

Ten-Vertex Iron–Monocarbollide Complexes: Synthesis and Reactivity of the Anion $[4,9-{Fe(CO)_4}-9,9,9-(CO)_3$ -arachno-9,6-FeCB₈H₁₁]⁻

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The reagent [*arachno*-4-CB₈H₁₄] reacts with [Fe₃(CO)₁₂] in tetrahydrofuran (THF) at reflux temperatures, followed by addition of [N(PPh₃)₂]Cl, to afford [N(PPh₃)₂][4,9-{Fe(CO)₄}-9,9,9-(CO)₃-*arachno*-9,6-FeCB₈H₁₁] (**3**). In the anion

of **3**, one iron atom is part of the open CBBFeBB face of a 10-vertex {*arachno*-9,6-FeCB₈} cage, to which the second iron atom is attached via an Fe–Fe bond and an additional exo-polyhedral Fe–B σ bond. Upon heating **3** in refluxing toluene, the closed 10-vertex species [N(PPh₃)₂][2,2,2-(CO)₃-*closo*-2,1-FeCB₈H₉] (**4**) is obtained, whereas the isomeric compound [N(PPh₃)₂][6,6,6-(CO)₃-*closo*-6,1-FeCB₈H₉] (**5**) is isolated upon heating [*closo*-4-CB₈H₉]⁻ and [Fe₃(CO)₁₂] in refluxing THF with subsequent addition of [N(PPh₃)₂]Cl. Protonation of **3** using CF₃SO₃H in CH₂Cl₂ gives the charge-compensated compound [4,9-{Fe(CO)₄}-4-(μ -H)-9,9,9-(CO)₃-*arachno*-9,6-FeCB₈H₁₁] (**6**), in which the B–Fe σ bond of the precursor has been converted to a B–H \rightarrow Fe linkage. In contrast, **3** with {M(PPh₃)}⁺ gives the trimetallic species [1,3,4,9-{MFe(CO)₄(PPh₃)}-1,3-(μ -H)₂-9,9,9-(CO)₃-*arachno*-9,6-FeCB₈H₉] (M = Cu (**7**), Ag (**8**)) in which the three metal centers form a V-shaped M–Fe–Fe unit. Compound **6** reacts with PEt₃ in the presence of Me₃NO to yield [4,9-(PEt₃)₂-9,9-(CO)₂-*nido*-9,6-FeCB₈H₁₀] (**9**). In the latter, the formerly exo-polyhedral {Fe(CO)₄} fragment has been replaced by a PEt₃ ligand, with a second PEt₃ substituting one CO group at the remaining cluster iron vertex. The novel structural features of compounds **3**–**9** have been confirmed by single-crystal X-ray diffraction studies.

Introduction

We have for some years been investigating the chemistry of metal-monocarbollide species^{1,2} in an attempt to redress a perceived imbalance between reports of these compounds in the literature relative to their much more well-studied dicarbollide counterparts.³ However, until recently, our studies have essentially been limited to icosahedral {MCB₁₀} clusters,^{1,2} a consequence of the difficulty of access to monocarboranes smaller than the {CB₁₀} system.⁴ The discovery of the so-called Brellochs reaction,⁵ as well as its

- (1) McGrath, T. D.; Stone, F. G. A. J. Organomet. Chem. 2004, 689, 3891.
- McGrath, T. D.; Stone, F. G. A. Adv. Organomet. Chem. 2005, 53, 1.
 Grimes, R. N. In Comprehensive Organometallic Chemistry; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 1, Section 5.5. Grimes, R. N. In Comprehensive Organometallic Chemistry II; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 1, Chapter 9. Grimes, R. N. Coord. Chem. Rev. 2000, 200–202, 773.
- (4) Stibr, B. Chem. Rev. 1992, 92, 225.
- (5) Brellochs, B. In *Contemporary Boron Chemistry*; Davidson, M. G., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000; p 212.

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subsequent elaboration,^{6–8} has allowed intermediate-sized monocarboranes to be synthesized readily and in good yields from commercially available decaborane ($B_{10}H_{14}$). As a consequence, metallacarborane chemists are presented with a "golden opportunity". Sub-icosahedral metal-monocarbollide complexes in principle are now within reach via the many smaller carboranes that are newly accessible. In expanding our studies in this direction, we have reported 11-vertex {MCB₉} clusters (M = Re,⁹ Mn,¹⁰ Mo¹¹) synthe-

- (7) Franken, A.; Kilner, C. A.; Thornton-Pett, M.; Kennedy, J. D. Collect. Czech. Chem. Commun. 2002, 67, 869. Jelínek, T.; Thornton-Pett, M.; Kennedy, J. D. Collect. Czech. Chem. Commun. 2002, 67, 1035.
- (8) Brellochs, B.; Backovsky, J.; Stíbr, B.; Jelínek, T.; Holub, J.; Bakardjiev, M.; Hnyk, D.; Hofmann, M.; Císarová, I.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **2004**, 3605.

(11) Lei, P.; McGrath, T. D.; Stone, F. G. A. Chem. Commun. 2005, 3706.

⁽⁶⁾ Stibr, B. Pure Appl. Chem. 2003, 75, 1295.

⁽⁹⁾ Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. Organometallics 2003, 22, 2842.

^{(10) (}a) Du, S.; Farley, R. D.; Harvey, J. N.; Jeffery, J. C.; Kautz, J. A.; Maher, J. P.; McGrath, T. D.; Murphy, D. M.; Riis-Johannessen, T.; Stone, F. G. A. *Chem. Commun.* **2003**, 1846. (b) Du, S.; Jeffery, J. C.; Kautz, J. A.; Lu, X. L.; McGrath, T. D.; Miller, T. A.; Riis-Johannessen, T.; Stone, F. G. A. *Inorg. Chem.* **2005**, *44*, 2815.



sized from $[6\text{-Ph-$ *nido* $-6-CB_9H_{11}}]^-$ and more recently a pair of 9- and 10-vertex ferracarboranes prepared from $[closo-1\text{-CB}_7\text{H}_8]^{-12}$ Following on from the latter, we have performed a comparative study upon 10-vertex ferracarboranes derived from {CB₈} precursors, the results of which we now present. (Vertex numbering in the 10-vertex (**A**) *closo*-FeCB₈, and (**B**) *nido*- or *arachno*-FeCB₈, cages discussed herein is shown in Chart 1.)

Results and Discussion

We have recently prepared the salts $[N(PPh_3)_2][7,7,7-$ (CO)₃-closo-7,1-FeCB₇H₈] (1) and [N(PPh₃)₂][6,6,6,10,10,- $10-(CO)_6-closo-6, 10, 1-Fe_2CB_7H_8$ (2) by heating [NBuⁿ₄]- $[closo-1-CB_7H_8]$ with $[Fe_3(CO)_{12}]$ in THF followed by addition of [N(PPh₃)₂]Cl (Chart 2).¹² Using a similar methodology, we obtained $[N(PPh_3)_2][4,9-{Fe(CO)_4}-9,9,9 (CO)_3$ -arachno-9,6-FeCB₈H₁₁] (3) from [arachno-4-CB₈H₁₄] with $[Fe_3(CO)_{12}]$ in THF at reflux temperatures followed by addition of [N(PPh₃)₂]Cl. An X-ray diffraction study upon the product was required to establish definitively its molecular structure. One of the three crystallographically independent anions of **3** is presented in Figure 1. Two iron atoms are present and are connected via an Fe-Fe bond (Fe(1A)-Fe(2A) = 2.7033(6) Å), with one of them a vertex in the arachno-10-vertex cluster system, and the other bonded exopolyhedrally to the cage via a direct Fe-B σ bond (Fe(1A)-B(4A) = 1.996(3) Å). Both iron centers possess pseudooctahedral coordination spheres and are formally in the +2oxidation state.

Chart 2



Figure 1. Structure of one of the three crystallographically independent anions of compound **3** showing the crystallographic labeling scheme; the other two anions are essentially identical. In this and subsequent figures, thermal ellipsoids are drawn with 40% probability Selected distances (Å) and angles (deg) are Fe(1A)–Fe(2A), 2.7033(6); Fe(1A)–B(4A), 1.996-(3); Fe(1A)–B(8A), 2.205(3); Fe(1A)–B(10A), 2.213(3); Fe(1A)–C(11A), 1.789(3); Fe(1A)–C(12A), 1.761(3); Fe(1A)–C(13A), 1.779(3); Fe(2A)–B(4A), 2.140(3); Fe(2A)–C(21A), 1.810(3); Fe(2A)-C(22A), 1.803(3); Fe(2A)–C(23A), 1.799(3); Fe(2A)–C(24A), 1.773(3); B(4A)–Fe(1A)–Fe(2A), 51.54(9); B(8A)–Fe(1A)–Fe(2A), 83.25(8); B(10A)–Fe(1A)–Fe(2A), Fe(2A), 51.54(1).

Data characterizing compound **3** are listed in Tables 1–3. Its IR spectrum shows four CO bands between 2055 and 1916 cm⁻¹, while its ¹¹B NMR spectrum contains a 1:1:2: 2:2 set of resonances, consistent with the molecular mirror symmetry seen in the solid state. One of these resonances, at δ 61.4, remains a singlet upon retention of proton coupling and may be assigned to the *B*–Fe nucleus.¹³ Attempts to substitute the Fe-bonded CO groups by other donor mol-



Table 1. Analytical and Physical Data

| | | yield | IR $\nu_{\rm max}({\rm CO})^a$ | | anal. ^b | |
|---|--------|-------|--|--------------------------|--------------------|-----------|
| compd | color | (%) | (cm^{-1}) | С | Н | Ν |
| [N(PPh ₃) ₂][4,9-{Fe(CO) ₄ }-9,9,9-(CO) ₃ -arachno-9,6- FeCB ₈ H ₁₁] (3) | yellow | 47 | 2055 s, 1986 s, 1946 m, 1916 m | 55.1 (55.3) | 4.1 (4.3) | 1.6 (1.5) |
| $[N(PPh_3)_2][2,2,2-(CO)_3-closo-2,1-FeCB_8H_9]$ (4) | yellow | 79 | 2053 s, 1985 s | 59.9 (59.9) ^c | 5.0 (4.9) | 1.7 (1.7) |
| $[N(PPh_3)_2][6,6,6-(CO)_3-closo-6,1-FeCB_8H_9]$ (5) | yellow | 40 | 2033 s, 1964 s | 61.0 (61.1) | 5.2 (5.0) | 1.8 (1.8) |
| [4,9-{Fe(CO) ₄ }-4-(<i>µ</i> -H)-9,9,9-(CO) ₃ -arachno-9,6- FeCB ₈ H ₁₁] (6) | yellow | 73 | 2121 m, 2063 s, 2046 s, 2027 w, 1985 w, 1967 w | 22.8 (23.0) | 2.7 (2.9) | |
| [1,3,4,9-{CuFe(CO) ₄ (PPh ₃)}-1,3-(µ-H) ₂ -9,9,9-(CO) ₃ - arachno-9,6-FeCB ₈ H ₉] (7) | orange | 87 | 2075 s, 2023 s, 2005 s, 1972 w, 1950 w | 41.3 (41.2) ^c | 3.6 (3.5) | |
| [1,3,4,9-{AgFe(CO) ₄ (PPh ₃)}-1,3-(µ-H) ₂ -9,9,9-(CO) ₃ - arachno-9,6-FeCB ₈ H ₉] (8) | orange | 82 | 2071 s, 2021 s, 2002 s, 1971 w, 1950 w | 39.4 (39.7) | 3.3 (3.3) | |
| $[4,9-(PEt_3)_2-9,9-(CO)_2-nido-9,6-FeCB_8H_{10}]$ (9) | pink | 44 | 2008 s, 1960 s | 39.0 (39.4) | 8.4 (8.8) | |

^{*a*} Measured in CH₂Cl₂; in addition, the spectra of all compounds show a broad, medium-intensity band at ca. 2500-2550 cm⁻¹ due to B-H absorptions. ^{*b*} Calculated values are given in parentheses. ^{*c*} Crystallizes with 0.25 equiv of CH₂Cl₂.

Table 2. ¹H and ¹³C NMR Data^a

| compd | $^{1}\mathrm{H}^{b}\left(\delta ight)$ | $^{13}\mathrm{C}^{c}\left(\delta ight)$ |
|-------|---|--|
| 3 | 7.75-7.43 (m, 30H, Ph), 0.61 (br s, 1H, cage CH), 0.46 (br s, 1H, | 216.9 (CO), 215.6 (CO), 133.7-126.5 (Ph), 30.6 (br, |
| | cage CH), -3.22 (br, 2H, B-H-B) | cage C) |
| 4 | 7.66-7.47 (m, 30H, Ph), 5.79 (br s, 1H, cage CH) | 210.6 (CO), 134.0-126.5 (Ph), 76.2 (br, cage C) |
| 5 | 7.68-7.43 (m, 30H, Ph), 5.10 (br s, 1H, cage CH) | 214.0 (CO), 133.7–126.4 (Ph), 67.8 (br, cage C) |
| 6 | 0.91 (br s, 1H, cage CH), 0.42 (br s, 1H, cage CH), -3.11 (br, 2H, | 211.6 (CO), 211.4 (CO), 207.0 (2 × CO), 202.4 |
| | $B-H-B$, -10.25 (q, J(BH) = 67, 1H, $B-H \rightarrow Fe$) | $(2 \times CO)$, 198.3 (CO), 14.0 (br, cage C) |
| 7 | 7.75–7.49 (m, 15H, Ph), 1.03 (br s, 1H, cage CH), 0.94 (br s, 1H, | 214.3 (CO), 212.2 (CO), 133.7–129.2 (Ph), 44.4 (br, |
| | cage CH), -3.42 (br, 2H, B-H-B) | cage C) |
| 8 | 7.72–7.41 (m, 15H, Ph), 1.18 (br s, 1H, cage CH), 1.02 (br s, 1H, | 212.2 (CO), 209.8 (CO), 133.8–129.3 (Ph), 30.6 (br, |
| | cage CH), -3.02 (br, 2H, B-H-B) | cage C) |
| 9 | 6.00 (br s, 1H, cage CH), 1.72 (m, 6H, PCH ₂), 1.48 (m, 6H, | 214.0 (d, $J(PC) = 30$, CO), 107.9 (br, cage C), 19.5 |
| | PCH_2), 1.16 (m, 9H, CH_3), 0.55 (m, 9H, CH_3), -11.38 (q, $J(BH) =$ | $(d, J(PC) = 29, PCH_2), 14.6 (d, J(PC) = 42, PCH_2),$ |
| | 50, 2H, B-H \rightarrow Fe) | 7.0 (br, PCH_2CH_3), 6.3 (br, PCH_2CH_3) |
| | | |

^{*a*} Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, measurements taken at ambient temperatures in CD₂Cl₂. ^{*b*} Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. -1 to +3. ^{*c*} ¹H-decoupled chemical shifts are positive to high frequency of SiMe₄.

Table 3. ¹¹B and ³¹P NMR Data^a

| compd | $^{11}\mathrm{B}^{b}\left(\delta ight)$ | $^{31}\mathrm{P}^{c}\left(\delta ight)$ |
|---------------------------------|---|---|
| 3 4 5 6 7 8 9 | | 5.8 (br) 13.8 (vbr d, $J(AgP) \approx 555$, $AgPPh_3$) 57.9 (s, FePEt ₃), 7.2 (q, $J(BP) \approx 132$, $B-PEt_3$) |

^{*a*} Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, measurements taken at ambient temperatures in CD₂Cl₂. ^{*b*} ¹H-decoupled chemical shifts are positive to high frequency of BF₃·Et₂O (external); resonances are of unit integral except where indicated. ^{*c*} ¹H-decoupled chemical shifts are positive to high frequency of 85% H₃PO₄ (external). Compounds **3–5** show an additional singlet at δ 21.7 for the [N(PPh₃)₂]⁺ cation.

ecules failed, even in the presence of Me₃NO. In this respect, the anion of **3** displays similar chemical behavior to both **1** and 2.¹²

Other 10-vertex metallaheteroboranes with the cluster formulation {*arachno*-9,6-MEB₈} (E = C, N, O, S, Se) are also known, with the majority (as here) formed by addition of the metal center to a preformed open-cage heteroborane.¹⁴ However, the synthesis of compound **3** may also appropriately be compared with the formation of neutral, *arachno*-10-vertex nickel– and platinum–dicarbollide derivatives reported approximately three decades ago from reaction of the nine-vertex carboranes 4,6-R₂-*arachno*-4,6-C₂B₇H₁₁ (R = H, Me) with zero-valent nickel or platinum reagents.¹⁵ In all three of the latter systems, incorporation of the metal vertex (Ni, Pt, Fe) into the cluster may be viewed as an oxidative insertion, with the ultimate products all having an arachno geometry and with the metal center in the three-connected 9-position in the cage. Compound **3**, upon dissolution in toluene and heating to reflux temperature for 4 h, yielded the closed 10-vertex species $[N(PPh_3)_2][2,2,2-(CO)_3-closo-2,1-FeCB_8H_9]$ (**4**) as the only metallacarborane product. Formally, the reaction appears straightforward, with the four electrons available from the arachno \rightarrow closo conversion utilized in the evolution of 1 equiv of H₂ by reduction of two formerly bridging protons and in the reductive loss of the former exo-{Fe(CO)₄}²⁺ moiety as Fe(0). The precise details of the reaction, of course, may be more complex. The ¹¹B{¹H} NMR spectrum of **4** showed a 1:1:2:2:2 set of resonances, all of which showed coupling with terminal hydrogens in a fully coupled ¹¹B spectrum, confirming the loss of the exo-polyhedral iron unit. Other data for compound **4** (Tables 1–3) are straightforward.

In contrast with the thermal closure of **3** to give **4**, it was subsequently found that the carborane $[closo-4-CB_8H_9]^-$ and $[Fe_3(CO)_{12}]$ react in THF under reflux to form the anion $[6,6,6-(CO)_3-closo-6,1-FeCB_8H_9]^-$ via an oxidative insertion



Figure 2. Structure of the anions of (a) compound **4** and (b) compound **5**, showing their crystallographic labeling schemes. For clarity, hydrogen atoms are omitted. Selected internuclear distances (Å) are as follows. For **4**: Fe(2)-C(1), 1.992(3); Fe(2)-B(3), 2.205(3); Fe(2)-B(5), 2.201(3); Fe(2)-B(6), 2.221-(3); Fe(2)-B(9), 2.208(3); Fe(2)-C(21), 1.780(3); Fe(2)-C(22), 1.787(3); Fe(2)-C(23), 1.777(3). For **5**: $B(2)\cdots B(3)$, 2.044(6); Fe(6)-B(2), 2.210(4); Fe(6)-B(3), 2.185(4); Fe(6)-B(7), 2.221(4); Fe(6)-B(9), 2.270(4); Fe(6)-B(10), 2.073(4); Fe(6)-C(61), 1.770(4); Fe(6)-C(62), 1.779(4); Fe(6)-C(63), 1.772(3).

of the iron moiety. This anion was isolated as its $[N(PPh_3)_2]^+$ salt (**5**) following addition of $[N(PPh_3)_2]Cl$. The reaction whereby **5** is formed is analogous to the formation of **1** from $[closo-1-CB_7H_8]^-$ and $[Fe_3(CO)_{12}]$.¹² We note in passing that the anion of **5** is also obtained (albeit in poor yield and with considerable contamination) from $[nido-1-CB_8H_{12}]$ and $[Fe_3(CO)_{12}]$. This is unsurprising as $\{arachno-4-CB_8\}$ species are converted quite readily to their $\{nido-1-CB_8\}$ counterparts upon heating.^{6–8}

The ¹¹B{¹H} NMR spectrum for **5** is quite similar to that of its isomer **4** and shows a 1:3:2:2 set of resonances, all of which likewise become doublets upon retention of proton coupling. It may be of significance that the CO stretching frequencies for **5** are some 20 cm⁻¹ lower than the ones for **4**, perhaps a reflection of the differing donor properties toward the iron vertex of CB₄ (**4**) versus B₅ (**5**) faces of the different {*nido*-CB₈} ligands in the two compounds. This phenomenon is readily understood (at least qualitatively) by consideration of the different electronegativities of boron versus carbon. Other spectroscopic data for **5** (Tables 1–3) are uncomplicated.

X-ray diffraction experiments were required to initially and definitively establish the structures of the ferracarborane anions of compounds **4** and **5**, in particular the relative positions of the carbon and iron vertexes. Given the C_s symmetry implied by the ¹¹B NMR data and with the ¹H NMR data showing only a single cage CH and the absence of any B-H-B protons, a closed-cage structure was likely, with only 2,1- or 6,1-{FeCB₈} isomers possible. This reasonably assumes that carbon will occupy a four-connected site¹⁶ and that iron will be in the higher, five-connected one;¹⁷ otherwise, 1,2- or 1,6-{FeCB8} isomers would also be conceivable. The results of the structural studies are shown in Figure 2 and merit little further comment, save to note that in both cases the carbon and iron vertexes do indeed occupy four- and five-coordinate sites, as expected.^{16,17} A (presumably unfavorable) {closo-10,1-FeCB₈} isomer is not observed. Perhaps surprisingly, we also found no evidence of isomerization of either 4 or 5 upon prolonged heating in refluxing toluene.

Although metallacarboranes with a { $closo-MCB_8$ } architecture are known,^{10b,18} they are relatively rare. These are limited primarily to clusters with 2,1- and 6,1-MCB₈ atom arrangements; we are aware of only one example^{18a,b,f} with a {10,1-MCB₈} architecture. Moreover, the structurally characterized isomeric pair **4** and **5** is particularly interesting, and it will be important in the future to compare their respective reactivities.

 (16) (a) Williams, R. E. Adv. Inorg. Chem. Radiochem. 1976, 18, 67. (b) Ott, J. J.; Gimarc, B. M. J. Am. Chem. Soc. 1986, 108, 4303.

⁽¹²⁾ Franken, A.; McGrath, T. D.; Stone, F. G. A. Organometallics 2005, 24, 5157.

⁽¹³⁾ Brew, S. A.; Stone, F. G. A. Adv. Organomet. Chem. 1993, 35, 135.
(14) Jones, J. H.; Stíbr, B.; Kennedy, J. D.; Thornton-Pett, M. Inorg. Chim. Acta 1994, 227, 163. Hilty, T. K.; Thompson, D. A.; Butler, W. M.; Rudolph, R. W. Inorg. Chem. 1979, 18, 2642. Alcock, N. A.; Jasztal, M. J.; Wallbridge, M. G. H. J. Chem. Soc., Dalton Trans. 1987, 2793. Faridoon; Dhubhghaill, O. N.; Spalding, T. R.; Ferguson, G.; Kaitner, B.; Fontaine, X. L. R.; Kennedy, J. D. J. Chem. Soc., Dalton Trans. 1989, 1657. Fontaine, X. L. R.; Kennedy, J. D.; Thornton-Pett, M.; Nestor, K.; Stíbr, B.; Jelínek, T.; Base, K. J. Chem. Soc., Dalton Trans. 1990, 2887. Stíbr, B.; Jelínek, T.; Kennedy, J. D.; Fontaine, X. L. R.; Thornton-Pett, M. J. Chem. Soc., Dalton Trans. 1993, 1261. Kim, Y.-H.; Brownless, A.; Cooke, P. A.; Greatrex, R.; Kennedy, J. D.; Thornton-Pett, M. Inorg. Chem. Commun. 1998, 1, 19.

⁽¹⁵⁾ Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1975, 2274.

⁽¹⁷⁾ For example: Miller, V. R.; Sneddon, L. G.; Beer, D. C.; Grimes, R. N. J. Am. Chem. Soc. 1974, 96, 3090.

^{(18) (}a) Salentine, C. G.; Rietz, R. R.; Hawthorne, M. F. Inorg. Chem. 1974, 13, 3025. (b) Stíbr, B.; Janousek, Z.; Base, K.; Dolansky, J.; Hermánek, S.; Solntsev, K. A.; Butman, L. A.; Kuznetsov, I. I.; Kuznetsov, N. T. Polyhedron 1982, 1, 831. (c) Crooke, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. J. Chem. Soc., Chem. Commun. 1983, 83. (d) Solntsev, K. A.; Butman, L. A.; Kuznetsov, I. I.; Kuznetsov, N. T.; Stíbr, B.; Janousek, Z.; Base, K. Koord. Khim. 1983, 9, 993. (e) Alcock, N. W.; Taylor, J. G.; Wallbridge, M. G. H. J. Chem. Soc., Chem. Commun. 1983, 1168. (f) Stíbr, B.; Janousek, Z.; Base, K.; Plesek, J.; Hermánek, S.; Solntsev, K. A.; Butman, L. A.; Kuznetsov, I. I.; Kuznetsov, N. T. Collect. Czech. Chem. Commun. 1984, 49, 1660. See also: Carr, M. J.; Franken, A.; Kennedy, J. D. Dalton Trans. 2004, 2612.



Figure 3. Structure of compound **6** showing the crystallographic labeling scheme. Selected distances (Å) and angles (deg) are Fe(1)-Fe(2), 2.6885(2); Fe(1)-B(4), 2.0213(11); Fe(1)-B(8), 2.2387(11); Fe(1)-B(10), 2.2573(12); Fe(1)-C(11), 1.8015(11); Fe(1)-C(12), 1.7742(10); Fe(1)-C(13), 1.7916(10); Fe(2)-F(4), 2.2923(11); Fe(2)-H(4), 1.592(13); B(4)-H(4), 1.245(13); Fe(2)-C(21), 1.8192(11); Fe(2)-C(22), 1.8313(10); Fe(2)-C(23), 1.8420(10); Fe(2)-C(24), 1.8226(10); B(4)-Fe(1)-Fe(2), 56.12(3); B(8)-Fe(1)-Fe(2), 85.52(3); B(10)-Fe(1)-Fe(2), 85.17(3); B(4)-Fe(2)-Fe(1), 47.06(3); Fe(1)-Fe(2), 76.83(4).

Mention was made earlier of the difficulty of substituting the iron-bound CO groups in **3**. In an attempt to make these ligands more susceptible to replacement, we attempted to convert the anion of **3** to a neutral, zwitterionic species following a typical protocol, namely abstraction of a boronbound hydride (using H⁺) in the presence of a donor solvent.² Although an apparently neutral species was obtained, preliminary ¹H NMR evidence showed no donor molecule to be present and the same product was obtained regardless of the donor chosen. Ultimately, the identity of this product was established as the complex $[4,9-{Fe(CO)_4}-4-(\mu-H) 9,9,9-(CO)_3-arachno-9,6-FeCB_8H_{11}]$ (**6**). This was readily and cleanly obtained by protonation of **3** with CF₃SO₃H in CH₂-Cl₂, and its precise nature was confirmed by an X-ray diffraction study (Figure 3).

The overall constitution of the starting compound **3** is seen to have been retained. As in the anion of the precursor, two iron atoms are connected via an Fe–Fe bond (Fe(1)–Fe(2) = 2.6885(2) Å), this being slightly shorter than in the parent. The exo-polyhedral iron unit (Fe(2)) is again bonded to a boron atom (B(4)) adjacent to the cage iron vertex (Fe(1)), but the Fe(2)···B(4) distance (2.2923(11) Å) is much longer than that in **3**. This is due to the presence of a hydrido ligand bridging this connectivity. Thus, a B–Fe σ bond in **3** has been protonated to form a B–H \rightarrow Fe three-center, twoelectron agostic-type linkage. This process is readily reversible upon treatment of **6** with even mild bases to regenerate the anion of **3**. The introduction or removal of a B···H···M bridging hydride (as here) by protonation or deprotonation at a {B····M} site has been observed previously.¹⁹

The NMR data for **6** (Tables 2 and 3) are in complete agreement with the structure established in the solid state. In the ¹H NMR spectrum, a diagnostic¹³ broad quartet

resonance of unit integral is seen at $\delta -10.25$ (*J*(BH) = 67 Hz) and is assigned to the B-H \rightarrow Fe linkage, and a further signal at $\delta -3.11$ of relative intensity of 2 is in the region characteristic for B-H-B bridging hydrogens. The presence of a mirror plane of symmetry through C(6), B(2), B(4), Fe-(1), Fe(2), and the midpoint of the B(1)-B(3) bond is reflected in the observed ¹¹B{¹H} NMR spectrum, the latter showing a 1:1:2:2:2 set of resonances, with one resonance at δ 36.7 showing only a relatively small *J*(HB) value of 67 Hz in a fully coupled ¹¹B NMR spectrum, again characteristic of the B-H \rightarrow Fe bond.

Since the groups $\{M(PPh_3)\}^+$ (M = Cu, Ag) are isolobal with the proton,²⁰ it seemed likely that these cations would also react with the anion of 3, in this case to afford trimetallic species. Accordingly, 3 was dissolved in CH₂Cl₂ and treated with 1 equiv of $\{M(PPh_3)\}^+$ (from $[CuCl(PPh_3)]_4/Tl[PF_6]$ or $Ag[PF_6]/PPh_3$). These reactions yielded the compounds $[1,3,4,9-{MFe(CO)_4(PPh_3)}-1,3-(\mu-H)_2-9,9,9-(CO)_3-arachno-$ 9,6-FeCB₈H₉] (M = Cu (7), Ag (8)), whose structures were definitively established by X-ray diffraction studies. The structure of compound 7 and geometric data for both 7 and 8 are presented in Figure 4. The two compounds gave isomorphous crystals and, as expected, are essentially isostructural, with some slight differences in geometric parameters arising merely as a result of the differing radii of Cu versus Ag. In both species, there is the same arrangement of iron atoms with Fe(1)-Fe(2) = 2.7543(4) Å in 7 and 2.7485(5) Å in 8. As in the starting anion of 3, the iron atom Fe(1) that is a cluster vertex is coordinated by three CO molecules and the exo-polyhedral Fe(2) center bears four such groups. The appended $\{M(PPh_3)\}$ moiety is attached to the $\{arachno-FeCB_8\}$ framework in a site that is distant

from the open CBBFeBB face. Thus, the metal center M is bonded to Fe(2) (Fe(2)-Cu(1) = 2.5655(4) Å; Fe(2)-Ag(1) 2.6755(4) Å) and also approaches B(4), so that this boron is in contact with all three metal atoms (for 7: Fe(1)-B(4) = 1.9937(15) Å, Fe(2)-B(4) = 2.2018(15), $B(4)\cdots Cu(1) = 2.2082(15)$ Å; for 8: Fe(1)-B(4) =1.9881(19) Å, Fe(2)-B(4) = 2.245(2) Å, $B(4)\cdots Ag(1) =$ 2.4876(19) Å). The *exo*-{M(PPh₃)} unit is further supported by interactions with the $\{BH(1)\}\$ and $\{BH(3)\}\$ vertexes, which partake in weak $B-H \rightarrow M$ three-center, two-electron bonds (for 7: $B(1)\cdots Cu(1) = 2.4474(15) \text{ Å}, B(3)\cdots Cu(1)$ = 2.3309(15) Å; for 8: B(1)···Ag(1) = 2.753(2) Å, $B(3) \cdot \cdot \cdot Ag(1) = 2.624(2) \text{ Å}$. Although in both 7 and 8, the interaction with $\{BH(3)\}$ is significantly stronger than that with $\{BH(1)\}$, both of these B····M distances are nevertheless rather long.

Spectroscopic data for compounds 7 and 8 (Tables 1–3) are consistent with their solid-state structures. Their ¹H NMR spectra display broad signals for the two B–H–B bridging hydrogens at δ –3.42 (7) and –3.02 (8), but no peaks were

⁽¹⁹⁾ Examples include: (a) Vites, J.; Housecroft, C. E.; Eigenbrot, C.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. J. Am. Chem. Soc. **1986**, 108, 3304.
(b) Ellis, D. D.; Jelliss, P. A.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. **2000**, 2113. (c) Yasue, T.; Kawano, Y.; Shimoi, M. Angew. Chem., Int. Ed. **2003**, 42, 1727.

⁽²⁰⁾ Stone, F. G. A. Angew. Chem., Int. Ed. Engl. 1984, 23, 89.



Figure 4. Structure of compound 7 showing the crystallographic labeling scheme; that of compound 8 is very similar. For clarity, all but the ipso carbons of phenyl rings are omitted. Selected distances (Å) and angles (deg) are as follows. For 7: Fe(1)-Fe(2), 2.7543(4); Fe(1)-B(4), 1.9937(15); Fe(1)-B(8), 2.2304(17); Fe(1)-B(10), 2.2376(17); Fe(2)-Cu(1), 2.5655(4); Fe(2)-B(4), 2.2018(15); B(1)···Cu(1), 2.4474(15); B(3)···Cu(1), 2.3309(15); B(4)···Cu(1), 2.2082(15); B(4)-Fe(1)-Fe(2), 52.32(4); B(4)-Fe(2)-Cu(1), 54.54(4); B(4)-Fe(2)-Fe(1), 45.78(4); Cu(1)-Fe(2)-Fe(1), 100.269(10); Fe(1)-B(4)-Fe(2), 81.90(6); Fe(1)-B(4)-Cu(1), 152.87(8); Fe(2)-B(4)-Cu(1), 71.15(5). For 8: Fe(1)-Fe(2), 2.7485(5); Fe(1)-B(4), 1.9881(19); Fe(1)-B(8), 2.228(2); Fe(1)-B(10), 2.226(2); Fe(2)-Ag(1), 2.6755(4); Fe(2)-B(4), 2.245(2); B(1)···Ag(1), 2.753(2); B(3)···Ag(1), 2.624(2); B(4)···Ag(1), 2.4876(19); C(24)···Ag(1), 2.699(2); B(4)-Fe(1)-Fe(2), 53.73(6); B(4)-Fe(2)-Ag(1), 59.98(5); B(4)-Fe(2)-Fe(1), 45.55(5); Ag(1)-Fe(2)-Fe(1), 105.444(12); Fe(1)-B(4)-Fe(2), 80.72(7); Fe(1)-B(4)-Ag(1), 149.11(10); Fe(2)-B(4)-Ag(1), 68.63(5).

observed that could be assigned to the agostic $B-H \rightarrow$ Mbridges. The absence of the latter signals is not unusual and results from solution dynamic processes that are rapid on the NMR time scale, even at low temperature.²¹ The boron atom (B(4)) that is in contact with all three of the metal atoms gives rise to a rather deshielded signal at δ 49.0 (7) and 53.1 (8) in the respective ${}^{11}B{}^{1}H{}$ NMR spectra, this peak remaining a singlet upon retention of proton coupling. Other signals in the NMR spectra are in characteristic positions and need not be discussed further, save to note that the ³¹P-{¹H} NMR spectrum for 7 shows a broad resonance at δ 5.8 that is broadened by unresolved coupling to the adjacent copper and boron nuclei, while the corresponding signal for 8 occurs as a broad doublet ($J(AgP) \approx 555$ Hz) centered at δ 13.8 for which individual ¹⁰⁷Ag- and ¹⁰⁹Ag-³¹P couplings could not be resolved.



Chart 3

Despite the fact that compound **6** was prepared with a view to replacing its CO groups with other donor ligands, this proved difficult. With a number of reagents, the only process that occurred appeared to be decomposition—often via loss of the exo-polyhedral iron center. However, with strong donors, some products could be isolated. Thus, although no reaction occurred on stirring **6** with PEt₃, upon addition of excess Me₃NO to the reaction mixture, the pink monoiron species [4,9-(PEt₃)₂-9,9-(CO)₂-*nido*-9,6-FeCB₈H₁₀] (**9**) was formed.

The ${}^{11}B{}^{1}H{}$ NMR spectrum of **9** indicated a mirror symmetric structure with five resonances of relative intensity 2:2:2:1:1 (high to low frequency), in sharp contrast with the 1:1:2:2:2 pattern seen for 3 (and 6-8). This reversal of the intensity pattern was suggestive of a change in cluster character from arachno to nido, and is seen in other arachnoversus nido-10-vertex clusters, such as the $\{C_2B_8\}, \{CB_9\}, \{CB_9\}$ $\{SB_9\}$, and $\{B_{10}\}$ systems.^{8,22} For **9**, the highest field ¹¹B signal (δ -22.7) is a doublet that has characteristic coupling of J(PB) = 134 Hz and arises from PEt₃ substitution at one boron atom. A corresponding quartet signal appears in the ³¹P{¹H} NMR spectrum at δ 7.2 with J(BP) = 132 Hz plus a singlet at δ 57.9 that is assigned to an Fe-bound PEt₃ moiety. The presence of this phosphine at the metal center results in the sole signal for CO ligands being a doublet (δ 214.0; J(PC) = 30 Hz) in the ¹³C{¹H} NMR spectrum. Since no other signals for carbonyl ligands were found, it seemed likely that the exo-polyhedral iron unit had been lost and it was reasonably proposed that the boron-bound phosphine

^{(21) (}a) Jeffrey, J. C.; Ruiz, M. A.; Sherwood, P.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1989, 1845. (b) Carr, N.; Gimeno, M. C.; Goldberg, J. E.; Pilotti, M. U.; Stone, F. G. A.; Topaloglu, I. J. Chem. Soc., Dalton Trans. 1990, 2253. (c) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1993, 1073. (d) Jeffery, J. C.; Jelliss, P. A.; Rees, L. H.; Stone, F. G. A. Organometallics 1998, 17, 2258.

 ⁽²²⁾ Beckett, M. A.; Kennedy, J. D. J. Chem. Soc., Chem. Commun. 1983, 575. Bown, M.; Fontaine, X. L. R.; Kennedy, J. D. J. Chem. Soc., Dalton Trans. 1988, 1467. See also: Hermánek, S. Chem. Rev. 1992, 92, 325 and references therein.

Ten-Vertex Iron-Monocarbollide Complexes

had become attached at B(4). This last proposal is also consistent with the observed retention of mirror symmetry, as B(2) is the only other boron that lies on the mirror plane. In the ¹H NMR spectrum, multiplet signals for the ethyl protons of the two different PEt₃ ligands are evident, along with only a single cage CH resonance at δ 6.00 of unit relative intensity. There is also a broad, integral-2 quartet to high field (δ -11.38; J(BH) = 50 Hz) that is suggestive of B-H-Fe bridges, which one would expect to be located between the Fe center and the adjacent boron vertexes (B(8))and B(10)). Such hydrogen atoms, bridging the cluster 8,9 and 9,10 connectivities, plus the absence of an endo hydrogen on the carbon vertex are also typical of the nido structure that the ¹¹B NMR data suggests. In contrast, the 5,10- and 7,8-bridging hydrogens in 3, along with the endo hydrogen on the cage carbon atom, are characteristic of arachno-10vertex clusters.

Although the structure of 9 was evident from the NMR spectral data, crystals of 9 suitable for study by X-ray diffraction were grown to confirm the proposed architecture. The result of this experiment is shown in Figure 5. Although the crystals were only of modest quality, the above formulation of 9 was verified unequivocally. The central {9,6-FeCB₈ cage is seen to have been retained, with substitution by PEt₃ moieties at iron and at boron (Fe(1)–P(1) = 2.216(2) Å; B(4)–P(2) = 1.890(8) Å) and loss of the second iron fragment. The Fe(1)-B(8) (2.178(8) Å) and Fe(1)-B(10) (2.188(9) Å) bonds are bridged by hydrido ligands (H(89) and H(91), respectively) as expected, the siting of these hydrogens being consistent with the NMR data and with the proposed nido character of the cluster. This is further corroborated by the B(5)-B(10) and B(7)-B(8) bond lengths in 9, 1.941(12) and 1.945(11) Å, respectively, which are rather longer than the corresponding distances (typically 1.876(5) and 1.880(5) Å, respectively, for one of the crystallographically independent anions) in 3. This elongation is well established as typical of nido-10-vertex clusters. The arachno \rightarrow nido conversion involved in the formation of 9 may be viewed as a simple oxidation of the cluster, possibly effected by the presence of excess Me₃NO or alternatively by the reductive loss of the formerly exo-polyhedral iron fragment, formally Fe(II), as Fe(0).

In contrast with the above reaction of **6** with PEt₃ in the presence of Me₃NO, a preliminary investigation of the reaction of **6** with CNBu' and Me₃NO suggests that the product(s) retain an arachno-10-vertex character and that the exo-polyhedral iron center is still present. However, yields in this system are very low and products with various multiple degrees of substitution are evident, making separation very difficult. Notably, though, it appears that substitution occurs exclusively at the exo iron atom. We hope to report more upon this system in the future.

Conclusion

Several new 10-vertex ferracarboranes have been prepared starting from 8-boron-atom substrates, and their reactivity has been studied. The carborane [*arachno*-4-CB₈H₁₄] adds two iron fragments upon heating with [Fe₃(CO)₁₂]: one as



Figure 5. Structure of one of the crystallographically independent molecules of compound **9** showing the crystallographic labeling scheme. For clarity, only the major component of the disordered Et group is shown and ethyl hydrogens are omitted. Selected distances (Å) and angles (deg) are as follows. Fe(1)–P(1), 2.216(2); Fe(1)–C(41), 1.769(8); Fe(1)–C(42), 1.758(8); Fe(1)–H(89), 1.59(4); B(8)–H(89), 1.19(2); Fe(1)–H(91), 1.75(4); B(10)–H(91), 1.20(2); B(4)–Fe(1), 2.209(8); B(8)–Fe(1), 2.178(8); B(10)–Fe(1), 2.188(9); B(4)–P(2), 1.890(8); B(4)–Fe(1)–P(1), 156.1(2); B(8)–Fe(1)–P(1), 115.8(2); B(10)–Fe(1)–P(1), 120.2(2); C(41)–Fe(1)–P(1), 92.7(3); C(42)–Fe(1)–P(1), 92.1(2); P(2)–B(4)–Fe(1), 116.6(4).

a vertex and the second in an exo-polyhedral site, giving the anion of compound **3**. The latter upon thermolysis undergoes a cage-closure reaction to afford the anion of **4**, whereas the isomeric anion in **5** is produced by direct iron insertion into $[closo-4-CB_8H_9]^-$ in its reaction with $[Fe_3(CO)_{12}]$. The isomeric pair **4** and **5** themselves represent useful starting substrates for which a comparative reactivity study will be of interest, bearing in mind their isolobal relationship with $[Mn(CO)_3(\eta-C_5H_5)]$.²³ They should also provide useful comparisons with the {CB₇} derivatives **1** and **2** and with the corresponding 12-vertex {FeCB₁₀} system.^{24–26} Moreover, compound **3** contains both Fe–Fe and Fe–B linkages to the exo-polyhedral iron, and upon protonation, it is the Fe–B σ -bond that is attacked, converting it cleanly to a B–H \rightarrow Fe agostic-type bridge.

⁽²³⁾ Hata, M.; Kautz, J. A.; Lu, X. L.; McGrath, T. D.; Stone, F. G. A. *Organometallics* **2004**, *23*, 3590.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk line techniques. Solvents were stored over and distilled from appropriate drying agents under dinitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40–60 °C. Chromatography columns (typically ca. 15 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60–200 mesh). NMR spectra were recorded at the following frequencies (MHz): ¹H, 360.1; ¹³C, 90.6; ¹¹B, 115.5; and ³¹P, 145.8. The compounds [*arachno*-4-CB₈H₁₄],⁸ [NBuⁿ₄][*closo*-4-CB₈H₉],⁸ and [CuCl-(PPh₃)]₄²⁷ were prepared according to the literature; all other materials were used as received.

Synthesis of $[N(PPh_3)_2][4,9-{Fe(CO)_4}-9,9,9-(CO)_3-arachno-9,6-FeCB_8H_{11}]$. The compounds $[Fe_3(CO)_{12}]$ (0.50 g, 1.0 mmol) and $[arachno-4-CB_8H_{14}]$ (0.056 g, 0.5 mmol) were dissolved in THF (10 mL) and heated to reflux for 24 h. The mixture was cooled to room temperature, and $[N(PPh_3)_2]Cl$ (0.29 g, 0.5 mmol) was added. Solvent was removed in vacuo, and the residue was dissolved in CH₂Cl₂ (2 mL) and transferred to the top of a chromatography column. Elution with CH₂Cl₂-petroleum ether (4:1) gave a yellow fraction from which was obtained, after removal of solvent in vacuo and then crystallization from CH₂Cl₂-petroleum ether, yellow microcrystals of $[N(PPh_3)_2][4,9-{Fe(CO)_4}-9,9,9-(CO)_3-arachno-9,6-FeCB_8H_{11}]$ (3; 0.23 g).

Synthesis of $[N(PPh_3)_2][2,2,2-(CO)_3-closo-2,1-FeCB_8H_9]$. Compound 3 (0.23 g, 0.25 mmol) was dissolved in toluene (10 mL) and heated to reflux for 4 h. Volatiles were removed in vacuo, and the residue was dissolved in CH₂Cl₂ (2 mL) and subjected to column chromatography. Elution with neat CH₂Cl₂ gave a yellow fraction. Removal of solvent in vacuo, followed by crystallization from CH₂-Cl₂-petroleum ether, yielded yellow microcrystals of $[N(PPh_3)_2]$ -[2,2,2-(CO)₃-closo-2,1-FeCB₈H₉] (4; 0.14 g).

Synthesis of $[N(PPh_3)_2][6,6,6-(CO)_3-closo-6,1-FeCB_8H_9]$. The compounds $[Fe_3(CO)_{12}]$ (0.40 g, 0.79 mmol) and $[NBu^n_4][closo-4-CB_8H_9]$ (ca. 0.18 g, 0.5 mmol) were heated to reflux in THF (10 mL) for 18 h. The mixture was then cooled to room temperature, and $[N(PPh_3)_2]Cl$ (0.29 g, 0.5 mmol) was added. Solvent was removed in vacuo, and the residue was dissolved in CH₂Cl₂ (2 mL) and transferred to the top of a chromatography column. Elution with CH₂Cl₂ gave a pale yellow fraction. Removal of solvent in vacuo followed by crystallization from CH₂Cl₂—petroleum ether yielded yellow microcrystals of $[N(PPh_3)_2][6,6,6-(CO)_3-closo-6,1-FeCB_8H_9]$ (5; 0.16 g).

Synthesis of [4,9-{Fe(CO)₄}-4-(μ -H)-9,9,9-(CO)₃-arachno-9,6-FeCB₈H₁₁]. Compound 3 (0.23 g, 0.25 mmol) was dissolved in CH₂Cl₂ (10 mL), CF₃SO₃H (0.25 mL) was added, and the mixture was stirred at room temperature for 30 min. After filtration through Celite, the filtrate was evaporated in vacuo. The residue was dissolved in CH₂Cl₂ (2 mL) and transferred to the top of a chromatography column. Elution with CH₂Cl₂-petroleum ether (1: 1) gave a yellow fraction from which removal of solvent in vacuo followed by crystallization from CH₂Cl₂-petroleum ether afforded yellow microcrystals of [4,9-{Fe(CO)₄}-4-(μ -H)-9,9,9-(CO)₃arachno-9,6-FeCB₈H₁₁] (6; 0.080 g). Synthesis of $[1,3,4,9-{MFe(CO)_4(PPh_3)}-1,3-(\mu-H)_2-9,9,9-(CO)_3-arachno-9,6-FeCB_8H_9]$. (i) Compound 3 (0.23 g, 0.25 mmol), [CuCl(PPh_3)]_4 (0.09 g, 0.06 mmol), and Tl[PF₆] (0.09 g, 0.25 mmol) were stirred in CH₂Cl₂ (10 mL) at room temperature for ca. 18 h. The resulting mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The residue was taken up in CH₂Cl₂ (2 mL) and applied to a chromatography column. Elution with CH₂Cl₂—petroleum ether (1:1) gave an orange fraction that was collected, evaporated in vacuo, and crystallized from CH₂Cl₂—petroleum ether to give orange microcrystals of $[1,3,4,9-{CuFe(CO)_4(PPh_3)}-1,3-(\mu-H)_2-9,9,9-(CO)_3-arachno-9,6-FeCB_8H_9]$ (7; 0.16 g). (ii) Similarly, compound 3 (0.23 g, 0.25 mmol), Ag[PF₆] (0.070 g, 0.25 mmol), and PPh₃ (0.070 g, 0.25 mmol) yielded orange microcrystals of $[1,3,4,9-{AgFe(CO)_4-(PPh_3)}-1,3-(\mu-H)_2-9,9,9-(CO)_3-arachno-9,6-FeCB_8H_9]$ (8; 0.16 g).

Synthesis of [4,9-(PEt₃)₂-9,9-(CO)₂-*nido*-9,6-FeCB₈H₁₀]. Compound 6 (0.10 g, 0.25 mmol) was dissolved in CH₂Cl₂ (10 mL), PEt₃ (0.25 mL, 0.20 g, 1.69 mmol) and Me₃NO (0.075 g, 1.0 mmol) were added, and the mixture was stirred at room temperature for ca. 5 days. Volatiles were removed under reduced pressure, and the residue was redissolved in CH₂Cl₂ (2 mL) and transferred to the top of a chromatography column. Elution with CH₂Cl₂-petroleum ether (4:1) gave a pink fraction from which removal of solvent in vacuo and crystallization from Et₂O (-30 °C) yielded red microcrystals of [4,9-(PEt₃)₂-9,9-(CO)₂-*nido*-9,6-FeCB₈H₁₀] (9; 0.050 g).

Structure Determinations. Diffraction-quality crystals of compounds 3–5 were obtained by slow diffusion of petroleum ether into CH₂Cl₂ solutions at -30 °C; those of **6** and **9** were grown by slow cooling of saturated hexane solutions to -30 °C, while those of **7** and **8** were grown similarly from pentane solutions at the same temperature. Experimental data for compounds **3–9** are reported in Table 4. Diffraction data were acquired at 110(2) K using a Bruker–Nonius X8 Apex area-detector diffractometer (graphitemonochromated Mo K α radiation, $\lambda = 0.71073$ Å). Several sets of data frames were collected at different θ values for various initial values of ϕ and ω , each frame covering a 0.5 increment in ϕ or ω . The data frames were integrated using SAINT;²⁸ the substantial redundancy in data allowed empirical absorption corrections (SADABS)²⁸ to be applied on the basis of multiple measurements of equivalent reflections.

The structures were solved (SHELXS-97) via conventional direct methods and-for all but 3-were refined (SHELXL-97) by fullmatrix least-squares on all F² data using SHELXTL.^{28,29} All nonhydrogen atoms were assigned anisotropic displacement parameters. The locations of the cage carbon atoms were verified by examination of the appropriate internuclear distances and the magnitudes of their isotropic thermal displacement parameters. All of the hydrogen atoms in organic functions, plus terminal cluster H atoms in the structure of 9, were set riding on their parent atoms in calculated positions; all other cluster H atoms were located in difference maps and allowed positional refinement-with the exception of the B-H-Fe bridging hydrogens in 9, which could only be positionally refined subject to restraints (DFIX card in SHELXL with B-H 1.20(5) Å and Fe-H 1.60(5) Å). All hydrogen atoms were assigned fixed isotropic thermal parameters calculated as $U_{iso}(H) = 1.2 \times U_{iso}(parent)$, or $U_{iso}(H) = 1.5 \times U_{iso}(parent)$ for methyl hydrogens.

Crystals of **3** contained three formula units per asymmetric fraction, with the three independent units differing primarily in the

⁽²⁴⁾ Ellis, D. D.; Franken, A.; Jelliss, P. A.; Stone, F. G. A.; Yu, P.-Y. Organometallics 2000, 19, 1993.

⁽²⁵⁾ Ellis, D. D.; Franken, A.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A.; Yu, P.-Y. J. Chem. Soc., Dalton Trans. 2000, 2509.

⁽²⁶⁾ Franken, A.; Du, S.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A. Organometallics 2001, 20, 1597.
(27) Jardine, F. H.; Rule, J.; Vohra, G. A. J. Chem. Soc. A 1970, 238.

 ⁽²⁸⁾ APEX 2, version 1.0; Bruker AXS: Madison, WI, 2003–2004.
 (29) SHELXTL, version 6.12; Bruker AXS: Madison, WI, 2001.

Ten-Vertex Iron-Monocarbollide Complexes

| Table 4. Crystallographic Data for Compounds 3- | -9 |
|---|----|
|---|----|

| | 3 | 4 | 5 | 6 |
|---|--|--|---|-----------------------|
| formula | $C_{44}H_{41}B_8Fe_2NO_7P_2$ | C40H39B8FeNO3P2 | C40H39B8FeNO3P2 | $C_8H_{12}B_8Fe_2O_7$ |
| fw | 955.90 | 785.99 | 785.99 | 418.36 |
| space group | $P2_1/n$ | $P\overline{1}$ | $P2_{1}/n$ | Pbca |
| <i>a</i> , Å | 16.2454(12) | 11.6121(6) | 14.990(3) | 11.8803(4) |
| <i>b</i> , Å | 56.345(4) | 11.7781(6) | 14.936(3) | 15.9624(7) |
| <i>c</i> , Å | 16.3333(13) | 14.4449(8) | 17.660(4) | 17.6111(7) |
| α, deg | 90 | 80.587(2) | 90 | 90 |
| β , deg | 113.414(4) | 85.802(2) | 94.854(10) | 90 |
| γ , deg | 90 | 82.398(2) | 90 | 90 |
| <i>V</i> , Å ³ | 13719.6(18) | 1929.19(18) | 3939.7(14) | 3339.7(2) |
| Z | 12 | 2 | 4 | 8 |
| $ ho_{ m calc}$, g cm ⁻³ | 1.388 | 1.353 | 1.325 | 1.664 |
| μ (Mo K α), mm ⁻¹ | 0.755 | 0.515 | 0.504 | 1.763 |
| reflns measured | 144 940 | 37 290 | 32 351 | 36 420 |
| indep reflns | 35 715 | 11 184 | 9070 | 6392 |
| R _{int} | 0.0456 | 0.0398 | 0.0557 | 0.0273 |
| wR2(all data), R1 ^a | 0.1105, 0.0524 | 0.1642, 0.0583 | 0.1301, 0.0581 | 0.0582, 0.0231 |
| | 7 •C ₅ H ₁₂ | 8.℃2H12 | 9 | |
| formula | C ₃₁ H ₃₈ B ₈ CuFe ₂ O ₇ P | C31H38AgB8Fe2O7P | $C_{15}H_{40}B_8FeO_2P_2$ | |
| fw | 815.30 | 859.63 | 456.74 | |
| space group | PI | D1 | D1 | |
| Space Broup | 1 1 | P1 | P1 | |
| a, Å | 11.4290(14) | P1 11.5823(17) | 12.6993(14) | |
| a, Å b, Å | 11.4290(14) 12.8599(17) | P1 11.5823(17) 12.8429(19) | 12.6993(14) 13.4499(16) | |
| a, Å b, Å c, Å | 11.4290(14) 12.8599(17) 14.3117(18) | P1 11.5823(17) 12.8429(19) 14.420(2) | F1 12.6993(14) 13.4499(16) 15.9396(18) | |
| $\begin{array}{c} a, \ \mathring{A} \\ b, \ \mathring{A} \\ c, \ \mathring{A} \\ \alpha, \ \deg \end{array}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) | 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) | |
| $\begin{array}{c} a, \dot{A} \\ b, \dot{A} \\ c, \dot{A} \\ \alpha, \deg \\ \beta, \deg \end{array}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) | 11 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) | |
| $\begin{array}{c} a, \dot{A} \\ b, \dot{A} \\ c, \dot{A} \\ \alpha, \deg \\ \beta, \deg \\ \gamma, \deg \end{array}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) | F1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) | |
| $\begin{array}{c} a, \text{\AA}\\ b, \text{\AA}\\ c, \text{\AA}\\ \alpha, \deg\\ \beta, \deg\\ \gamma, \deg\\ V, \text{\AA}^{3} \end{array}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) 1829.3(4) | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) 1851.6(5) | P1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) 2478.2(5) | |
| $\begin{array}{c} a, \dot{A} \\ b, \dot{A} \\ c, \dot{A} \\ \alpha, \deg \\ \beta, \deg \\ \gamma, \deg \\ V, \dot{A}^{3} \\ Z \end{array}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) 1829.3(4) 2 | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) 1851.6(5) 2 | P1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) 2478.2(5) 4 | |
| $\begin{array}{l} a, \dot{A} \\ b, \dot{A} \\ c, \dot{A} \\ \alpha, \deg \\ \beta, \deg \\ \gamma, \deg \\ \gamma, \deg \\ V, \dot{A}^{3} \\ Z \\ \rho_{calc}, g \ cm^{-3} \end{array}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) 1829.3(4) 2 1.480 | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) 1851.6(5) 2 1.542 | P1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) 2478.2(5) 4 1.224 | |
| $\begin{array}{l} p_{\text{calc}} p_{\text{calc}}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) 1829.3(4) 2 1.480 1.447 | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) 1851.6(5) 2 1.542 1.384 | P1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) 2478.2(5) 4 1.224 0.747 | |
| a, Å b, Å c, Å α, \deg β, \deg γ, \deg γ, \deg γ, A^3 Z $\rho_{calc}, g cm^{-3}$ μ (Mo K α), mm ⁻¹ reflns measured | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) 1829.3(4) 2 1.480 1.447 36 939 | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) 1851.6(5) 2 1.542 1.384 37 597 | P1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) 2478.2(5) 4 1.224 0.747 39 747 | |
| β_{A} , \hat{A} β_{a} , \hat{A} c_{a} , \hat{A} α_{a} , deg β_{a} , deg γ_{a} , deg γ_{a} , deg γ_{a} , deg γ_{a} , deg γ_{a} , deg γ_{a} , deg μ_{a} | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) 1829.3(4) 2 1.480 1.447 36 939 11 143 | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) 1851.6(5) 2 1.542 1.384 37 597 12 108 | P1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) 2478.2(5) 4 1.224 0.747 39 747 11 168 | |
| $\beta_{\rm A}$ \dot{A} \dot{a} , \dot{A} \dot{b} , \dot{A} c , \dot{A} α , deg β , deg γ , deg γ , deg γ , deg V , \dot{A}^3 Z $\rho_{\rm calc}$, g cm ⁻³ μ (Mo K α), mm ⁻¹ reflns measured indep reflns $R_{\rm int}$ | 11.4290(14) 12.8599(17) 14.3117(18) 96.175(6) 110.698(5) 106.957(5) 1829.3(4) 2 1.480 1.447 36.939 11.143 0.0309 | P1 11.5823(17) 12.8429(19) 14.420(2) 97.590(4) 112.387(4) 104.934(4) 1851.6(5) 2 1.542 1.384 37 597 12 108 0.0425 | P1 12.6993(14) 13.4499(16) 15.9396(18) 114.448(5) 90.694(4) 90.124(4) 2478.2(5) 4 1.224 0.747 39 747 11 168 0.0724 | |

^{*a*} wR2 = $[\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$; R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$ with $F_o > 4\sigma(F_o)$.

dispositions of the cations. The large number of data and parameters required refinement by blocked-matrix least-squares on F^2 , with one cation and one anion per block (and some atoms common to two blocks), but the model was otherwise as described above.

For both **7** and **8**, one molecule of pentane as solvate cocrystallized in the asymmetric unit along with one molecule of the compound. In both cases, the solvate had two disordered methylene units, of which the two parts were assigned refining complementary occupancies, in the approximate ratios 60:40 (**7**) and 58:42 (**8**) at convergence. The geometries within the two parts of the solvate were restrained to be similar using the SAME card in SHELXL, but treatment was otherwise as above.

Two independent molecules were also found in the asymmetric fraction of crystals of 9 with the molecules differing in the site of a disordered ethyl group in the PEt₃ ligand bound to iron. In each

case, the two parts were assigned refining complementary occupancies, with approximate ratios of 71:29 and 76:24 at convergence. The structure was otherwise refined as above.

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Supporting Information Available: Full details of the crystal structure analyses in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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