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Preparation and Characterization of Macropolyhedral Metallaborane Clusters from the *anti*-$B_{18}H_{22}$ Borane Cluster: Crystal Structure of $[(CH_3)_4N][anti\text{-}B_{18}H_{20}Co(CO)_3]$

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Summary: The reaction of anti-$B_{18}H_{22}$ *with* $[Co_2(CO)_8]$ *and* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_{10})]^+$ *yields the macropolyhedral metallaboranes* $[anti\text{-}B_{18}H_{20}Co(CO)_3][(CH_3)_4N]$ *(**1**) and* $[9\text{-}(Fe(CO)_2(\eta^5\text{-}C_5H_5))\text{-}anti\text{-}B_{18}H_{21}]$ *(**2**), respectively. Single-crystal X-ray diffraction analysis of complex **1** showed that the structure consists of an 11-vertex nido-cobaltaborane subunit edge shared with a 10-vertex nido-borane fragment.*

The initial synthesis of several 19-vertex metallaborane compounds, in which nickel, cobalt, palladium, platinum, and rhodium organometallic fragments were incorporated into the macropolyhedral framework of either the *anti* or *syn* configurations of $B_{18}H_{22}$, was first reported in 1973 by Todd and Sneath.[1] These compounds were prepared by employing a synthetic pathway involving the initial deprotonation of the $B_{18}H_{22}$ cage to form the $[B_{18}H_{20}]^{2-}$ species, followed by reaction with an appropriate organometallic reagent, such as $[Co_2(CO)_8]$, $[Cl_2Ni(Ph_2PCH_2CH_2PPh_2)]$, or $[RhCl(CO)(PPh_3)_2]$, to produce the corresponding 19-vertex metallaborane. In 1982, Greenwood and co-workers reported the synthesis of platinum derivatives of the $B_{18}H_{22}$ cluster, including $[(Pt\text{-}\eta^4\text{-}anti\text{-}B_{18}H_{20})(PMe_2Ph)_2]$, from the reaction of *anti*-$[B_{18}H_{22}]$ with *cis*-$[PtCl_2(PMe_2Ph)_2]$.[2] A more compact diplatinum derivative, $[(Pt_2B_{18}H_{16})(PMe_2Ph)_4]$, was also formed from this reaction. Sneath and Todd proposed that the structures for their 19-vertex complexes consisted of 11-vertex *nido*-metallaborane fragments edge-shared with 10-vertex *nido*-borane subunits, illustrated in Figure 1, but spectroscopic characterization and structural studies were not provided.[1]

The first unsubstituted 19-vertex borane species, nonadecaborane $[B_{19}H_{20}]^{n-}$, was reported in 2000,[3] although some questions have recently arisen, on the basis of computational studies, as to whether this species is best formulated as a 1− or 3− anionic compound.[4,5] Nonadecaborane displays essentially the same structure as the previously described 19-vertex metallaboranes, except that a B−H unit is inserted into the *anti*-$B_{18}H_{22}$ framework instead of an organometallic subunit.

In this paper, we report the first complete spectroscopic and structural characterization of the previously reported 19-vertex metallaborane $[(CH_3)_4N][anti\text{-}B_{18}H_{20}\text{-}Co(CO)_3]$ (**1**).[1] In addition, we report the first example of the formation of an *anti*-$B_{18}H_{21}$ cluster with an *exo*-bound organometallic moiety, $[9\text{-}(Fe(CO)_2(\eta^5\text{-}C_5H_5))anti\text{-}B_{18}H_{21}]$ (**2**).

Experimental Section

Physical Measurements. ^{11}B NMR spectra were recorded on a Brüker DPX-300 NMR spectrometer operating at 96.3 MHz. Typical ^{11}B NMR acquisition parameters were a relaxation delay of 0.1 ms and a 90° pulse of 10 μs. Proton (^1H) and carbon (^{13}C) NMR spectra were recorded on a Brüker DPX-300 spectrometer operating at 300.15 and 77.47 MHz, respectively. Mass spectra were obtained in the Mass Spectrometry Laboratory, University of Illinois. The 70-VSE mass spectrometer was purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648). Unit resolution mass spectra were obtained on a Hewlett-Packard Model 5989B gas chromatograph/mass spectrometer (GC/MS) using an ionization potential of between 11 and 70 eV. FT-IR spectra were measured on a Mattson Galaxy 2020 spectrometer and were referenced to the 1602.8 cm^{-1} band of polystyrene. UV−vis spectral data were collected on a Cary 1 UV−vis spectrophotometer in a quartz cell.

Materials. All solvents were reagent grade or better. Tetrahydrofuran (THF) and hexanes were distilled over potassium metal prior to use. The reagents *anti*-$B_{18}H_{22}$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_{10})][PF_6]$ were synthesized as previously described.[1,7] TLC plates were purchased from the Aldrich Chemical Co. All other commercially available reagents were used as received.

Synthesis and X-ray Crystallographic Studies of $[(CH_3)_4N][B_{18}H_{20}Co(CO)_3]$ (1). Compound **1** was synthesized from the reaction of deprotonated $[B_{18}H_{22}]$ and $Co_2(CO)_8$, as previously described.[8] ^{11}B NMR (CD_3CN; δ (ppm)): 14.86 (s, B(12,18), J_{BH} = 127.6 Hz), 13.79 (s, B(5), J_{BH} = 180.3 Hz), 11.16 (s, B(10) unresolved), 6.15 (s, B(2,3) unresolved), 4.26 (s, B(11,9,8) unresolved), 0.05 (s, B(1,19), J_{BH} = 116.3 Hz), −2.65 (s, B(14), J_{BH} = 148.6 Hz), −4.37 (s, B(16), J_{BH} = 159.7 Hz), −16.40 (s, B(13), J_{BH} = 151.8 Hz), −22.29 (s, B(4), J_{BH} = 144.4 Hz), −26.34 (s, B(17), J_{BH} = 130.6 Hz), −30.17 (s, B(6), J_{BH} = 143.6 Hz), −37.66 (s, B(15), J_{BH} = 150.0 Hz). ^1H NMR (CD_3CN; δ (ppm)): 3.85 (s, $B_{18}H_{20}$), 3.66 (s, $B_{18}H_{20}$), 3.43 (s, $B_{18}H_{20}$), 3.31 (s, $B_{18}H_{20}$), 3.07 (s, $B_{18}H_{20}$), 2.95 (s, $(CH_3)_4N$), 2.83

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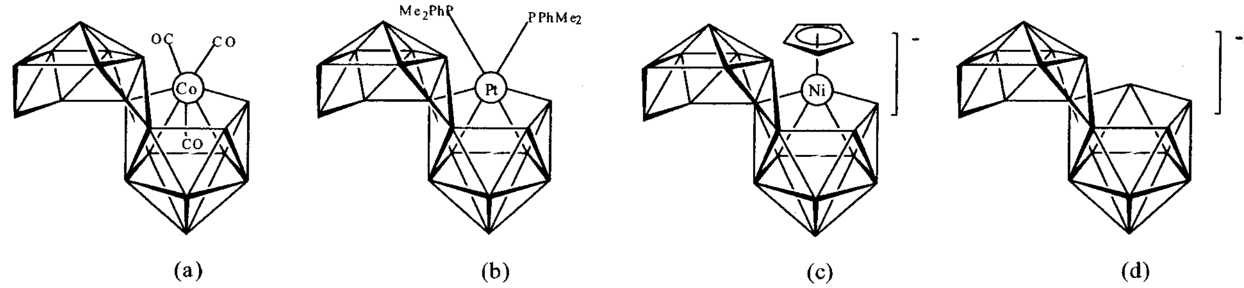

Figure 1. Structures of 19-vertex metallaboranes: (a) $[(CH_3)_4N][$*anti*-$B_{18}H_{20}Co(CO)_3]$ (**1**); (b) $[(Pt$-η^4-*anti*-$B_{18}H_{20})(PMe_2Ph)_2]$; (c) $[B_{18}H_{19}(2\text{-THF})Ni(\eta^5\text{-}C_5H_5)]$; (d) $[B_{19}H_{20}]^{n-}$. Terminal hydrogen atoms have been omitted for clarity.

(s, $B_{18}H_{20}$), 2.68 (s, $B_{18}H_{20}$), 2.22 (s, $B_{18}H_{20}$), 2.15 (s, $B_{18}H_{20}$), 1.84 (s, $B_{18}H_{20}$), 1.52 (s, $B_{18}H_{20}$), 1.17 (s, $B_{18}H_{20}$), 0.53 (s, $B_{18}H_{20}$), 0.14 (s, $B_{18}H_{20}$), 0.06 (s, $B_{18}H_{20}$), −0.04 (s, $B_{18}H_{20}$), −0.37 (s, $B_{18}H_{20}$), −2.27 (s, $B_{18}H_{20}$), −2.78 (s, $B_{18}H_{20}$). FT-IR (KBr plates; cm^{-1}): 2521 (s), 2075 (s), 2035 (s), 2020 (s). Anal. Calcd for $C_7H_{32}B_{18}CoNO_3$: C, 19.47; H, 7.47; N, 3.24; Co, 13.65. Found: C, 19.67; H, 7.46; N, 3.87; Co, 13.44. UV−visible (CD_3CN; nm): 384, 336.

A suitable crystal of **1** for X-ray analysis was grown by layering hexanes over a solution of **1** in methylene chloride. The crystal was then attached to a glass fiber and immediately placed in the low-temperature nitrogen stream of the diffractometer.[10] Data were collected using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at −54 °C. The data set was collected at 150 K by employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data collection nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different φ angle, and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. No decay was observed. An absorption correction was applied utilizing the program SADABS.[11] The crystal structure was solved by direct methods included in the SHELX program package.[12] The structures were refined by full-matrix least-squares refinement on F^2 (SHELXL-96).[11] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms on the boron cage were found in difference Fourier maps and refined with U_{iso} constrained at 1.2 times the U_{eq} value of the carrier atom. Scattering factors were those provided with the SHELX program system.[12] Crystal data for **1**: space group $P2_1/c$, monoclinic, $a = 13.9472(1)$ Å, $b = 10.1795(1)$ Å, $c = 19.5337(1)$ Å, $\beta = 107.02(1)°$, $V = 2651.90(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.294$ g/cm^3, $T = 150(1)$ K, 16 319 reflections collected, 6209 reflections with $I > 2\sigma(I)$, 378 parameters, R1 = 0.0592, wR2 = 0.1562.

[9-(Fe(CO)$_2$(η^5-C$_5$H$_5$))-*anti*-B$_{18}$H$_{21}$] (2). Under an inert atmosphere, 375 mg (0.82 mmol) of $[Et_4N][B_{18}H_{21}]$[9] was placed in a dry Schlenk flask. To the borane solid was added 25 mL of dry THF. This solution was then degassed with three freeze−pump−thaw cycles. The borane solution was added by cannula to a dry Schlenk flask containing 331 mg (0.82 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_{10})][PF_6]$. This mixture was stirred at room temperature for 10 h, after which time the solvent was removed *in vacuo*. The reaction mixture was then eluted on a silica gel column (3 cm × 30 cm) with a 9:1 mixture of CH_2Cl_2 and hexanes. The fastest moving yellow band was collected, and the solvent was removed *in vacuo* immediately to produce a yellow-brown solid. The yellow-brown solid was then extracted with dry and degassed hexanes and filtered, and the solvent was removed *in vacuo*. Pure product, **2**, was collected in 50% yield as a bright yellow solid. ^{11}B NMR (CD_3CN; δ (ppm)): 32.56 (s, B(9)), 14.52 (s, B(3,13), $J_{BH} = 127.4$ Hz), 10.43 (s, B(10) unresolved), 9.88 (s, B(18) unresolved), 6.06 (s, B(6)), 3.82 (s, B(5)), 2.81 (s, B(1,17), $J_{BH} = 224.0$ Hz), 0.47 (s, B(11), $J_{BH} = 167.0$ Hz), −2.33 (s, B(8) unresolved), −3.35 (s, B(16) unresolved), −10.36 (s, B(7), $J_{BH} = 172.2$ Hz), −13.14 (s, B(15), $J_{BH} = 173.5$ Hz), 31.30 (s, B(12), $J_{BH} = 165.3$ Hz), −33.13 (s, B(2), $J_{BH} = 152.2$ Hz), −34.50 (s, B(4), $J_{BH} = 145.0$ Hz), −39.96 (s, B(14), $J_{BH} = 156.2$ Hz). ^1H NMR (CD_3CN; δ (ppm)): 4.87 (s, η^5-C_5H_5), 4.07 (s, $B_{18}H_{21}$), 3.91 (s, $B_{18}H_{21}$), 3.35 (s, $B_{18}H_{21}$), 3.04 (s, $B_{18}H_{21}$), 2.89 (s, $B_{18}H_{21}$), 0.91 (s, $B_{18}H_{21}$), 0.46 (s, $B_{18}H_{21}$), −0.11 (s, $B_{18}H_{21}$), −0.29 (s, $B_{18}H_{21}$), −0.41 (s, $B_{18}H_{21}$), −0.88 (s, $B_{18}H_{21}$), −1.03 (s, $B_{18}H_{21}$), −1.57 (s, $B_{18}H_{21}$), −2.98 (s, $B_{18}H_{21}$). $^{13}C\{^1H\}$ NMR (CD_3CN; δ (ppm)): 214.05 (s, *C*O), 84.93 (s, η^5-C_5H_5). FT-IR (KBr plates; cm^{-1}): 2574 (s), 2020 (sp), 1967 (sp). MS (nominal mass; *m*/*z*): 389 (found 41.0, calcd 17.0; P^+ envelope), 390 (found 56.1, calcd 37.0; P^+ envelope), 391 (found 76.9, calcd 65.8; P^+ envelope), 392 (found 90.1, calcd 92.7; P^+ envelope), 393 (found 100.0, calcd 100.0; P^+ envelope;$^{12}C_7{}^1H_{26}{}^{10}B_3{}^{11}B_{15}{}^{56}Fe^{16}O_2$), 394 (found 82.6, calcd 78.1; P^+ envelope), 395 (found 49.7, calcd 40.2; P^+ envelope), 396 (found 23.3, calcd 11.4; P^+ envelope), 177 (base peak; $^{12}C_7{}^1H_5{}^{56}Fe^{16}O_2$). UV−visible ($CD_3CN$; nm): 245, 270, 320, 380.

Results and Discussion

The initial synthesis of $[(CH_3)_4N][B_{18}H_{20}Co(CO)_3]$ (**1**) was reported in 1973 by Sneath and Todd, although structural confirmation by X-ray crystal analysis, assignment of the ^{11}B NMR signals, and ^1H NMR data were not reported.[1] We have now synthesized this compound and assigned the ^{11}B NMR signals unambiguously by $^{11}B-^{11}B$ COSY NMR. The ^{11}B NMR data for **1** consist of 13 resonances, very similar to those found for the $[B_{18}H_{20}Ni(\eta^5\text{-}C_5H_5)][N(CH_3)_4]$ and $[B_{18}H_{19}(2\text{-THF})Ni(\eta^5\text{-}C_5H_5)]$ complexes.[6] The data are consistent with a structure based upon two edge-fused *nido*-borane clusters.[1]

The X-ray crystal structure of **1**, shown in Figure 2, confirms the proposed structure as a 19-vertex metallaborane. The Co−B bond lengths of **1** are slightly larger, 2.131−2.250 Å, than found in the Ni analogues previously reported, $[B_{18}H_{20}Ni(\eta^5\text{-}C_5H_5)][N(CH_3)_4]$ and $[B_{18}H_{19}(2\text{-THF})Ni(\eta^5\text{-}C_5H_5)]$.[6] This is to be expected, however, because of the slightly larger size of the cobalt atom relative to nickel.

In an effort to extend the synthetic utility of the *anti*-$B_{18}H_{22}$ cluster to new structural motifs, we have explored the incorporation of other organometallic fragments into the macropolyhedral B_{18} cluster. The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_{10})]PF_6$ with $[B_{18}H_{21}]^-$ produces a new 18-vertex metallaborane with an *exo*-polyhedral-

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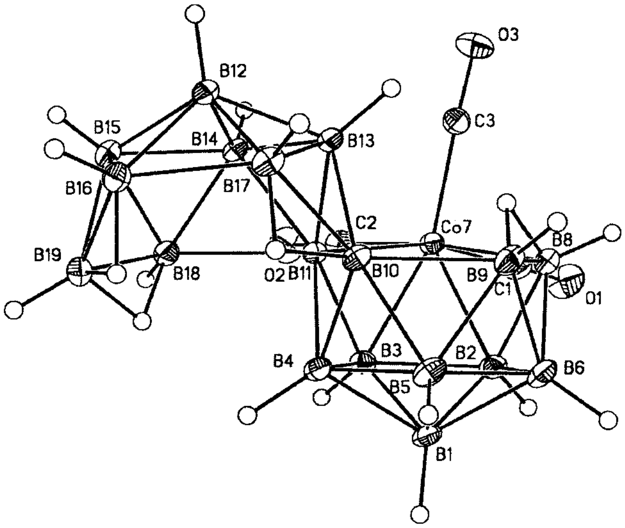

Figure 2. Crystallographically determined structure of $[(CH_3)_4N][B_{18}H_{20}Co(CO)_3]$ (**1**), with thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): average Co(7)−C(carbonyl) = 1.816; average C(carbonyl)−O(carbonyl) = 1.138; Co(7)−B(8) = 2.250(4); Co(7)−B(2) = 2.152(4); Co(7)−B(3) = 2.131(3); Co(7)−B(11) = 2.273(3); average Co(7)−C(carbonyl)−O(carbonyl) = 176.1; B(3)−Co(7)−B(8) = 85.9(1); Co(7)−B(11)−B(10) = 115.9(2); B(9)−B(10)−B(11) = 109.9(2); Co(7)−B(8)−B(9) = 117.6(2).

bound organometallic fragment, $[9\text{-}(Fe(CO)_2(\eta^5\text{-}C_5H_5))\text{-}anti\text{-}B_{18}H_{21}]$ (**2**). This *exo*-substitution pattern is in contrast with all the previously reported metallaboranes prepared from the B_{18} cluster, such as compound **1**, which incorporate the organometallic fragment directly within the cluster framework. Compound **2** is similar, however, to several known small metallaborane clusters with an *exo*-bound iron organometallic fragment, although none involved clusters with more than 10 vertexes. Literature examples of these small-cluster analogues are $[6\text{-}((\eta^5\text{-}C_5H_5)Fe(CO)_2)B_{10}H_{13}]$,[13] $[(PPh_2)B_5H_7(Fe(\eta^5\text{-}C_5H_5)(CO)_2)]$,[14] and $[B_5H_8(Fe(\eta^5\text{-}C_5H_5)(CO)_2)]$.[15] The synthesis of $[6\text{-}((\eta^5\text{-}C_5H_5)Fe(CO)_2)B_{10}H_{13}]$ was reported from the addition of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_{10})]PF_6$ to $[B_{10}H_{13}]^-$.[13] A similar procedure was previously used for the preparation of $[(PPh_2)B_5H_7(Fe(\eta^5\text{-}C_5H_5)(CO)_2)]$ and $[B_5H_8(Fe(\eta^5\text{-}C_5H_5)(CO)_2)]$ from the reaction of the sodium or potassium salt of the borane with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2I]$.[14,15]

The $^{11}B\{^1H\}$ and ^{11}B NMR of **2** are shown in Figure 3. The $^{11}B\{^1H\}$ NMR consists of 16 signals with 2 coincidental signals having an integration of 2 relative to the other 14 signals. The signal at 32.56 ppm remains as a broad singlet in the proton-coupled experiment. This signal arises from the 9-position of the *anti*-B_{18} cage, where a terminal hydrogen has been replaced by the $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ fragment. The signal is shifted downfield from its position in *anti*-$B_{18}H_{22}$ by approximately 30 ppm, indicating that significant electron density has been donated to the organometallic fragment. This is one of the largest downfield shifts reported for an *exo*-substituted cluster.[16] Literature examples of small-cage $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$-substituted compounds also show significant downfield shifts of the substituted boron. The smallest downfield shift is seen in the diiron-substituted compound $[B_5H_8(Fe(\eta^5\text{-}C_5H_5)(CO)_2)_2]$, with a 15 ppm downfield shift.[14] Interestingly, the corresponding monoiron-substituted species $[B_5H_8Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ has a 22 ppm downfield shift of the substituted boron, 7 ppm more than that observed for the disubstituted species.[14] In the monoiron-substituted decaborane species $[6\text{-}B_{10}H_{13}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)]$, the boron in the 6-position is shifted 29 ppm from that in the unsubstituted *nido*-$B_{10}H_{14}$.[13] The remainder of the ^{11}B signals for compound **2** were unambiguously assigned by a $^{11}B-^{11}B$ COSY experiment.

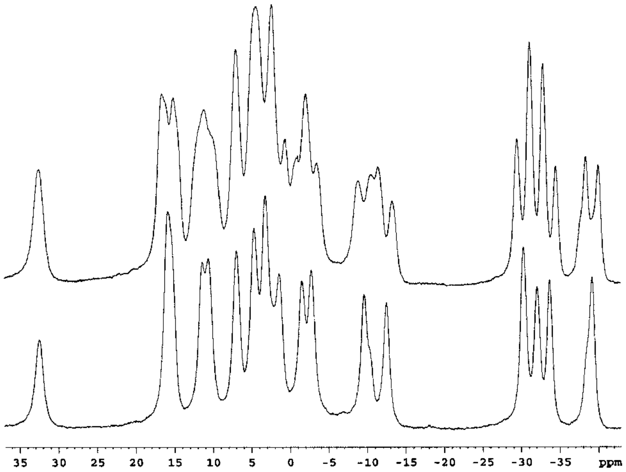

Figure 3. $^{11}B\{^1H\}$ (bottom) and ^{11}B (top) NMR spectra (96.3 MHz) of $[9\text{-}(Fe(CO)_2(\eta^5\text{-}C_5H_5))anti\text{-}B_{18}H_{21}]$ (**2**) in hexane.

Compounds **1** and **2** have structures fully consistent with recently reported electron-counting schemes for *conjuncto* cluster species.[5,6]

The IR spectrum of **2** shows the B−H stretching signal at 2574 cm^{-1} as well as two strong CO stretches at 2020 and 1966 cm^{-1}, also consistent with an *exo*-bound iron moiety. From these data, the proposed structure of compound **2** consists of an *anti*-$B_{18}H_{21}$ framework with an *exo*-bound $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ fragment in the 9-position on the cluster, as shown in Figure 4.

We have also explored the photochemistry of this new iron-containing metallaborane cluster, **2**, to compare it with the known photoreactions of $[(PPh_2)B_5H_7(Fe(\eta^5\text{-}C_5H_5)(CO)_2)]$ and $[B_5H_8(Fe(\eta^5\text{-}C_5H_5)(CO)_2)]$.[14,15] The photochemical irradiation of **2** was carried out in a quartz vessel using inert-atmosphere techniques, with hexane as the solvent, as previously described.[15] After irradiation with 254 nm light for 20 min, the yellow color of the reaction mixture was replaced with a deep purple. The infrared analysis of the reaction mixture showed an absence of any signals in the CO stretching region of the spectrum, indicating the loss of both carbonyl moieties. Inspection of the $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture revealed that no starting material, **2**, remained. The ^{11}B NMR spectrum showed the presence of neutral *anti*-$B_{18}H_{22}$ and a second unidentified

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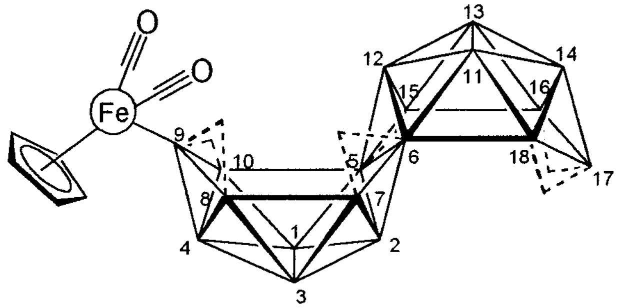

Figure 4. Proposed structure and numbering scheme of [9-(Fe(CO)$_2$(η^5-C$_5$H$_5$))*anti*-B$_{18}$H$_{21}$] (**2**). Bridging hydrogens are represented by dashed lines, and terminal hydrogens have been omitted for clarity.

product (^{11}B NMR (δ, ppm): 12.4, 10.3, 2.9, −0.8, −1.2, −5.1, −8.6, −21.9, −29.8, −38.4, −49.5). A more complete characterization of this new purple product was unsuccessful, however, due to its thermal instability, including attempts at low-temperature isolation and purification. Many attempts were made to try to stabilize this new species, including irradiation in different solvents such as diethyl ether, hexanes, dioxane, THF, and dibutyl ether. In other attempts to stabilize the photoproduct, the photoreactions were attempted in the presence of other ligands such as triphenylphosphine and 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane. Neither of these strategies proved to be successful. Attempts to synthesize different organometallic derivatives of **2,** including [Fe(CO)(PPh$_3$)(η^5-C$_5$H$_5$)]$^-$, [Fe(CO)$_2$(η^5-C$_5$Me$_5$)]$^-$, [Fe(CO)$_2$(η^5-C$_5$EtMe$_4$)]$^-$, and [Ru(CO)$_2$(η^5-C$_5$H$_5$)]$^-$ derivatives, also proved to be unsuccessful. From the infrared data and other spectroscopic data, it can be assumed that both carbonyl moieties were lost upon irradiation, but further structural characterization of the photoproduct was not possible.

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Supporting Information Available: A figure giving the ^{11}B−^{11}B COSY NMR spectrum for compound **1** and tables giving complete crystallographic experimental details, bond distances and angles, positional parameters for all atoms, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for compound **1** with a figure showing the thermal ellipsoid plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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