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Borane Cluster Photochemistry. 1. Photochemical Decarbonylation and Rearrangement Chemistry of the σ-Metalated Pentaborane Cluster $[Fe(\eta^5\text{-}C_5H_5)(CO)_2B_5H_8]$

While the photochemistry of organometallic compounds has yielded a rich array of interesting complexes,[1,2] the potentially fertile field of the photochemistry of boranes and their organometallic derivatives has not been well investigated.[3] In the relatively few reported photochemical studies of metallaborane complexes, the yields have typically been very low, usually less than 5%, with a multitude of product complexes generated.[3a,4,5] We have recently explored the photochemical conversion of the σ-metalated phosphinopentaborane cluster $[Fe(\eta^5\text{-}C_5H_5)(CO)_2B_5H_7(\mu\text{-}P(C_6H_5)_2)]$ into the organometallic tetraborane cluster complex $[Fe(\eta^5\text{-}C_5H_5)(CO)B_4H_6(P(C_6H_5)_2)]$.[6] In a continuation of our studies of the photochemistry of organometallic borane clusters, we have investigated the photochemical decarbonylation and rearrangement chemistry of the related σ-metalated pentaborane cluster $[2\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)_2B_5H_8]$ (**1**).

The photochemical irradiation of $[2\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)_2B_5H_8]$ (**1**) in 75 mL of THF was accomplished using a water-cooled quartz immersion-well photochemical reactor with an inert nitrogen atmosphere maintained in the reactor.[7] The THF solution of **1** was irradiated for 31 h, during which time the solution changed from clear yellow to clear red-brown. The steady disappearance of the ^{11}B NMR resonances of the starting material[8] and the appearance of several new peaks[9] was observed during the irradiation. At the end of the irradiation, the starting material had been completely consumed and the resonances for the new product, **2**, were observed. The photochemical conversion of complex **1** to **2** (as monitored by ^{11}B NMR spectroscopy) proceeded with 63% conversion. Complex **2** was purified by vacuum sublimation as a solid which melted into a red-brown oil at room temperature. The complex is slightly air-sensitive and is stable in an inert atmosphere at room temperature.

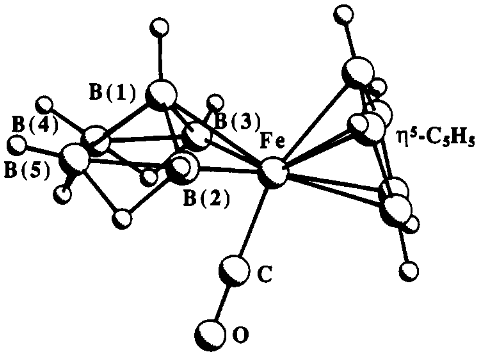

Figure 1. PLUTO[16] drawing of $[Fe(\eta^5\text{-}C_5H_5)(CO)B_5H_8]$ (**2**) showing the atomic numbering scheme. Selected intramolecular bond distances (bond distances are given in Å and the estimated standard deviations in the least significant figure are given in parentheses): Fe–C[CO] = 1.728 (4), C–O = 1.146 (5), Fe–C[η^5-C_5H_5] = 2.11 (3), Fe–B(2,3) = 1.968 (4), Fe–B(1) = 2.161 (4), B(2,3)–B(5,4) = 1.777 (5), B(1)–B(2,3) = 1.738 (4), B-(1)–B(4,5) = 1.767 (5). Selected intramolecular bond angles (bond angles are given in deg and the estimated standard deviations in the least significant figure are given in parentheses): C[CO]–Fe–B(2,3) = 84.7 (1), Fe–C–O = 178.1 (4), B(2,3)–B(1)–B(5,4) = 110.7 (3), B(2,3)–Fe–B(1) = 49.5 (1).

The spectroscopic characterization of **2** is consistent with a pentagonal pyramidal structure for a $[2\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)B_5H_8]$ complex in which an $Fe(\eta^5\text{-}C_5H_5)(CO)$ unit occupies a vertex in the basal plane of the B_5-cage.[9] This structure is shown in Scheme

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(7) In a typical experiment, 3.3 g (14 mmol) of $[2\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)_2B_5H_8]$ (**1**) in 150 mL of dry THF was placed in a water-cooled photochemical reactor (Ace No. 7841) with a quartz immersion well under a nitrogen atmosphere. The clear yellow solution was irradiated for 31 h using a Conrad-Hanovia Hg vapor lamp (Ace No. 7825-34). During the irradiation, the solution changed from clear yellow to clear red-brown. The solvent was removed in vacuo to give a red-brown oil. Pure $[2\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)B_5H_8]$ (**2**) was sublimed in 19% isolated yield (0.54 g) with decomposition from the residue by heating it to 40 °C at 10^{-5} Torr and collecting the sublimate in a trap held at −10 °C.

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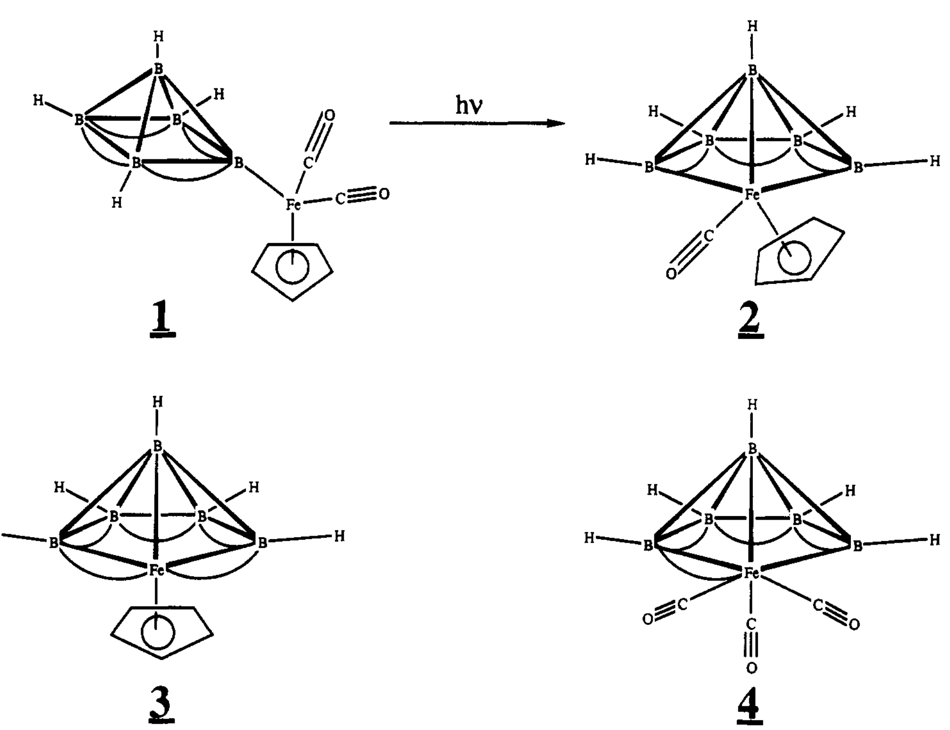
Scheme I. Organometallic Photochemistry of Compound **1** in the Formation of Compound **2**[a]



[a] An inverted arc indicates a bridging hydrogen atom.

I. The ^{11}B NMR spectrum consists of two basal resonances at +76.0 and +10.9 ppm with an intensity ratio of 2:2 and a resonance assigned to the apical boron atom at −45.5 ppm with a relative intensity of 1. Each resonance appears as a B–H-coupled doublet in the ^1H-coupled spectrum which collapses into a sharp singlet upon proton decoupling. The ^{11}B and ^1H NMR data for **2** are consistent with the proposed structures of the related [2-Fe(η^5-C_5H_5)B_5H_{10}] (**3**)[4] and [2-Fe(CO)$_3$$B_5H_9$] (unstable), (**4**)[5] complexes. Compounds **3** and **4** were prepared in very low yields from the reaction of $C_5H_5^-$ with $FeCl^2$ and B_5H_8 (2.5%) and from the thermal reaction (220 °C) of $Fe(CO)_5$ with B_5H_9 (5%), respectively. The proposed structures for complexes **3** and **4** are shown in Scheme I. Of note in the ^{11}B NMR spectrum of **2**, however, is the unusually large downfield shift (+76.0 ppm) assigned to the two basal boron atoms attached to the Fe(η^5-C_5H_5)(CO) unit. Analogous resonances for complexes **3** and **4** at room temperature were observed at +44.4 and +46.0, respectively. The large downfield shift in **2** can be attributed to the absence of Fe–H–B interactions in the complex. The ^1H NMR spectrum clearly showed the characteristic η^5-C_5H_5 resonance at 4.90 ppm as well as distinct boron-coupled quartets for the three types of terminal B–H protons in a 2:2:1 ratio. FT-IR spectroscopy showed a single CO stretch at 1940 cm^{-1}, consistent with the loss of one carbonyl group from the starting complex **1**.

Electron counting for complex **2** describes the cluster as a 16-electron, six vertex [2*n* + 4] cage system.[11] In this counting scheme, the Fe(η^5-C_5H_5)(CO) fragment contributes three electrons to the cage bonding, 10 electrons are contributed from the five BH units and three electrons are contributed from the three B–H–B bridging protons on the cage for a total of 16 skeletal electrons. Thus, the structure of complex **2** is expected to be based on the *nido* six-vertex B_6H_{10} parent structure,[12] as proposed. In the complimentary electron-counting scheme for **2** using the effective atomic number (EAN) rule,[2] the iron center (eight-electron core) achieves an 18-electron configuration through coordination to one CO ligand (two-electron donor), a cyclopentadienyl group (five-electron donor), and three Fe–B cage interactions (one-electron donor each).

Confirmation of the assignment of complex **2** as a basally substituted pentagonal pyramidal structure was obtained from a single-crystal X-ray analysis.[13] The molecular structure and numbering scheme for complex **2** are shown in Figure 1. In the structure, all the atoms in the complex, including the hydrogen atoms, were located and refined without difficulty. Selected bond angles and bond lengths are also given in Figure 1. The Fe–C(carbonyl) bond distance (1.723 (5) Å) is slightly shortened in comparison with other similar bond distances in iron carbonyl complexes (average Fe–C$_{(terminal)}$ ranging from approximately 1.74 to 1.82 Å).[14] The iron exhibits an approximate octahedral co-

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(9) Spectroscopic characterization for compound **2**: ^{11}B NMR ($CDCl_3$, s = singlet, d = doublet) δ +76.0 (d, B(2,3), J_{BH} = 158 Hz), +10.9 (d, B(4,5), J_{BH} = 158 Hz), −45.5 (d, B(1), J_{BH} = 129 Hz); ^1H NMR ($CDCl_3$, s = singlet, q = quartet) δ −15.1 (br s), −1.79 (q, 1 H, apical terminal H), 3.7 (q, 2 H, basal terminal H), 4.90 (s, 5 H, η^5-C_5H_5), 8.1 (q, 2 H, basal terminal H), centered near 0.5 (br s, 3H, B-H-B); FT-IR (KBr plates neat, w = weak, s = strong, m = moderate) 3116 (w, ν_{CH} of η^5-C_5H_5 group), 2565 (s, ν_{BH}), 2526 (s, ν_{BH}), 1940 (s, ν_{CO}), 1415 (m), 1360 (m), 1313 (m), 1016 (w), 1002 (w), 923 (m), 892 (m), 831 (m), 694 (m), 565 (m), 536 (m) cm^{-1}; MS (20 eV; relative intensities given with the largest peak in the envelope normalized to 100.0% with the calculated values *m*/*e* based on natural abundances and normalized to the most intense peak in the envelope) 213 (calcd 7.8, found 12.2; P$^+$ envelope), 212 (calcd 85.3, found 83.6; $^{12}C_6{}^1H_{13}{}^{11}B_5{}^{56}Fe^{16}O$; P$^+$ envelope), 211 (calcd 100.0, found 100.0; P$^+$ envelope), 210 (calcd 53.9, found 64.9; P$^+$ envelope), 209 (calcd 18.2, found 27.0; P$^+$ envelope).

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(13) Crystallographic data for **2**: orthorhombic space group *Pnma* (No. 62), a = 14.889 (1) Å, b = 9.4560 (9) Å, c = 7.2838 (9) Å, $\alpha = \beta = \gamma$ = 90.00°, V = 1025.5 (3) Å^3, Z = 4 molecules/cell, $2\theta_{max}$ = 69.9°, 1908 total reflections measured at 0 °C with 959 observed (with $I > 3\sigma(I)$) reflections used for refinement. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were then located on a difference map and were refined isotropically. The final cycle of a full-matrix least-squares refinement converged with $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.036 and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)]^{1/2}$ = 0.037. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and −0.33 e/Å^3, respectively. Final atom coordinates and *B*(eq) are available as supplementary materials.

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ordination and resides 0.34 Å below the B(2)–B(5) basal plane. The Fe-B(2,3) distances are significantly shorter (1.97 Å) than the analogous distances in $[N(n\text{-}C_4H_9)_4]^+[2\text{-}Fe(CO)_3B_5H_9]^-$ (2.08 and 2.13 Å),[5] $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ (2.075 and 2.115 Å),[5c] and $[\mu\text{-}(Fe(CO)_4B_7H_{12}]^-$ (2.22 and 2.20 Å)[15] due to the absence of Fe–H–B bonding in complex **2**. The structure of **2** represents the first crystallographically characterized neutral *nido*-ferrahexaborane cluster, although the structure of the directly related species $[N(n\text{-}C_4H_9)_4]^+[2\text{-}Fe(CO)_3B_5H_9]^-$ has been determined.[5]

The high-yield preparation of **2** by the irradiation of the σ-metalated complex **1** is in sharp contrast to the observed very low yield (1–3%) of the only product isolated from the irradiation of the related decaborane(14) cluster $[6\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)_2B_{10}H_{13}]$ (**5**).[3a] The product obtained from this reaction, $6\text{-}Fe(\eta^5\text{-}C_5H_5)(CB_{10}H_{13}L)$ (where L = $O(CH_2CH_3)_2$ or THF), was found to result from the photolytic insertion of the carbonyl carbon into a borane cluster framework. No analogue of this type of carbonyl-inserted complex was observed in the photochemistry of complex **1**.

The clean, high-yield photochemical synthesis of complex **2** provides an excellent route to this complex in relatively large quantities. The photochemistry of metal borane clusters is expected to allow for the observation of new structural types and reaction pathways. Insights into these processes are critical to the understanding of the reaction chemistry of other organometallic cluster species. The further study of the organometallic reactions and photochemistry of similar classes of organometallic cluster compounds is currently in progress in our laboratory.

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Supplementary Material Available: Tables of all atom coordinates including all hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for non-hydrogen atoms for **1** (5 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(17) National Science Foundation Research Experiences for Undergraduates Participant 1990–1992.

Department of Chemistry and Center for Molecular Electronics
Center for Science and Technology
Syracuse University
Syracuse, New York 13244-4100

Bruce H. Goodreau
Lianna R. Orlando[17]
James T. Spencer*

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Emission Spectroscopic Properties of 1,2-Bis(dicyclohexylphosphino)ethane Complexes of Gold(I)

Electronic emission has been reported for a few gold(I) dimers in solution at room temperature.[1-4] Formulations of the electronic structures of the emissive excited states of these complexes have emphasized the importance of Au–Au interactions (by analogy to d^8–d^8 Pt$_2$[5-7] and d^{10}–d^{10} Pt$_2$[8] species). In the course of our work on the coordination chemistry of the ligand 1,2-bis(dicyclohexylphosphino)ethane (dcpe), we have prepared and characterized an intensely emissive gold(I) complex containing *isolated* AuP_3 units. Our results suggest that excited-state Au–L bonding is a key factor in Au^I photophysics.

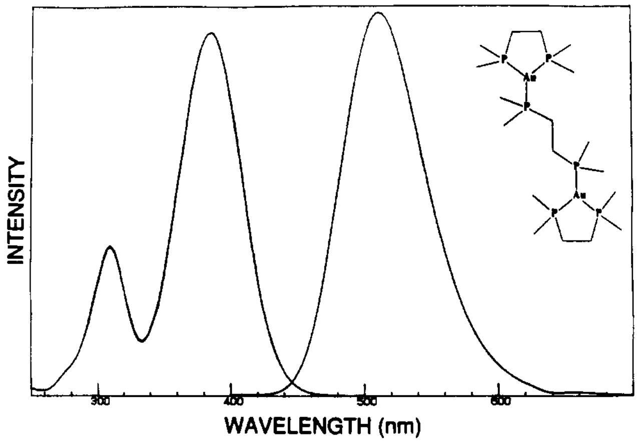

Figure 1. Excitation (left) and emission (right) spectra of $[Au_2(dcpe)_3](PF_6)_2$ (**3**) in acetonitrile at room temperature.

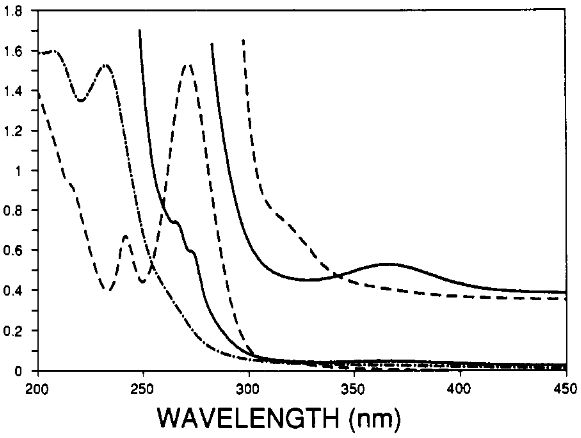

Figure 2. Absorption spectra in acetonitrile at room temperature: 5.02 × 10^{-4} and 5.02 × 10^{-5} M $[Au_2(dcpe)_3](PF_6)_2$ (—) (**3**), 7.32 × 10^{-4} and 7.32 × 10^{-5} M $[Au_2(dcpe)_2](PF_6)_2$ (--) (**1**), 4.18 × 10^{-5} M $[Au(dcpe)_2]PF_6$ (-··) (**4**).

Reaction of dcpe with ClAu(tetrahydrothiophene) in acetonitrile solution yields three principal products: a 1:1 (dcpe:Au) molar ratio gives $Au_2(dcpe)_2^{2+}$; a 1.5:1 (dcpe:Au) molar ratio produces $Au_2(dcpe)_3^{2+}$; and, with a large excess of dcpe, $Au(dcpe)_2^+$ is formed.[9,10] Crystal structures of $[Au_2(dcpe)_2](PF_6)_2$ (**1**) and $[Au_2(dcpe)_3][Au(CN)_2]_2$ (**2**) have been determined: **1** features

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(9) ^{31}P NMR data in acetonitrile-d_3 referenced to neat H_3PO_4: $[Au_2(dcpe)_2](PF_6)_2$ (**1**), 52.4 ppm (s); $[Au_2(dcpe)_3](PF_6)_2$ (**3**), 64.20 ppm (d), 57.49 ppm (t); $[Au(dcpe)_2]PF_6$ (**4**), 29.5 ppm (s). The ^{31}P spectrum of **3** was unchanged over a period of 4 days.

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