distortion that the trimetallic complexes could conceivably undergo to adopt a nido geometry were many, and the NMR data did not uniquely define a structure. Therefore the structure of III was determined via a single-crystal x-ray diffraction study. The results and a full discussion of the structure are reported below. Figures 2 and 3 show accurate representations of the molecular structure. Briefly, the nine-vertex polyhedron did indeed adopt a nido geometry, containing an open four-membered face composed of three nickel atoms and a boron atom. The polyhedron can be viewed as a slightly distorted monocapped square antiprism.

The structure of III established the preference of $\{NiC_5H_5\}$ to adopt a low-coordinate polyhedral position in the tri-

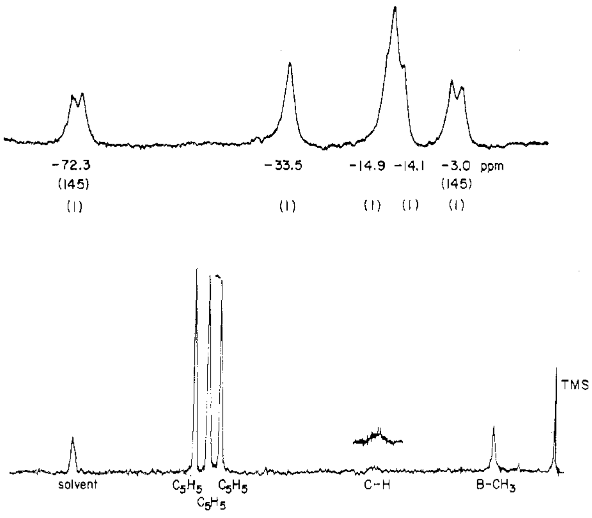

Figure 4. The 80.5-MHz ^{11}B NMR spectrum (top) and 60-MHz ^1H NMR spectrum (bottom) of *nido*-$(C_5H_5Ni)_3CB_5H_5CH_3$, VI.

metallocarborane, as all three nickel positions are formally four-coordinate. On the basis of the above considerations and the lack of a very low field resonance in the ^{11}B NMR spectrum,[6] we propose for II the structure *nido*-7,8,9-(η^5-$C_5H_5)_3$-7,8,9-Ni_3-6-CB_5H_6, using the numbering system of Figure 2. In this structure, all four heteroatoms reside at the low-coordinate open-face positions. This proposed structure would be expected to rearrange, if possible, and thus is substantiated by the slow polyhedral rearrangement of II to a new isomer, IV. The rearrangement occurred slowly in the solid state, with about 80% conversion after 1 year. Due to insufficient amount of sample, IV was characterized by mass and NMR spectra only. The mass spectrum of IV was identical with that of II or III. The 60-MHz ^1H NMR spectrum (in benzene-d_6) showed cyclopentadienyl resonances of equal area at τ 4.53, 4.81, and 5.00. The 80.5-MHz ^{11}B NMR spectrum showed resonances of area 1:1:1:1:1 at –70.9, –20.4, –15.5, –11.8, and –3.6 ppm, relative to $Et_2O\cdot BF_3$. The lack of symmetry, combined with the low-field ^{11}B NMR signal,[6] is consistent with the structure *nido*-1,7,8-(η^5-$C_5H_5)_3$-1,7,8-Ni_3-6-CB_5H_6 for IV. This transformation is in agreement with the established preference for carbon–metal separation in polyhedral rearrangement[18] and represents the first example of polyhedral rearrangement in an electron-rich metallocarborane. Rearrangement of the electron-rich carborane anions, $C_2B_{10}H_{12}^{2-}$, has previously been observed.[19]

The reaction of 2-carba-3-methyl-*nido*-hexaborane(9), $CB_5H_8CH_3$, with nickelocene and sodium amalgam in tetrahydrofuran produced two trimetallocarboranes of the formula $(C_5H_5Ni)_3CB_5H_5CH_3$, V and VI. Elemental analysis and mass spectra were consistent with these formulations; NMR data (Tables I and II) established that they were methyl derivatives of the parent compounds, V a derivative of II and VI a derivative of III. Methyl substitution removed the symmetry in both V and VI, so that three cyclopentadienyl resonances in the ^1H NMR and five boron resonances in the ^{11}B NMR spectra were observed. Figure 4 shows the NMR spectra of VI. The singlet in the ^{11}B NMR spectrum at –33.5 ppm is characteristic of the B–CH_3 moiety. The methyl-substituted boron atom was adjacent to carbon in the starting material and thus may remain adjacent in the product. Therefore V is formulated as *nido*-2-CH_3-7,8,9-(η^5-$C_5H_5)_3$-7,8,9-Ni_3-6-CB_5H_5, using the numbering system in Figure 2. There are two equally likely possibilities for the position of methyl substitution in VI, the 2 or 3 position. The 2 position may be slightly favored due to more steric crowding with the cyclopentadienyl groups at the 3 position.

Metallocarboranes II–VI can formally be constructed from the known metallocarborane[20] $(C_5H_5Ni^{III})_2C_2B_5H_7$ by replacement of a $\{CH\}^{3+}$ vertex with an "isoelectronic" $\{C_5H_5Ni\}^{3+}$ vertex. Thus they may be regarded as formal mixed-valence Ni(III)–Ni(III)–Ni(IV) systems. The near-infrared spectra (Table IV) exhibited broad bands in the region 800–1500 nm, indicating the possibility of mixed-valence charge transfer.[21] Using the crystallographic data (vide infra), an estimate of the interaction parameter, α, was made for complex III utilizing the equation[22]

$$\alpha^2 \cong (4.5 \times 10^{-4})\epsilon_{\max}\Delta_{1/2}/\nu r^2$$

where r is the distance separating the donor and acceptor in angstroms (2.404 Å), $\epsilon_{\max}$ is the molar absorptivity at the band maximum (700, from Table IV), $\Delta_{1/2}$ is the half-bandwidth in wavenumbers (2.86×10^4 cm^{-1}), and ν is the frequency in wavenumbers (850 nm, or 1.18×10^4 cm^{-1}, from Table IV). The interaction parameter is an indicator of the amount of valence delocalization or the extent of the interaction between the two moieties and is estimated at $\alpha = 0.363$ for III. With the nonbonded nickel–nickel distance of 3.250 Å for r (see below) the value of α is 0.269. These estimates place $(C_5H_5Ni)_3CB_5H_6$ among the class II mixed-valence compounds and indicate that the valences are not trapped.[21] Other class II mixed-valence compounds with smaller α values contain trapped valence states (α less than 0.25), such as the 1,1′-biferrocenylene[Fe(II),Fe(III)] salts.[22] Thus, a considerable amount of valence delocalization may occur in metallocarboranes II–VI, assuming correct assignment of the near-infrared band. It is unfortunate that no electronic spectral data for $(C_5H_5Ni^{III})_2C_2B_5H_7$ are available for comparison.

Cyclic voltammetry was performed with complex VI and showed a reversible reduction at $E_{p/2} = -0.95$ V, presumably a Ni(IV) → Ni(III) reduction by comparison with other formal Ni(IV)-containing heteroboranes.[4,5,7,8] Also observed was one well-defined irreversible oxidation wave at +0.49 V and two further irreversible oxidation waves at approximately +0.95 and +1.25 V. The oxidation wave (+0.49 V) occurs at a relatively low potential for most metallocarboranes and is consistent with previous cyclic voltammetry data for electron-rich metallocarboranes.[23]

Complexes II–VI are the first trimetallocarboranes containing nickel[24] and represent the only example of the synthesis of a trimetallic species by direct insertion of three transition metals into a *nido*-carborane. The process whereby three nickel atoms are inserted into *nido*-CB_5H_9 is unclear. Direct insertion of three $\{C_5H_5Co\}$ vertices into *closo*-$C_2B_5H_7$ has also been reported.[12] While the mechanisms of these unusual reactions are not known at this time, product stability certainly is of major importance, as exemplified by the metal insertion reactions of $CB_9H_{10}^-$ and $B_{10}H_{10}^{2-}$ whereby stable icosahedral products are formed from 10-vertex starting materials.

Crystal and Molecular Structure of *nido*-7,8,9-(η^5-$C_5H_5)_3$-7,8,9-Ni_3-1-CB_5H_6, III. Several recent crystal structures have established the existence of metal–metal bonds in bimetallocarboranes. These complexes were shown to contain cobalt–cobalt,[25,26] cobalt–nickel,[27] and iron–iron[28] bonds. With the exception of the electron-deficient biferracarborane,[28] these and other crystallographic studies of bimetallocarboranes involved species which satisfied the electronic requirements for *closo*-metallocarborane polyhedra. Previous crystallographic studies[29] of electron-rich metallocarboranes were limited to the monometallic icosahedral complexes $M(C_2B_9H_{11})_2^{n-}$ (M = Ni, n = 2; M = Cu, n = 1, 2) and showed that significant polyhedral distortion, though not to a formal nido structure, could occur as a result of excess electron density.

Because of the electron-rich nature of complex III, $(C_5H_5Ni)_3CB_5H_6$, we undertook the first crystallographic study of a trimetallocarborane to determine the extent of polyhedral distortion, if any, and to test the validity of the polyhedral electron-counting rules[10] and their applicability to the smaller polyhedral metallocarboranes.

Unit Cell and Space Group

Dark green-black crystals of III were air stable and did not decompose upon exposure to x-rays. Least-squares refinement of 15 automatically centered reflections from a rotation photograph revealed an orthorhombic unit cell of volume 1740.9 (5) Å^3, with dimensions a = 7.518 (1) Å, b = 14.740 (2) Å, and c = 15.711 (3) Å at 26 °C. The density, measured by flotation in aqueous cesium chloride solution, was 1.70 (2) g cm^{-3}, in agreement with the calculated density of 1.692 g cm^{-3} for $Z = 4$.

Examination of intensity data revealed the systematic absences $0kl$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, indicating space groups *Pbnm* and *Pbn*2$_1$, alternate settings of *Pnma* (D_{2h}^{16}, No. 62) and *Pna*2$_1$ (C_{2v}^{9}, No. 33), respectively.[30] Successful solution was accomplished in the former, centrosymmetric space group.

Collection and Reduction of the Diffraction Data

A sample of the compound was glued on a glass fiber and mounted on a Syntex $P\bar{1}$ automated diffractometer. The crystal had the form of a diamond-shaped plate, with an acute-angle corner missing. Distances from the existing acute corner on the (001) face to the other six faces were as follows: $(00\bar{1})$, 0.048 mm; $(\bar{1}10)$, 0; $(\bar{1}\bar{1}0)$, 0.415 mm; $(0\bar{1}0)$, 0.700 mm; $(1\bar{1}0)$, 0.357 mm; (110), 0.0.

Graphite crystal monochromatized Mo Kα radiation (λ 0.71069 Å) was utilized for data collection. A scan rate of 2.4°/min was employed over a scan interval from 0.9° below Mo Kα_1 to 0.9° above Mo Kα_2 with the θ–2θ scan technique. The ratio of time spent in counting background to time spent in counting the reflection was 0.8. The scintillation counter was 19.5 cm from the crystal, and a 1.8-mm beam collimator was used. A 4° takeoff angle was employed.

The intensities of 2931 independent reflections were collected to $2\theta = 60°$; of these, 1840 had $I > 3\sigma(I)$ and were used in subsequent calculations. The intensity of a reflection, $I(hkl)$, and $\sigma[I(hkl)]$, its estimated standard deviation, were calculated according to the equations $I = \mathrm{CT} - (t_c/t_b)(\mathrm{B1} + \mathrm{B2})/2$ and $\sigma = \{\sigma_s^2 + (0.04I)^2\}^{1/2}$, where I is the net integrated intensity, CT is the total integrated count, t_c and t_b are the times employed for counting the scan and background, respectively, B1 and B2 are the background counts on the low and high sides of the reflection, and σ_s is the standard deviation in the intensity due to counting statistics. The intensities of three standard reflections were remeasured every 97 reflections to monitor the tube efficiency and possible crystal deterioration. No significant deviations were observed. The reflections were corrected for Lorentz and polarization effects.

Solution and Refinement of the Structure

A three-dimensional Patterson map[31] showed a large vector along the z axis approximately 3.25 Å in length, suggesting space group *Pbnm* with the molecule bisected by a crystallographic mirror plane. The positions of the two independent nickel atoms were determined, and a Fourier synthesis based on these input parameters ($R = 0.264$, $R_w = 0.348$)[32] showed the positions of all of the remaining nonhydrogen atoms. Full-matrix least-squares refinement of the positional and isotropic temperature factors of the 14 independent atoms resulted in $R = 0.089$, $R_w = 0.111$. To this stage, all of the light atoms in the polyhedron were treated as boron atoms. The cage carbon atom was distinguished by its smaller temperature factor and bond distances and subsequently given carbon scattering factors. At this point an absorption correction was applied to the original data set ($\mu = 31.88$ cm^{-1}; maximum and minimum transmission factors were 0.8597 for (200) and 0.4425 for (022)). Another cycle of least-squares refinement, including anisotropic temperature factors for all atoms, was followed by a difference Fourier map which revealed the locations of all the hydrogen atoms. Least-squares refinement of all positional parameters, anisotropic thermal parameters of the nonhydrogen atoms, and isotropic thermal parameters of the hydrogen atoms, which anomalous dispersion corrections applied to the scattering of nickel, resulted in convergence at $R = 3.16\%$, $R_w = 3.93\%$. A final difference Fourier map was devoid of significant features; in particular, no peaks could reasonably be associated with any of the atoms constituting the open face (Ni6, Ni7, Ni8, and B9). The standard deviation of an observation of unit weight was 1.24.

Scattering factors for neutral nickel, carbon, and boron were taken from ref 33; hydrogen scattering factors were obtained from Stewart, Davidson, and Simpson;[34] and the real and imaginary corrections for anomalous scattering of nickel were taken from Cromer.[35] The function $\sum w\|F_o| - |F_c\|^2$ was minimized in the least-squares refinement.

Final positional and thermal parameters are listed in Tables V and VI. The final observed and calculated structure factors are available.[36]

Description of the Structure

The molecular structure of 7,8,9-$(\eta^5\text{-}C_5H_5)_3$-7,8,9-Ni_3-1-CB_5H_6, III, is shown in Figure 2. The molecular units are bisected by crystallographic mirror planes, in congruence with the molecular plane of symmetry established from the NMR data. The intramolecular distances and angles are tabulated in Tables VII and VIII.

In heteroborane chemistry the observed closo nine-vertex polyhedral geometry is the tricapped trigonal prism, as found for $B_9H_9^{2-}$,[37] $C_2B_7H_7(CH_3)_2$,[38] $[C_2B_6H_8Mn(CO)_3]^-$,[39] and $[C_5H_5CoCB_7H_8]^-$.[3b] The geometry observed for III consists of a nine-vertex "opened", or nido, polyhedron, which can be derived from a tricapped trigonal prism by the elongation of the Ni7–B9 polyhedral edge. The polyhedron is best described as a distorted monocapped square antiprism. Figure 3 shows a top view of the four-membered open face, composed of Ni6, Ni7, Ni8, and B9.

The unique nickel atom, Ni7, resides on the mirror plane and is bonded equivalently to the other nickel atoms at a distance of 2.404 (1) Å. This value is in the range of previously reported metal–metal distances in bimetallocarboranes, which range from 2.387 (2)[26] to 2.571 (1) Å.[28] For comparison, the range of bond lengths for nickel–nickel bonds in normal nickel cluster compounds[40] is about 2.33–2.51 Å. The Ni7–B9 separation, 2.991 (5) Å, is clearly a nonbonded distance and compares well with similar nonbonded distances found in *closo*-metallocarboranes (Co–B = 2.987 and 2.997 Å in $(C_5H_5Co)_2C_2B_6H_8$;[25] Co–B and Ni–B average 3.015 Å in $(C_5H_5)_2CoNiCB_7H_8$[27]).

Observed distortions from the idealized C_{4v} point symmetry appear to be a result of inclusion of the relatively large heteroatoms (Ni) into the carborane polyhedron and are as follows: (i) the open face departs substantially from the square form found in the regular capped square antiprism; however, only the angle about B9 (105.4 (2)°) deviates greatly from 90°; (ii) the B3–B4 bond distance, 1.977 (8) Å, is significantly longer than B2–B5, 1.798 (9) Å; the B2–B3 (B4–B5) distance of 1.916 (5) Å is also significantly longer than the normal boron–boron distance of about 1.78 Å found in carboranes;[41] and (iii) atom B9 is displaced 0.282 (6) Å from the plane of the three nickel atoms in the direction of B2 and B5. As expected, though, the Ni6–Ni7–Ni8 plane is nearly parallel (angle 2.2 (2)°) to the B2–B3–B4–B5 plane.

The cyclopentadienyl rings and the three nickel polyhedral bonding faces (B4–B5–B9–Ni7, B2–B3–B9–Ni7, and B3–B4–Ni6–Ni8) are planar within experimental error. In addition, the nickel atoms are sandwiched between nearly parallel bonding faces; the dihedral angle between the planes is 6.7 (2)° for Ni6 and 12.2 (2)° for Ni7. The average Ni–Cp distance is 2.13 (3) Å, slightly larger than Co–Cp distances of 2.03–2.08 Å found in other metallocarboranes,[25,26] while the average Ni–B distance (2.060 (16) Å) is shorter than the 2.10–2.15 Å typical for Ni–B bonds in other metallocarboranes.[42–44] The carbon–carbon bond distances average 1.415 (9) Å, in good agreement with previously observed values.[45] The dihedral angle between the two independent cyclopentadienyl rings is 88.3 (2)°.

Table V. Positional and Anisotropic Thermal Parameters for All Nonhydrogen Atoms[a,b]

Atom	x/a	y/b	z/c
Ni6	0.336 60 (5)	0.397 35 (3)	0.353 44 (2)
Ni7	0.527 03 (7)	0.326 57 (3)	0.250 00 (0)
C1	0.558 1 (7)	0.533 7 (3)	0.250 0 (0)
B2	0.376 9 (5)	0.527 7 (2)	0.307 2 (3)
B3	0.576 8 (4)	0.447 3 (2)	0.312 9 (3)
B9	0.229 1 (7)	0.461 0 (4)	0.250 0 (0)
Cp61	0.357 5 (6)	0.381 9 (4)	0.489 6 (2)
Cp62	0.206 4 (6)	0.433 2 (3)	0.466 9 (3)
Cp63	0.093 0 (5)	0.377 8 (3)	0.416 9 (3)
Cp64	0.175 6 (6)	0.293 5 (3)	0.405 7 (3)
Cp65	0.339 8 (6)	0.295 3 (3)	0.450 1 (3)
Cp71	0.783 5 (6)	0.270 8 (3)	0.250 0 (0)
Cp72	0.691 1 (5)	0.240 0 (2)	0.322 5 (2)
Cp73	0.543 5 (5)	0.187 0 (2)	0.294 6 (3)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni6	69 (1)	20.8 (2)	13.7 (2)	2.3 (3)	3.1 (3)	−2.3 (1)
Ni7	59 (1)	12.5 (2)	14.3 (2)	3.4 (4)	0 (0)	0 (0)
C1	183 (10)	32 (2)	53 (3)	−7 (4)	0 (0)	0 (0)
B2	172 (7)	29 (1)	45 (2)	5 (3)	−3 (3)	−7 (1)
B3	123 (6)	34 (2)	37 (2)	−4 (2)	−5 (3)	−5 (1)
B9	127 (8)	43 (3)	31 (2)	8 (4)	0 (0)	0 (0)
Cp61	228 (9)	116 (4)	24 (1)	−21 (5)	3 (3)	1 (2)
Cp62	272 (10)	68 (2)	39 (2)	−2 (4)	37 (3)	−12 (2)
Cp63	161 (7)	74 (3)	45 (2)	6 (3)	25 (3)	5 (2)
Cp64	231 (8)	57 (2)	40 (2)	−16 (3)	26 (3)	8 (2)
Cp65	229 (9)	78 (3)	36 (2)	28 (4)	23 (3)	20 (2)
Cp71	124 (8)	44 (2)	44 (2)	12 (3)	0 (0)	0 (0)
Cp72	180 (7)	44 (2)	39 (2)	19 (3)	−6 (3)	7 (1)
Cp73	208 (7)	32 (1)	56 (2)	11 (3)	13 (3)	8 (1)

[a] The β_{ij}'s have been multiplied by 10^4. The anisotropic temperature factors are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The numbers in parentheses are the estimated standard deviations in the last digits.

Table VI. Positional and Isotropic Thermal Parameters for Hydrogen Atoms[a]

Atom	x/a	y/b	z/c	B, Å^2
HC1	0.6452 (55)	0.5918 (27)	0.2500 (0)	0.1 (8)
HB2	0.3225 (50)	0.5830 (25)	0.3530 (25)	2.7 (9)
HB3	0.6929 (46)	0.4447 (24)	0.3602 (22)	1.6 (7)
HB9	0.0788 (63)	0.4664 (31)	0.2500 (0)	1.5 (10)
H61	0.4716 (79)	0.4116 (31)	0.5317 (37)	7.6 (15)
H62	0.1826 (58)	0.5035 (34)	0.4853 (33)	5.2 (12)
H63	−0.0421 (70)	0.4033 (30)	0.3898 (31)	5.2 (12)
H64	0.0767 (80)	0.2245 (39)	0.3673 (37)	8.9 (17)
H65	0.4346 (61)	0.2349 (31)	0.4630 (32)	5.3 (12)
H71	0.9069 (92)	0.3099 (42)	0.2500 (0)	4.4 (16)
H72	0.7438 (62)	0.2533 (31)	0.3863 (29)	4.1 (11)
H73	0.4383 (59)	0.1398 (28)	0.3359 (30)	5.7 (12)

[a] See footnote *b* of Table V.

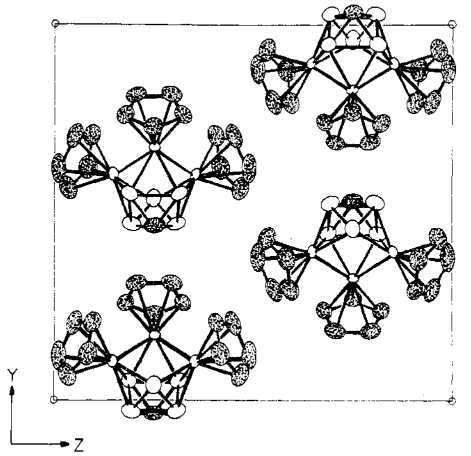

Figure 5. Projection of the unit cell for $(C_5H_5Ni)_3CB_5H_6$ along the *x* direction. Hydrogen atoms have been omitted.

Table VII. Interatomic Distances (Å)[a]

I. Distances around Nickel Atoms			
Ni6–Cp61	2.157 (4)	Ni6–Ni7	2.4040 (5)
Ni6–Cp62	2.101 (4)	Ni6···Ni8	3.2503 (8)
Ni6–Cp63	2.105 (4)	Ni6–B2	2.077 (4)
Ni6–Cp64	2.117 (4)	Ni6–B3	2.051 (4)
Ni6–Cp65	2.137 (4)	Ni6–B9	2.043 (3)
Ni7–Cp71	2.096 (5)	Ni7–B3	2.070 (3)
Ni7–Cp72	2.109 (3)	Ni7···B9	2.991 (5)
Ni7–Cp73	2.177 (3)		
II. Cyclopentadienyl Ring Distances			
Cp61–Cp62	1.410 (6)	Cp64–Cp65	1.418 (6)
Cp61–Cp65	1.426 (7)	Cp71–Cp72	1.410 (5)
Cp62–Cp63	1.418 (6)	Cp72–Cp73	1.426 (5)
Cp63–Cp64	1.401 (6)	Cp73–Cp74	1.403 (8)
III. Boron-Boron Distances			
B2–B3	1.916 (5)	B2–B9	1.735 (6)
B2–B5	1.798 (9)	B3–B4	1.977 (8)
IV. Boron-Carbon Distances			
B2–C1	1.634 (6)	B3–C1	1.618 (5)
V. Boron-Hydrogen and Carbon-Hydrogen Distances			
B2–HB2	1.16 (4)	Cp63–H63	1.16 (5)
B3–HB3	1.15 (3)	Cp64–H64	1.40 (6)
B9–HB9	1.13 (5)	Cp65–H65	1.16 (5)
C1–HC1	1.08 (4)	Cp71–H71	1.09 (7)
Cp61–H61	1.17 (6)	Cp72–H72	1.10 (5)
Cp62–H62	1.09 (5)	Cp73–H73	1.24 (5)

[a] See footnote *b* of Table V.

The crystal packing of the unit cell is shown in Figure 5 as a projection along the *x* direction. The molecules are bisected by crystallographic mirror planes at $z = {}^1/_4$ and $z = {}^3/_4$. The shortest intermolecular contacts are 2.14 (6) Å between HB3 and H63, 2.15 (6) Å between HB2 and H73, and 2.23 (7) Å between HB2 and H64. All other contacts are greater than 2.38 Å.

The trimetallocarborane III possesses two more electrons than required for a closo geometry and is predicted[10,16,17] to be nido, as crystallographically found. However, the nido configuration is achieved through the theoretical elongation of the Ni7–B9 polyhedral edge (in a tricapped-trigonal-

Table VIII. Interatomic Angles (deg)[a]

I. Angles about Nickel Atoms			
B2-Ni6-B3	55.3 (1)	Ni7-Ni6-Cp64	106.8 (1)
-Cp61	115.7 (2)	-Cp65	99.7 (1)
-Cp62	97.6 (2)	-B9	84.1 (1)
-Cp63	114.8 (2)	B9-Ni6-Cp61	150.0 (2)
-Cp64	152.7 (2)	-Cp62	112.0 (2)
-Cp65	153.9 (2)	-Cp63	95.5 (2)
-Ni7	94.5 (1)	-Cp64	114.5 (2)
-B9	49.8 (2)	-Cp65	153.2 (2)
B3-Ni6-Cp61	106.4 (2)	B3-Ni7-B4	57.1 (2)
-Cp62	125.7 (2)	-Ni6	54.0 (1)
-Cp63	164.1 (2)	-Cp71	99.9 (2)
-Cp64	152.0 (2)	-Cp72	99.0 (1)
-Cp65	117.6 (2)	-Cp73	130.4 (2)
-Ni7	54.7 (1)	-Cp74	162.9 (1)
-B9	86.4 (2)	-Cp75	132.3 (1)
Cp61-Ni6-Cp62	38.7 (2)	-Ni8	93.3 (1)
-Cp63	65.1 (2)	Ni6-Ni7-Cp71	135.89 (4)
-Cp64	65.2 (2)	-Cp72	104.2 (1)
-Cp65	38.8 (2)	-Cp73	103.1 (1)
Cp62-Ni6-Cp63	39.4 (2)	-Cp74	131.4 (1)
-Cp64	65.6 (2)	-Cp75	167.5 (1)
-Cp65	65.1 (2)	-Ni8	85.07 (2)
Cp63-Ni6-Cp64	38.8 (2)	Cp71-Ni7-Cp72	39.2 (1)
-Cp65	65.0 (2)	-Cp73	65.0 (2)
Cp64-Ni6-Cp65	38.9 (2)	Cp72-Ni7-Cp73	38.8 (1)
Ni7-Ni6-Cp61	125.5 (1)	-Cp74	64.5 (1)
-Cp62	163.8 (1)	-Cp75	65.4 (2)
-Cp63	141.2 (1)	Cp73-Ni7-Cp74	37.6 (2)
II. Angles around Cp Carbon Atoms			
Cp62-Cp61-Ni6	68.5 (2)	Cp61-Cp65-Ni6	71.4 (2)
Cp65-Cp61-Ni6	69.8 (2)	Cp64-Cp65-Ni6	69.8 (2)
Cp65-Cp61-Cp62	107.1 (4)	Cp64-Cp65-Cp61	108.2 (4)
Cp61-Cp62-Ni6	72.8 (2)	Cp72-Cp71-Ni7	70.9 (2)
Cp61-Cp62-Cp63	108.4 (4)	Cp72-Cp71-Cp75	107.9 (5)
Cp63-Cp62-Ni6	70.4 (2)	Cp71-Cp72-Ni7	69.9 (2)
Cp62-Cp63-Ni6	70.2 (2)	Cp71-Cp72-Cp73	108.1 (4)
Cp62-Cp63-Cp64	108.2 (4)	Cp73-Cp72-Ni7	73.2 (2)
Cp64-Cp63-Ni6	71.1 (2)	Cp72-Cp73-Ni7	68.0 (2)
Cp63-Cp64-Ni6	70.2 (2)	Cp72-Cp73-Cp74	107.9 (2)
Cp63-Cp64-Cp65	107.9 (4)	Cp73-Cp74-Ni7	71.2 (1)
Cp65-Cp64-Ni6	71.3 (2)		
III. Angles around Carbon			
B2-C1-B3	72.2 (2)	B3-C1-B4	75.3 (3)
B2-C1-B5	66.7 (3)	B3-C1-B5	111.5 (3)
IV. Angles around Boron Atoms			
C1-B2-B3	53.5 (2)	C1-B3-Ni6	113.3 (3)
-B5	56.6 (2)	-Ni7	111.7 (2)
-Ni6	111.3 (3)	B2-B3-B4	87.3 (2)
-B9	106.2 (3)	-Ni6	63.0 (2)
B3-B2-B5	92.7 (2)	-Ni7	111.6 (2)
-Ni6	61.7 (2)	B4-B3-Ni6	108.1 (1)
-B9	100.1 (3)	-Ni7	61.5 (1)
B5-B2-Ni6	110.5 (1)	Ni6-B3-Ni7	71.4 (1)
-B9	58.8 (2)	B2-B9-B5	62.4 (3)
Ni6-B2-B9	64.1 (2)	-Ni6	66.1 (2)
C1-B3-B2	54.3 (2)	-Ni8	114.8 (3)
-B4	52.3 (2)	Ni6-B9-Ni8	105.4 (2)
V. Angles Involving Hydrogen Atoms			
HC1-C1-B2	123 (2)	H63-Cp63-Cp62	123 (2)
-B3	125 (1)	-Cp64	129 (2)
HB2-B2-C1	127 (2)	H64-Cp64-Ni6	132 (2)
-B3	133 (2)	-Cp63	118 (2)
-B5	128 (2)	-Cp65	134 (2)
-Ni6	112 (2)	H65-Cp65-Ni6	132 (2)
-B9	120 (2)	-Cp61	124 (2)
HB3-B3-C1	119 (2)	-Cp64	127 (2)
-B2	130 (2)	H71-Cp71-Ni7	125 (3)
-B4	130 (2)	-Cp72	126.0 (2)
-Ni6	117 (2)	H72-Cp72-Ni7	127 (2)
-Ni7	115 (2)	-Cp71	120 (2)
H61-Cp61-Ni6	125 (3)	-Cp73	131 (2)
-Cp62	122 (3)	H73-Cp73-Ni7	132 (2)
-Cp65	131 (3)	-Cp72	130 (2)
H62-Cp62-Ni6	123 (3)	-Cp74	122 (2)
-Cp61	125 (2)	HB9-B9-B2	127 (2)
-Cp63	127 (2)	-Ni6	115 (1)
H63-Cp63-Ni6	123 (2)	-Ni7	143 (2)

[a] See footnote *b* of Table V. Within each group, angles are listed in increasing numerical order of the central atom and then increasing numerical order of the first atom.

prismatic geometry) to generate a four-membered open face, rather than by the elongation of two edges (such as Ni7–B3 and Ni7–B4) to generate a five-membered open face. This latter nido geometry has been predicted[16] for $C_4B_5H_9$, postulated[46] for the known borane anion $B_9H_{12}^-$, crystallographically shown[47] for $C_2B_7H_9(CH_3)_2$, but was not found here. It is interesting that molecular orbital calculations[37] performed on $B_9H_9^{2-}$ indicated that upon two-electron reduction the preferred structure would be the C_{4v} monocapped square antiprism. Presented here is the first confirmed example of this gross geometry in polyhedral borane chemistry.

The above observations may be pertinent to the determination of how the closo nine-vertex polyhedron opens upon addition of two electrons.[48] In fact, it has been observed[49] that $B_9H_9^{2-}$ opens in the presence of $[C_5H_5NiCO]_2$ to produce the previously reported[8] metalloborane anion 1-(η^5-C_5H_5)-1-$NiB_9H_9^-$. It is noted that III contains all three nickel atoms at low-coordinate polyhedral vertices, further evidence of the ability,[5,6] and even preference,[8] of $\{C_5H_5Ni\}$ to reside in a low-coordinate position.

The crystallographic results reported here imply that $(C_5H_5Ni)_2C_2B_5H_7$[20] would also possess a nido geometry, rather than the proposed closo structure. Based on the NMR data,[20] a probable structure would then be *nido*-8,9-(η^5-$C_5H_5)_2$-8,9-Ni_2-6,7-$C_2B_5H_7$, using the numbering system in Figure 2. This structure is similar to that proposed for II, with $\{C_5H_5Ni\}$ replaced by $\{CH\}$.

Electron-rich metallocarboranes of the formula Cu-$(C_2B_9H_{11})_2^{n-}$ (n = 1, 2) were found to possess "slipped sandwich" structures[29] containing weak Cu–C interactions of length ~2.52 Å while the electron-rich 2,2′-Ni-(1,7-$C_2B_9H_{11})_2^{2-}$ was found to exhibit only a slight "slip" distortion[29] resulting in a Ni–C distance of 2.39 Å. These results with $(C_5H_5Ni)_3CB_5H_6$ indicate that electronic effects upon geometry are more pronounced in the smaller polyhedral systems, as fewer atoms are available to disperse excess electron density. Also, because the carboranyl ligand is a three-dimensional aromatic ligand capable of delocalizing electron density over as many as 12 atoms as opposed to the smaller cyclopentadienyl ligand, the use of cyclopentadienyl over carboranyl ligands (L) in complexes of the formula $(LM)_xC_2B_nH_{n+2}$ would be expected to enhance electronic effects upon polyhedral geometry, increasingly as x increases. This factor as well as polyhedral size appears to play the most significant role in determining the effects of excess electron density upon polyhedral geometry.

Experimental Section

Physical Measurements. Ultraviolet–visible–near-ir spectra were measured with a Cary 14 spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Proton NMR spectra were obtained on a Varian A-60D spectrometer. The 80.5-MHz ^{11}B NMR spectra were obtained with an instrument designed by Professor F. A. L. Anet of this department. Electrochemical data were obtained with an instrument described previously.[50] Mass spectra were measured using an Associated Electrical Industries MS-9 spectrometer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Melting points are uncorrected.

Materials. Literature methods were used to prepare $CsCB_9H_{10}$ (from pyrolysis of $CsCB_{10}H_{13}$),[2] cobaltocene,[51] nickelocene,[51] 2-CB_5H_9,[52] and 3-CH_3-2-CB_5H_8.[52] Sodium amalgam (about 0.5% Na) was prepared by careful treatment of molten sodium under xylene with mercury. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ and stored under nitrogen prior to use. Other solvents were reagent grade and used without further purification. Spectroquality acetonitrile and tetramethylammonium chloride were obtained from Matheson Coleman and Bell. Sodium metal was purchased from Allied Chemical Co. Silica gel powder, 60–200 mesh, was obtained from J. T. Baker Chemical Co. for use in column chromatography. Preparative thick-layer chromatography was performed with Chrom AR Sheet purchased from Mallinckrodt Chemical Co.

[$(CH_3)_4N$][2,11-(η^5-C_5H_5)$_2$-2,11-Co_2-1-CB_9H_{10}], I. $CsCB_9H_{10}$ (0.454 g, 1.8 mmol) was converted to the Na^+ salt by passage down a Na^+-ion-exchange column in CH_3CN–H_2O (1:2 v/v). Solvents were removed under vacuum and nitrogen was admitted, followed by 100 ml of THF, 0.76 g of $Co(C_5H_5)_2$ (4 mmol), and 15 g of sodium amalgam. The solution was refluxed 20 h under N_2, another 10 g of sodium amalgam was added (total 5 mmol of sodium), and reflux was continued another 20 h. The solution was cooled and decanted from mercury. Oxygen was bubbled through the solution for 15 min. Filtration through Celite gave a deep green solution. The THF was removed under reduced pressure, 100 ml of H_2O was added, and the solution was again filtered. Addition of an aqueous solution of excess $(CH_3)_4NCl$ caused precipitation of a green compound. Acetone was added to clarity and the solution was rotary evaporated to a small volume under reduced pressure. The dark green crystals which formed were filtered and washed with water, followed by a small amount of cold 20% ethanol; yield 0.32 g (40% based on $CB_9H_{10}^-$) of green platelets of I, dec pt 250–270 °C. Anal. Calcd for $C_{15}H_{32}B_9Co_2N$: B, 22.03; C, 40.80; H, 7.30; Co, 26.69; N, 3.17. Found: B, 21.89; C, 40.52; H, 7.28; Co, 26.91; N, 3.32.

Trimetallocarboranes from CB_5H_9. Into a 250-ml three-necked flask, in a nitrogen-filled drybox, were placed 100 ml of THF, 0.19 g (2.5 mmol) of CB_5H_9, and 0.6 g (3.0 mmol) of $Ni(C_5H_5)_2$. The flask was removed from the drybox and cooled to 0 °C under N_2. Then was added ~40 g of sodium amalgam, and the solution was stirred 18 h. The solution was exposed to air, decanted from mercury, and treated with O_2 for 15 min. Filtration through Celite yielded a deep green solution, which was added to 20 g of silica gel. The solvent was removed and the solids were placed atop a 5 × 25 cm silica gel chromatography column prepared in hexane. [Note: The dry green silica gel containing the trimetallocarboranes slowly decomposed in air, yielding uncharacterizable yellow compounds also soluble in hexane. Exclusion of air was not necessary if chromatography of the silica gel took place within a few hours.] Two major green bands were eluted in hexane: complex II was followed closely by III. Solvent was removed and the bands were recrystallized from cold pentane, yielding 7 mg of II and 9 mg of III, both as green-black crystals. Anal. Calcd for $C_{16}H_{21}B_5Ni_3$: B, 12.19; C, 43.33; H, 4.77; Ni, 39.71. Found for III: C, 42.70; H, 5.00; Ni, 40.32.

Trimetallocarboranes from $CB_5H_8CH_3$. This reaction was performed as above except for the following changes: (a) 0.42 g of $CB_5H_8CH_3$ (4.5 mmol) was used, (b) 2.28 g of $Ni(C_5H_5)_2$ (12 mmol) was added, followed by 65 g of Na/Hg, and (c) the solution was stirred 12 h at −78 °C and then slowly warmed to room temperature over a period of 6 h. After Celite filtration and the removal of THF, addition of CH_2Cl_2 produced a deep green solution with much insoluble red material. The green solution was chromatographed on thick-layer paper, showing two bands moving closely in hexane. The fastest moving band yielded, upon evaporation of solvent, 25 mg (1.4%) of black crystals of V, mp 161–162 °C. Anal. Calcd for $C_{17}H_{23}B_5Ni_3$: C, 44.63; H, 5.07. Found: C, 44.65; H, 5.30. The second band yielded, upon slow evaporation of solvent with cooling to −78 °C, 60 mg (3.3%) of black crystals of VI, mp 157–158 °C. Anal. Found: C, 44.39; H, 4.88. The infrared spectra of V and VI contained a characteristic B–CH_3 deformation band[53] at 1330 cm^{-1}. Complexes II–VI are very soluble in benzene, CH_2Cl_2, and THF and moderately soluble in hexane, acetone, CH_3CN, $CHCl_3$, CCl_4, and CS_2.

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Registry No. I, 59463-28-4; II, 59331-90-7; III, 58527-65-4; IV, 59349-62-1; V, 59331-91-8; VI, 59349-63-2; $Co(C_5H_5)_2$, 1277-43-6; $Ni(C_5H_5)_2$, 1271-28-9; CB_5H_9, 12385-35-2; $CB_5H_8CH_3$, 23087-40-3; ^{11}B, 14798-13-1.

Supplementary Material Available: Listing of observed and calculated structure factors for 6,7,8-(η^5-C_5H_5)$_3$-6,7,8-Ni_3-1-CB_5H_6 (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Crystal and Molecular Structure of Tetra-*n*-butylammonium Di-*μ*-sulfido-bis(oxo-1,1-dicyanoethylene-2,2-dithiolatomolybdate(V)), $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$

JOHN I. GELDER and JOHN H. ENEMARK*

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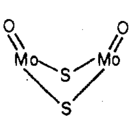
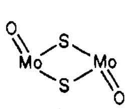
The crystal and molecular structure of tetra-*n*-butylammonium di-*μ*-sulfido-bis(oxo-1,1-dicyanoethylene-2,2-dithiolatomolybdate(V)), $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$, has been determined from three-dimensional x-ray diffraction data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 16.696$ (4), $b = 13.370$ (7), and $c = 13.265$ (7) Å, with $\alpha = 78.85$ (4), $\beta = 109.08$ (3), and $\gamma = 123.43$ (3)°. The calculated and observed densities are 1.30 and 1.28 (1), g cm^{-3}, respectively. Blocked-matrix, least-squares refinement has resulted in $R = 0.054$ for the 3933 data with $F_o^2 \geq 3\sigma(F_o^2)$. The anion has effective $mm\text{-}C_{2v}$ symmetry and contains an $Mo_2O_2S_2^{2+}$ core with cis-bent geometry and two S_b bridging atoms. The Mo···Mo distance is 2.821 (2) Å and the dihedral angle between the two $Mo(S_b)_2$ planes is 153.1°. Each Mo atom possesses distorted square-pyramidal coordination geometry with the two S_b atoms and two S_l atoms from an $[S_2C_2(CN)_2]^{2-}$ ligand forming the basal plane and an O atom in the axial position. The Mo–O distances for the two Mo atoms are not significantly different (1.661 (7) and 1.667 (7) Å). The average Mo–S_b distance is 2.300 (4) Å, and the average Mo–S_l distance is 2.434 (3) Å. It is proposed that the steric requirements of the coordinating ligands determine whether an $Mo_2O_2S_2^{2+}$ core adopts cis-bent or trans-planar geometry.

Introduction

Recent studies of the chemistry of sulfido complexes of molybdenum have been stimulated by the general interest in polynuclear metal compounds[1,2] and by the proposal[3,4] that sulfur is a donor atom in molybdenum-containing enzymes, especially xanthine oxidase. The existence of stable di-*μ*-sulfido-bis(oxomolybdenum) complexes is now well established[1,5-8] and two distinct geometries are known for the $Mo_2O_2S_2^{2+}$ core. Complexes of cysteine,[5,7] histidine,[6] and EDTA[8] contain a cis-bent core (**1a**) with a dihedral angle between the two MoS_2 planes of ~150°, whereas the cyclopentadienyl compound[1] has a trans-planar core (1b). Surprisingly, no structures have been reported for complexes of the $Mo_2O_2S_2^{2+}$ core with ligands containing only sulfur donor atoms.[9] The paucity of accurate structural data for dimeric molybdenum complexes of ligands with sulfur donor atoms and the existence of two geometries for the $Mo_2O_2S_2^{2+}$ core prompted the present determination of the structure of tetra-*n*-butylammonium di-*μ*-sulfido-bis(oxo-1,1-dicyanoethylene-2,2-dithiolatomolybdate(V)), $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$ (I).



1a



1b

Experimental Section

Very fine yellow air-stable crystals of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$ were prepared by Dr. J. McDonald and provided by Dr. William E. Newton. Crystals suitable for diffraction studies were grown as long plates by slow evaporation of a saturated 2:1 solution of acetone–ethanol. A crystal that exhibited sharp extinction under polarized light was selected for preliminary x-ray photographs using a precession camera and Mo Kα radiation. A systematic search of reciprocal space revealed no symmetry elements and suggested space groups $P1$ or $P\bar{1}$. Space group $P\bar{1}$ was assumed and confirmed by successful refinement of the structure.

Unit cell constants were determined from a least-squares refinement of the setting angles of 20 reflections which had been centered automatically on a Picker FACS-I diffractometer using Mo K$\bar{\alpha}$ radiation (λ 0.710 69 Å). The dimensions of the working cell are $a = 16.696$ (4), $b = 13.370$ (7), and $c = 13.265$ (7) Å, with $\alpha = 78.85$ (4), $\beta = 109.08$ (3), and $\gamma = 123.43$ (3)°. A Delauney cell reduction[10] yielded no additional symmetry. The dimensions of the reduced cell are $a = 16.620$, $b = 13.370$, and $c = 13.265$ Å, with $\alpha = 101.15$, $\beta = 99.95$, and $\gamma = 123.43$°. The reduced cell is related to the working cell by $a_r = a_w - b_w$, $b_r = -b_w$, and $c_r = c_w$. All computations and results are based upon the working cell. The experimental density of 1.28 (1) g cm^{-3} obtained by flotation in an aqueous KI solution requires two formula units of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$ per cell. The calculated density is 1.30 g cm^{-3}.

Single-crystal diffraction data were collected from a crystal of dimensions 0.127 × 0.127 × 0.019 mm using graphite-monochromatized Mo Kα radiation, the θ–2θ scan technique, and a takeoff angle of 1.9°. The scan rate was 1°/min and 10-s backgrounds were taken at each end of the scans. The scan range was $2\theta_{MoK\alpha_1} - 0.7°$ to $2\theta_{MoK\alpha_2} + 0.7°$. Three standard reflections were checked every 100 reflections, and their intensities did not change significantly during data collection. A total of 7037 independent reflections with $3° < 2\theta < 50°$ were collected and reduced to F^2 and $\sigma(F^2)$ as described previously.[11,12] The factor p introduced to prevent overweighting of strong reflections was set at 0.04. Of the 7037 reflections, 3933 had $F_o^2 \geq 3\sigma(F_o^2)$. The absorption coefficient for the compound for Mo Kα radiation is only 7.0 cm^{-1}, and consequently no absorption correction was needed for the crystal used for data collection.