

51.39; H, 5.31; Ni, 20.12; Fe, 9.43.

$(\mu_3\text{-CO})_2[(\eta^5\text{-Cp}^*)\text{Ni}]_2(\eta^5\text{-Cp})\text{Co}$ (**5**) and $(\mu_3\text{-CO})_2[(\eta^5\text{-Cp}^*)(\eta^5\text{-Cp})\text{Ni}]_2(\eta^5\text{-Cp})\text{Co}$ (**6**). The vessel of the metal vapor reactor was charged with 10 g (74 mmol) of Cp*H and 8 g (44 mmol) of CpCo(CO)₂ dissolved in 300 mL of methylcyclohexane. Nickel vaporization was started at -120 °C/10⁻⁴ Torr and continued for 90 min (ca. 1 g of Ni vaporized). The initial red color of the solution turned to a dark brown toward the end of the reaction. Filtration and removal of all volatiles and then chromatography (Al₂O₃, 5% H₂O) afford three different zones. First zone (pentane): traces of *cis/trans*-**2**. Second zone: trace amounts of **3**. Third zone (pentane/diethyl ether): 0.9 g, ≈20% as a mixture of complexes **5** and **6** (black-brown crystals, hexane, -30 °C); even repeated rechromatography of this single zone did not result in a splitting of this fraction; MS (EI, 120 °C) *m/e* 566 (3, M⁺, **5**), 496 (10, M⁺, **6**), 259 (73), 189 (100); IR (ν , cm⁻¹) 2970, 2905, 2835, 1705, 1410, 1370, 1350, 1150, 1105, 1045, 1000, 830, 810, 785, 560, 550. Anal. Calcd for C₂₇H₃₅O₂Ni₂Co: C, 57.10; H, 6.17; Ni, 20.70; Co, 10.39. Calcd for C₂₂H₂₅O₂Ni₂Co: C, 53.10; H, 5.02; Ni, 23.60; Co, 11.86. Found: C, 56.12; H, 6.19; Ni, 20.08; Co, 10.21.

Reaction of Cp*H with Ni Atoms and Fe(CO)₂(NO)₂ in Methylcyclohexane. Into a solution of 7 g (47 mmol) of Fe(CO)₂(NO)₂ and 6 g (44 mmol) of Cp*H in 250 mL of methyl-

cyclohexane was vaporized 1 g (17 mmol) of Ni atoms over 1 h. After vaporization of all volatiles and filtration a large amount of unreacted metal was left on the filter frit. Column chromatography of the residue yielded three different zones. First zone: trace amounts of **2**. Second zone: trace amounts of Fe(NO)₂(CO)₂. Third zone (pentane): 0.5 g (2.3 mmol), 14% of **7** (shiny red crystals, pentane, -30 °C); MS (EI, 30 °C) *m/e* 225 (38), 223 (98), 195 (32), 193 (100), 191 (68), 177 (14), 119 (18); IR (ν , cm⁻¹) 3550 (overtone), 3500 (overtone), 2985, 2910, 2930, 1795, 1760, 1465, 1382, 1065, 1025, 645; ¹H NMR (toluene-*d*₆) 1.83 ppm (s, 15 H); ¹³C NMR (toluene-*d*₆) 94.5 ppm (s). Anal. Calcd for C₁₀H₁₅NONi: C, 53.64; H, 6.71; N, 6.25; Ni, 26.24. Found: C, 53.57; H, 6.74; N, 6.19; Ni, 26.28.

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Supplementary Material Available: Detailed information on the crystal structure determination of **1**, including tables of final atomic positional parameters, final thermal parameters, and interatomic distances and angles (7 pages); a list of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Synthesis and Structural Characterization of Mononuclear Iron(II) Ferracarboranes

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Neutral iron(II) ferracarboranes of the type [*closo*-3-CO-3-L-3-L'-3,1,2-FeC₂B₉H₁₁] (**3**, L = CO, L' = PPh₃; **4**, L = PPh₃, L' = CH₃CN; **5**, L = CO, L' = CH₃CN; **6**, L = CO, L' = P(OCH₃)₃; **7**, L = L' = P(OCH₃)₃; **8**, L = L' = CO) have been prepared by the Cu(I) oxidation of the dimeric iron dicarbollide complex [*closo*-3-CO-3,3'-(μ-CO)-3,1,2-FeC₂B₉H₁₁]₂²⁻ (**2**) in the presence of the designated monodentate ligands. Complexes **3**, **4**, **7**, and **8** have been structurally characterized by single-crystal X-ray diffraction. Crystallographic parameters are as follows (compound: crystal system; space group; crystal parameters; Z; unique data (*I* > 3σ(*I*); *R*, *R*_w). **3**: monoclinic; *A2/a*; *a* = 18.384 (3) Å, *b* = 12.762 (2) Å, *c* = 23.059 (3) Å, β = 104.081 (4)°; **8**: 1780; 7.4, 8.8. **4**: monoclinic; *C2/c*; *a* = 28.050 (2) Å, *b* = 11.5715 (9) Å, *c* = 19.042 (2) Å, β = 116.846 (2)°; **8**: 1702; 6.5, 7.7. **7**: orthorhombic; *Pbnm* (standard setting *Pnma*); *a* = 10.397 (2) Å, *b* = 14.419 (3) Å, *c* = 15.092 (3) Å; **4**: 1051; 7.1, 8.9. **8**: monoclinic; *P2₁/n*; *a* = 6.971 (4) Å, *b* = 15.900 (9) Å, *c* = 11.237 (7) Å, β = 91.42 (2)°; **4**: 1108; 6.2, 7.4. The *closo* 12-vertex icosahedral geometry comprising a polyhedral (d⁶Fe)C₂B₉ framework and the pseudooctahedral coordination exhibited by the iron atom are common structural features displayed by all four ferracarboranes.

Introduction

Cyclopentadienyliron compounds¹ are among the most widely studied species in transition-metal organometallic chemistry. Although the structural and electronic similarities between the dicarbollide anion and the cyclopentadienide anion were demonstrated long ago² in the synthesis of the carborane analogue of ferrocene, [*com*-*o*-3,3'-Fe[3,1,2-FeC₂B₉H₁₁]₂]²⁻ (**1**), ferracarboranes remained relatively unexplored. An exception is the recently reported synthesis and structural characterization of (η⁶-arene)iron dicarbollide complexes.³ However, the in-

tensely studied field of mononuclear cyclopentadienyliron compounds containing simple monodentate ligands still lacks counterparts in carborane chemistry.

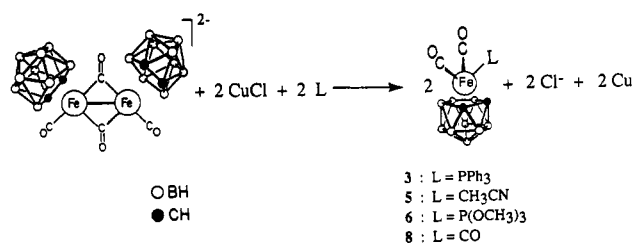
Although evidence of arene substitution by carbon monoxide and trimethyl phosphite in (η⁶-arene)-FeMe₂C₂B₉H₉ systems was reported by Stone and co-workers,^{3c} neither ¹¹B NMR, ¹H NMR, nor X-ray structural characterization data were reported. As part of our ongoing investigation of metallacarborane derivatives, we have prepared a series of novel monodicarbollide complexes that contain iron. In addition, we report herein the

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Scheme I



full spectroscopic and structural characterization of four new ferracarboranes.

Results and Discussion

Synthesis. Early attempts to expand the small family of ferracarboranes consisted of attaching the dicarbollide anion to a variety of metal sources, a methodology which was generally successful in the development of metalla-carborane chemistry. Repeated production of the iron dicarbollide sandwich (1) from a wide array of different methods led us to the intense investigation of the only readily available simple ferracarborane moiety; the dimeric iron dicarbonyl carborane [*closo*-3-CO-3,3'-(μ -CO)-3,1,2-FeC₂B₉H₁₁]₂²⁻ (2).⁴

The anaerobic heterogeneous reaction of 2 with 2 equiv of anhydrous copper(I) chloride and various monodentate ligands resulted in the formation of Cu metal and mononuclear complexes of the type [*closo*-3,3-(CO)₂-3-L-3,1,2-FeC₂B₉H₁₁] (3, L = PPh₃; 5, L = CH₃CN; 6, L = P(OCH₃)₃; 8, L = CO), as shown in Scheme I. Oxidation of the iron-iron bond in Fp₂ (where Fp = (η^5 -C₅H₅)Fe(CO)₂) by transition metals Ag(I)⁵ and Fe(III)⁶ provides precedents in metallocene chemistry.

Although their solutions show signs of decomposition after exposure to air for several days, complexes 3, 5, 6, and 8 are thermally stable compounds in the solid state. Their characteristic ¹¹B FT NMR spectra, showing six resonances with an area ratio of 1:1:1:2:2:2, are consistent with an icosahedral geometry for the carborane cage found in other iron dicarbollide complexes.²⁻⁴ A common feature displayed in their ¹H FT NMR spectra is the broad singlet observed in the region of 2-4 ppm, assigned to the carbonyl C-H.

Two strong frequencies observed in the infrared spectra of 3, 5, 6, and 8 are characteristic of terminal carbonyl groups. These data demonstrate the influence of ligand substitution on metal electron density, as suggested by the comparison of two isoelectronic trends. Examination of the IR data available for the analogous Cp series [(C₅H₅)Fe(CO)₂L]⁺ (L = PPh₃,⁷ CH₃CN,⁸ P(OCH₃)₃,⁹ CO¹⁰) shows that the carbonyl stretching frequencies for the carborane counterparts are consistently lower by ~20 cm⁻¹. Such reductions can be traced to greater M→CO back-bonding, which stems ultimately from an electron-enriched

metal center. The relative electronic properties of the monodentate ligands are also mirrored in the carbonyl stretching frequencies of these ferracarboranes, which suggest that the order of increasing electron density at the transition metal in (C₂B₉H₁₁)Fe(CO)₂L derivatives is CO < CH₃CN < P(OCH₃)₃ < PPh₃. This relative order is in excellent agreement with the well-established increase in the σ -donor: π -acceptor ratios of these ligands. This trend is corroborated by ¹³C NMR¹¹ and Mossbauer studies.¹²

The CuCl oxidation of the dicesium salt Cs₂[2]·CH₃CN·H₂O in the presence of 2 equiv of PPh₃ afforded a mixture of products. After the isolation of 3, red crystals of [*closo*-3-CO-3-PPh₃-3-CH₃CN-3,1,2-FeC₂B₉H₁₁] (4) were obtained from the reaction mixture. Since the oxidation was carried out in THF, the acetonitrile was undoubtedly present in the starting material, 2. An attempt to synthesize 4 with various salts of 2 (N(CH₃)₄⁺, Na⁺, PPN⁺) in acetonitrile solutions was unsuccessful. Although Cs₂[2]·CH₃CN·H₂O was used in other oxidation reactions that employed a variety of ligands, no other mixed-ligand products were isolated.

The 160-MHz ¹¹B{¹H} FT NMR spectrum of 4 exhibited eight peaks with the area ratio of 1:1:1:1:1:1:1:2, although a nine-line pattern is expected due to the asymmetry introduced by the chiral iron center. Most probably, the upfield resonance results from the coincidental overlap of two resonances. The unsymmetrical nature of 4 is also demonstrated in the ¹H NMR spectrum, in which two broad singlets assigned to the nonequivalent carbonyl C-H vertices are observed at 3.17 and 2.71 ppm.

In an attempt to synthesize the ferracarborane containing three trimethyl phosphite ligands, oxidation of 2 by CuCl was carried out in the presence of 6 equiv of P(OCH₃)₃. As monitored by ¹¹B NMR, the reaction mixture after 2 days of stirring at room temperature showed the presence of 6 and [*closo*-3-CO-3,3-[P(OCH₃)₃]₂-3,1,2-FeC₂B₉H₁₁] (7) in the approximate ratio of 1:2. Neither prolonged stirring nor additional excess of P(OCH₃)₃ affected the ratio of products of 6 and 7. Although the Cp analogue of 6 is known, the Cp analogue of 7 has not been reported.

Nucleophilic attack on the coordinated CO followed by subsequent loss of carbon monoxide of the ruthenacarborane tricarbonyl [*closo*-3,3,3-(CO)₃-3,1,2-RuC₂B₉H₁₁] has resulted in the formation of the hydride complex.¹³ Reaction of 1 molar equiv of NaBH₄ with 8 in THF at room temperature, afforded the iron dimer 2. Dimerization to form [C₅H₅Fe(CO)₂]₂ via C₅H₅Fe(CO)₂CHO and C₅H₅Fe(CO)₂H intermediates is known in FeCp chemistry.¹⁴

Quantitative production of complex 5, as monitored by ¹¹B NMR spectroscopy, was obtained via photolysis of 8 in acetonitrile. Although successive exchange of CO for CH₃CN has resulted in the isolation of [CpFe(CH₃CN)₃]⁺ from photolysis of [CpFe(CO)₃]⁺,¹⁵ further ligand substitution was not observed by prolonged exposure of 8 to ultraviolet radiation. The versatility of 8 as a synthon has also been demonstrated in the synthesis of an η^6 -benzene ferracarborane.^{3e}

Structural Analysis. Since no mononuclear ferracarboranes containing monodentate ligands have been crystallographically elucidated, four representative com-

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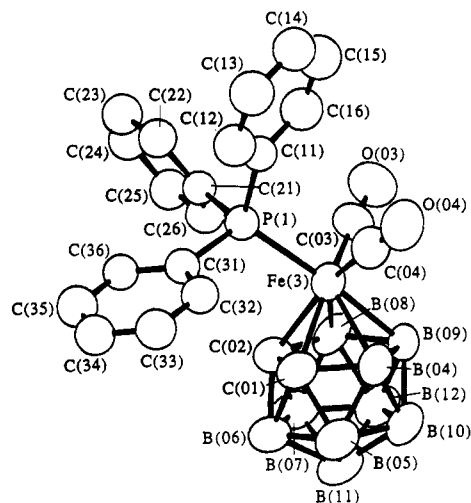


Figure 1. Structure of [*closo*-3,3-(CO)₂-3-PPh₃-3,1,2-FeC₂B₉H₁₁] (3) showing atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

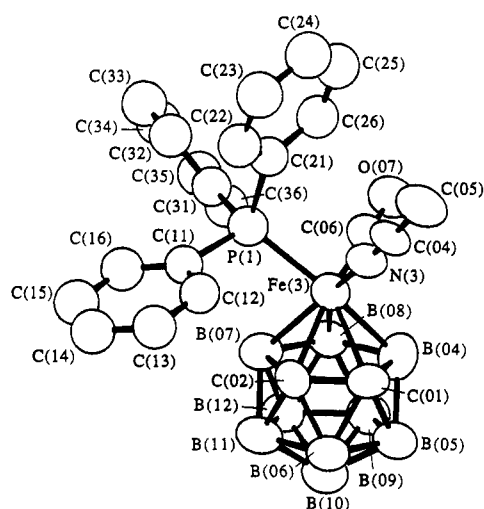


Figure 2. Structure of [*closo*-3-CO-3-PPh₃-3-CH₃CN-3,1,2-FeC₂B₉H₁₁] (4) showing atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

pounds of this series were studied by X-ray diffraction. The polyhedral FeC₂B₉ unit and the pseudooctahedral coordination exhibited by the iron atom are common structural features displayed by all four ferracarboranes.

In the structures of 3 and 4, shown in Figures 1 and 2, respectively, each displays three monodentate ligands and one C₂B₉H₁₁ unit occupying three facial coordination sites around the iron atom. Although a racemic mixture is found in the unit cell, the structure of one enantiomeric form of 4 is illustrated. The C₂B₉ bonding faces in 3 and 4 are planar (maximum deviation of 0.024 and 0.025 Å, respectively) with the iron approximately centered over the ring at distances of 1.574 and 1.545 Å, respectively, from the C₂B₉ plane.¹⁶ The Fe-P distance of 2.293 (2) Å

(16) Fe-C₂B₉ plane distances are as follows. (a) 1.487 Å in (C₆H₅)₃FeC₂B₉H₁₁.^{3a} (b) 1.494 Å in [(CH₃)₂C₆H₄]₂FeC₂B₉H₁₁ and 1.480 Å in [(C₆H₅)₂C₆H₄]₂FeC₂B₉H₁₁.^{3d} (c) 1.480 Å in [(CH₃)₂C₆H₄]₂FeC₂B₉H₁₁.^{3b} (d) 1.49 Å in (C₆H₅)₃FeC₂B₉H₁₁ (Zalkin, A.; Templeton, D. H.; Hopkins, T. E. *J. Am. Chem. Soc.* 1965, 87, 3988). (e) 1.58 Å in Cs₂[(C₂B₉H₁₁)₂Fe₂(C₂O)₄](CH₃)₂CO·H₂O (Greene, P. T.; Bryan, R. F. *Inorg. Chem.* 1970, 9, 1464). (f) 1.606 Å in (C₁₀H₈)₂Fe[(C₂H₅)₂C₂B₄H₄] and 1.73 Å in (C₁₄H₁₀)₂Fe[(C₂H₅)₂C₂B₄H₄] (Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* 1985, 4, 896). (g) The observed geometry in the Fe compounds characterized in the text is in accord with normal cluster-bonding effects, as described by: Barreto, R. D.; Fehlner, T. P.; Hosmane, N. S. *Inorg. Chem.* 1988, 27, 453.

Table I. Selected Interatomic Distances and Angles for 3

Distances (Å)			
Fe(3)-C(04)	1.754 (12)	Fe(3)-C(03)	1.762 (12)
Fe(3)-C(01)	2.105 (10)	Fe(3)-C(02)	2.112 (10)
Fe(3)-B(04)	2.172 (12)	Fe(3)-B(08)	2.178 (13)
Fe(3)-B(09)	2.219 (11)	Fe(3)-P(1)	2.293 (3)
C(01)-C(02)	1.621 (13)	C(01)-B(04)	1.679 (15)
C(01)-B(05)	1.694 (16)	C(01)-B(06)	1.772 (17)
O(04)-C(04)	1.154 (11)	O(03)-C(03)	1.143 (11)
B(10)-B(05)	1.768 (19)	B(10)-B(04)	1.772 (18)
B(10)-B(11)	1.777 (20)	B(10)-B(12)	1.778 (19)
B(10)-B(09)	1.820 (17)	B(11)-B(12)	1.753 (19)
B(11)-B(06)	1.774 (17)	B(11)-B(05)	1.777 (19)
B(11)-B(07)	1.781 (18)	B(06)-B(05)	1.755 (20)
B(06)-C(02)	1.757 (16)	B(06)-B(07)	1.791 (20)
B(08)-C(02)	1.702 (15)	B(08)-B(07)	1.783 (19)
B(08)-B(12)	1.803 (16)	B(08)-B(09)	1.837 (17)
C(02)-B(07)	1.673 (16)	B(05)-B(04)	1.780 (19)
B(04)-B(09)	1.833 (17)	B(07)-B(12)	1.751 (20)
B(12)-B(09)	1.800 (18)		
Angles (deg)			
C(04)-Fe(3)-C(03)	91.32 (57)	C(04)-Fe(3)-C(01)	106.40 (52)
C(04)-Fe(3)-C(02)	151.54 (53)	C(04)-Fe(3)-B(04)	79.43 (53)
C(04)-Fe(3)-B(08)	147.30 (52)	C(04)-Fe(3)-B(09)	99.37 (49)
C(04)-Fe(3)-P(1)	90.28 (38)	C(03)-Fe(3)-C(01)	160.19 (46)
C(03)-Fe(3)-C(02)	117.00 (48)	C(03)-Fe(3)-B(04)	132.53 (50)
C(03)-Fe(3)-B(08)	79.44 (50)	C(03)-Fe(3)-B(09)	87.58 (56)
C(03)-Fe(3)-P(1)	89.72 (36)	C(01)-Fe(3)-C(02)	45.20 (38)
C(01)-Fe(3)-B(04)	46.20 (42)	C(01)-Fe(3)-B(08)	80.84 (44)
C(01)-Fe(3)-B(09)	80.97 (41)	C(01)-Fe(3)-P(1)	98.79 (28)
C(02)-Fe(3)-B(04)	79.04 (45)	C(02)-Fe(3)-B(08)	46.73 (43)
C(02)-Fe(3)-B(09)	80.23 (41)	C(02)-Fe(3)-P(1)	92.49 (28)
B(04)-Fe(3)-B(08)	83.97 (48)	B(04)-Fe(3)-B(09)	49.33 (45)
B(04)-Fe(3)-P(1)	136.20 (35)	B(08)-Fe(3)-B(09)	49.39 (44)
B(08)-Fe(3)-P(1)	120.66 (33)	B(09)-Fe(3)-P(1)	170.03 (33)
O(03)-C(03)-Fe(3)	176.69 (108)	O(04)-C(04)-Fe(3)	174.53 (120)

Table II. Selected Interatomic Distances and Angles for 4

Distances (Å)			
Fe(03)-C(06)	1.749 (11)	Fe(03)-N(03)	1.935 (9)
Fe(03)-C(02)	2.103 (9)	Fe(03)-C(01)	2.118 (9)
Fe(03)-B(07)	2.122 (11)	Fe(03)-B(04)	2.163 (11)
Fe(03)-B(08)	2.185 (11)	Fe(03)-P(01)	2.265 (3)
O(07)-C(06)	1.151 (10)	C(04)-N(03)	1.109 (10)
C(04)-C(05)	1.476 (14)	B(04)-C(01)	1.693 (14)
B(04)-B(09)	1.808 (16)	B(04)-B(05)	1.819 (16)
B(04)-B(08)	1.843 (16)	C(02)-C(01)	1.605 (12)
C(02)-B(11)	1.724 (14)	C(02)-B(07)	1.739 (14)
C(02)-B(06)	1.745 (13)	B(07)-B(12)	1.793 (16)
B(07)-B(08)	1.819 (16)	B(07)-B(11)	1.828 (15)
B(12)-B(10)	1.775 (17)	B(12)-B(11)	1.787 (16)
B(12)-B(09)	1.813 (16)	B(12)-B(08)	1.822 (15)
C(01)-B(05)	1.727 (14)	C(01)-B(06)	1.748 (14)
B(10)-B(06)	1.753 (16)	B(10)-B(11)	1.772 (17)
B(10)-B(05)	1.777 (17)	B(10)-B(09)	1.814 (17)
B(05)-B(06)	1.763 (16)	B(05)-B(09)	1.800 (17)
B(06)-B(11)	1.768 (17)	B(09)-B(08)	1.801 (16)
Angles (deg)			
C(06)-Fe(3)-N(03)	93.93 (40)	C(06)-Fe(3)-C(02)	161.83 (41)
C(06)-Fe(3)-C(01)	126.97 (43)	C(06)-Fe(3)-B(07)	119.95 (45)
C(06)-Fe(3)-B(04)	84.66 (46)	C(06)-Fe(3)-B(08)	79.90 (43)
C(06)-Fe(3)-P(1)	91.76 (34)	N(3)-Fe(3)-C(02)	100.55 (34)
N(3)-Fe(3)-C(01)	85.16 (33)	N(3)-Fe(3)-B(07)	145.01 (40)
N(3)-Fe(3)-B(04)	107.97 (40)	N(3)-Fe(3)-B(08)	157.45 (39)
N(3)-Fe(3)-P(1)	86.41 (25)	C(02)-Fe(3)-C(01)	44.70 (34)
C(02)-Fe(3)-B(07)	48.60 (39)	C(02)-Fe(3)-B(04)	80.48 (41)
C(02)-Fe(3)-B(08)	82.55 (39)	C(02)-Fe(3)-P(1)	99.99 (26)
C(01)-Fe(3)-B(07)	81.15 (39)	C(01)-Fe(3)-B(04)	46.56 (40)
C(01)-Fe(3)-B(08)	81.51 (39)	C(01)-Fe(3)-P(1)	140.79 (29)
B(07)-Fe(3)-B(04)	85.27 (46)	B(07)-Fe(3)-B(08)	49.93 (41)
B(07)-Fe(3)-P(1)	84.24 (32)	B(04)-Fe(3)-B(08)	50.14 (44)
B(04)-Fe(3)-P(1)	165.35 (34)	B(08)-Fe(3)-P(1)	115.26 (32)
N(3)-C(4)-C(5)	177.15 (107)	C(4)-N(3)-Fe(3)	173.39 (87)
O(7)-C(06)-Fe(3)	176.67 (94)		

in 3 and 2.265 (3) Å in 4 are similar to those of analogous cyclopentadienyliron complexes, e.g. 2.242 (1) Å in [(C₅H₅)₂Fe(CO)₂(PPh₃)]Cl·3H₂O¹⁷ and 2.227 (2) Å in

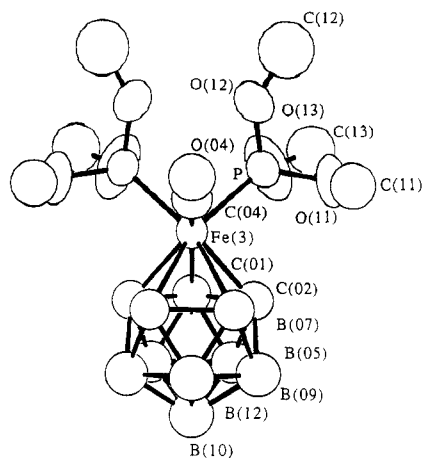


Figure 3. Structure of [closo-3-CO-3,3-[P(OCH₃)₃]₂-3,1,2-FeC₂B₉H₁₁] (7) showing atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

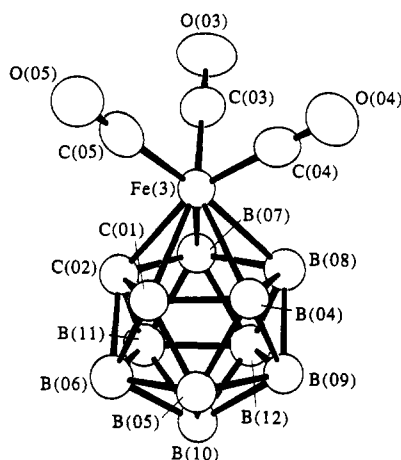


Figure 4. Structure of [closo-3,3,3-(CO)₃-3,1,2-FeC₂B₉H₁₁] (8) showing atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

[(C₅H₅)Fe(CO)(PPh₃)N≡CCH₃]₂BF₄.¹⁸ These distances are also in excellent agreement with the prediction of the quantitative analysis of ligand effects (QALE),¹⁹ that the ligand PPh₃, a pure σ donor, should give rise to relatively long Fe-P bond lengths of 2.20 Å. The CH₃CN ligand is essentially linear with the N(3)-C(4)-C(5) angle of 177.15°. Tables I and II list selected interatomic distances and angles for 3 and 4, respectively.

Complex 7 crystallizes from THF/heptane as yellow parallelepiped crystals. As shown in Figure 3, 7 possesses a crystallographic disorder imposed by mirror symmetry. On the basis of temperature factors and bond lengths, one of the atoms in the five-membered face coordinated to the iron atom was identified as a carbon and the two adjacent atoms in this face were assigned scattering factors of statistically disordered carbon and boron atoms. This disorder is not uncommon in that it is also a structural characteristic of [closo-3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₁₁].²⁰ Cage atoms Fe(03), C(01), B(10), and B(12), and the carbonyl atoms C(04) and O(04) lie on the crystallographic mirror plane. The iron atom bonds symmetrically to the

Table III. Selected Interatomic Distances and Angles for 7^a

Distances (Å)			
Fe(03)-P(01)	2.181 (3)	Fe(03)-C(04)	1.770 (14)
Fe(03)-C(01)	2.096 (14)	Fe(03)-C(02)	2.122 (11)
Fe(03)-B(07)	2.176 (12)	P(01)-O(11)	1.566 (7)
P(01)-O(12)	1.521 (9)	P(01)-O(13)	1.592 (9)
O(04)-C(04)	1.13 (2)	C(01)-C(02)	1.640 (14)
C(01)-B(05)	1.74 (2)	C(02)-B(05)	1.76 (2)
C(02)-B(07)	1.733 (16)	C(02)-B(09)	1.76 (2)
B(05)-B(09)	1.75 (2)	B(05)-B(10)	1.74 (2)
B(05)-B(05)*	1.75 (2)	B(07)-B(09)	1.78 (2)
B(07)-B(12)	1.76 (2)	B(07)-B(07)*	1.79 (2)
B(09)-B(10)	1.76 (2)	B(09)-B(12)	1.73 (2)
B(10)-B(12)	1.81 (3)	O(11)-O(12)	2.401 (11)
O(11)-O(13)	2.407 (11)	O(11)-C(11)	1.405 (15)
O(12)-C(12)	1.24 (2)	O(13)-C(13)	1.290 (16)

Angles (deg)			
P(01)-Fe(03)-C(04)	90.9 (3)	P(01)-Fe(03)-C(01)	100.6 (3)
P(01)-Fe(03)-C(02)	84.4 (3)	P(01)-Fe(03)-B(07)	110.7 (3)
P(01)-Fe(03)-P(01)*	89.7 (1)	P(01)-Fe(03)-C(02)*	143.2 (3)
P(01)-Fe(03)-B(07)*	159.2 (3)	C(04)-Fe(03)-C(01)	163.8 (4)
C(04)-Fe(03)-C(02)	125.4 (4)	C(04)-Fe(03)-B(07)	85.1 (4)
C(01)-Fe(03)-C(02)	45.7 (4)	C(01)-Fe(03)-B(07)	80.1 (4)
C(02)-Fe(03)-B(07)	47.5 (4)	C(02)-Fe(03)-C(02)*	79.2 (4)
C(02)-Fe(03)-B(07)*	81.4 (4)	B(07)-Fe(03)-B(07)*	48.7 (5)
Fe(03)-P(01)-O(11)	120.8 (3)	Fe(03)-P(01)-O(12)	113.5 (4)
Fe(03)-P(01)-O(13)	111.4 (3)	O(11)-P(01)-O(12)	102.1 (5)
O(11)-P(01)-O(13)	99.3 (4)	O(12)-P(01)-O(13)	108.3 (5)
Fe(03)-C(04)-O(04)	178.4 (9)	Fe(03)-C(01)-C(02)	68.0 (5)
C(02)-C(01)-C(02)*	111.1 (8)	P(01)-O(11)-C(11)	123.6 (7)
P(01)-O(12)-C(12)	137.4 (11)	P(01)-O(13)-C(13)	134.8 (9)

^a Positions marked by asterisks are related to tabulated positions by $x, y, 1/2 - z$.

C₂B₃ with a Fe-C₂B₃ face (centroid) distance¹⁶ of 1.570 Å. Selected interatomic distances and angles for 7 are listed in Table III.

In the structure of 8, illustrated in Figure 4, the iron atom is flanked by three carbonyl groups and the C₂B₃ face of the C₂B₉ cage. The C₂B₃ bonding face in 8 is essentially planar with no deviation from the least-squares plane by more than 0.012 Å. The iron is approximately centered over the ring, giving rise to a Fe-C₂B₃ face (centroid) distance¹⁶ of 1.562 Å. The C-O distances (1.131 (9), 1.143 (9), and 1.118 (10) Å) are slightly longer than those of 1.111 (7), 1.112 (7), and 1.113 (7) Å found in [CpFe(CO)₃]PF₆^{21a} and are similar to C-O distances of 1.136 (3) and 1.138 (2) Å found in (CO)₃Fe(C₂B₃H₇).^{21b} This is in accord with the higher carbonyl stretching frequencies observed for the Cp compound compared to those for 8. Table IV lists the selected interatomic distances and angles for 8. Overall, the bond lengths and bond angles within the carborane ligand of 3, 4, 7, and 8 are not unusual. As expected, in all of these ferracarboranes the Fe-B distances are longer (2.122-2.219 Å) than the Fe-carboranyl carbon distances (2.096-2.118 Å).^{16g}

Experimental Section

All manipulations were carried out under an argon or dinitrogen atmosphere by employing standard Schlenk techniques.²² All solvents were reagent grade and distilled from appropriate drying agents.²³ Iron pentacarbonyl (Aldrich) and cesium chloride (Aldrich) were purchased and used as received. After opening,

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Table IV. Selected Interatomic Distances and Angles for 8

Distances (Å)			
C(01)-Fe(3)	2.113 (8)	C(05)-Fe(3)	1.844 (11)
C(02)-Fe(3)	2.106 (8)	C(04)-Fe(3)	1.777 (9)
C(03)-Fe(3)	1.792 (9)	B(04)-Fe(3)	2.168 (9)
B(08)-Fe(3)	2.173 (9)	B(07)-Fe(3)	2.160 (9)
B(04)-B(08)	1.823 (13)	B(04)-B(09)	1.782 (13)
B(04)-C(01)	1.692 (12)	B(05)-C(01)	1.713 (11)
B(05)-B(06)	1.753 (13)	B(05)-B(10)	1.779 (12)
B(05)-B(09)	1.781 (12)	B(08)-B(09)	1.796 (13)
B(09)-B(12)	1.765 (12)	B(09)-B(10)	1.794 (12)
B(11)-C(02)	1.696 (12)	B(11)-B(12)	1.785 (13)
B(06)-C(01)	1.738 (12)	B(10)-B(11)	1.807 (13)
C(03)-O(03)	1.131 (9)	B(06)-B(10)	1.778 (13)
C(04)-O(04)	1.143 (9)	B(04)-B(05)	1.793 (13)
C(05)-O(05)	1.118 (10)	B(07)-B(12)	1.779 (13)
C(01)-C(02)	1.630 (10)	B(08)-B(12)	1.774 (13)
B(10)-B(12)	1.782 (13)	B(06)-C(02)	1.763 (12)
B(06)-B(11)	1.809 (13)	B(07)-C(02)	1.689 (11)
B(07)-B(11)	1.767 (13)	B(07)-B(08)	1.802 (13)
Angles (deg)			
C(04)-Fe(3)-C(03)	89.81 (41)	C(04)-Fe(3)-C(05)	92.56 (39)
C(04)-Fe(3)-C(02)	160.38 (34)	C(04)-Fe(3)-C(01)	118.29 (36)
C(04)-Fe(3)-B(07)	129.80 (38)	C(04)-Fe(3)-B(04)	80.17 (37)
C(04)-Fe(3)-B(08)	85.93 (37)	C(03)-Fe(3)-C(05)	91.85 (40)
C(03)-Fe(3)-C(02)	106.39 (35)	C(03)-Fe(3)-C(01)	151.71 (34)
C(03)-Fe(3)-B(07)	78.77 (37)	C(03)-Fe(3)-B(04)	147.55 (37)
C(03)-Fe(3)-B(08)	99.22 (36)	C(05)-Fe(3)-C(02)	97.78 (34)
C(05)-Fe(3)-C(01)	90.17 (35)	C(05)-Fe(3)-B(07)	135.98 (38)
C(05)-Fe(3)-B(04)	119.17 (39)	C(05)-Fe(3)-B(08)	168.82 (39)
C(02)-Fe(3)-C(01)	45.46 (28)	C(02)-Fe(3)-B(07)	46.63 (31)
C(02)-Fe(3)-B(04)	80.23 (32)	C(02)-Fe(3)-B(08)	80.70 (32)
C(01)-Fe(3)-B(07)	80.25 (31)	C(01)-Fe(3)-B(04)	46.53 (32)
C(01)-Fe(3)-B(08)	80.85 (32)	B(07)-Fe(3)-B(04)	84.17 (34)
B(07)-Fe(3)-B(08)	49.16 (34)	B(04)-Fe(3)-B(08)	49.65 (34)
O(03)-C(03)-Fe(3)	179.10 (80)	O(04)-C(04)-Fe(3)	175.88 (88)
O(05)-C(05)-Fe(3)	179.24 (91)		

anhydrous cuprous chloride (Cerac) and sodium hydride (Aldrich) were stored in a Vacuum Atmospheres inert-atmosphere glovebox. Trimethyl phosphite (MCB) was distilled from calcium hydride prior to use. Triphenylphosphine (Aldrich) was recrystallized from ethyl alcohol. Carbon monoxide was obtained from Air Products and used directly from the cylinder. [*closo*-3-CO-3,3'-(μ -CO)-3,1,2-FeC₂B₉H₁₁]₂²⁻ (2)⁴ was prepared according to literature methods.

Photochemical experiments were carried out by using a Hanovia 550-W medium-pressure mercury lamp. Solutions to be irradiated were placed in Pyrex Schlenk tubes supported 4 in. away from the light source.

¹H FT NMR spectra were recorded on a Bruker AF-200 (200.133 MHz) spectrometer. ¹¹B NMR spectra were obtained on a Bruker AM-500 FT-NMR spectrometer at 160.463 MHz. Proton and boron chemical shifts were referenced to residual solvent protons (CD₂Cl₂, 5.32 ppm) and external BF₃·OEt₂, respectively. All chemical shifts downfield of the reference are designated as positive. Infrared spectra were recorded as Nujol mulls (NaCl) on a Beckman FT-1100 instrument. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, FRG.

Preparation of Compounds. Although the following procedures utilize purified salts of the iron dicarbollide dimer 2, compounds 3 and 5-8 can be obtained from solutions of unisolated and unpurified Na₂[2]. Unlike its cyclopentadienyl analogue, 2 is commercially unavailable, and purification involves repeated fractional recrystallization. Since all subsequent compounds derived from 2 are neutral, methathesis of Na₂[2] with different cations for the purpose of isolating a purified starting material can be avoided.

[*closo*-3,3-(CO)₂-3-PPH₃-3,1,2-FeC₂B₉H₁₁] (3). To a bright red solution of Cs₂[2]·CH₃CN·H₂O (1.43 g, 1.75 mmol) in 40 mL of THF was added a beige solution generated by stirring an equimolar slurry of anhydrous CuCl (350 mg, 3.5 mmol) and triphenylphosphine (920 mg) in 40 mL of THF for 1 h at room temperature. Stirring of the resulting pink slurry for 48 h at room temperature was followed by removal of a pink solid and shiny Cu metal by filtration over a Celite pad. The orange-yellow filtrate

was reduced in volume, and heptane was added. The resulting yellow crystals were collected, washed twice with heptane, and dried in vacuo. Recrystallization from CH₂Cl₂/heptane afforded an analytically pure product in a yield of 31% (550 mg). Anal. Calcd for C₂₂H₂₆B₉O₂PF₆: C, 52.16; H, 5.18; B, 19.20; P, 6.11; Fe, 11.02. Found: C, 52.04; H, 5.08; B, 19.07; P, 6.13; Fe, 10.08. IR (cm⁻¹): 2552, 2537 (B-H), 2031, 1996 (MC=O). ¹H NMR (ppm, CD₂Cl₂): 7.56-7.50 (m, 15 H, phenyl H), 2.12 (br s, 2 H, carboranyl C-H). ¹¹B{¹H} NMR (ppm, THF): 5.7, -2.6, -5.1, -8.4, -17.3, -20.7 (1:1:2:2:2:1).

[*closo*-3-CO-3-PPH₃-3-CH₃CN-3,1,2-FeC₂B₉H₁₁] (4). After the isolation of complex 3, excess heptane was added to the remaining orange filtrate from the previous reaction. The cloudy solution was allowed to stand for a period of 2 days. Red triangular plates were formed (165 mg, 18%). Anal. Calcd for C₂₃H₂₈B₉O₂PNFe: C, 53.16; H, 5.64; N, 2.70. Found: C, 53.02; H, 5.78; N, 2.69. IR (cm⁻¹): 2541, 2510 (B-H), 1967 (MC=O). ¹H NMR (ppm, CD₂Cl₂): 7.61-7.47 (m, 15 H, phenyl H), 3.17 (br s, 1 H, carboranyl C-H), 2.71 (br s, 1 H, carboranyl C-H), 1.69 (s, 3 H, NC-CH₃). ¹¹B{¹H} NMR (ppm, THF): 0.1, -4.1, -7.7, -9.6, -11.8, -15.4, -17.0, -22.0 (1:1:1:1:1:1:2).

[*closo*-3,3-(CO)₂-3-CH₃CN-3,1,2-FeC₂B₉H₁₁] (5). A red slurry was generated by stirring Cs₂[2]·CH₃CN·H₂O (200 mg, 0.25 mmol) and anhydrous CuCl (50 mg, 0.50 mmol) in 40 mL of CH₃CN. After stirring for 2 days at room temperature, a pink solid and shiny Cu metal were removed by filtration over a Celite pad. The filtrate was reduced in volume, and the residue was recrystallized from THF/heptane followed by a second recrystallization from CH₂Cl₂/heptane to yield reddish brown microcrystals (44 mg, 31%). Anal. Calcd for C₉H₁₄B₉O₂NFe: C, 25.25; H, 4.96; B, 34.09; N, 4.91; Fe, 19.57. Found: C, 25.09; H, 5.04; B, 33.96; N, 4.74; Fe, 19.80. IR (cm⁻¹): 2579, 2546 (B-H), 2058, 2016 (MC=O). ¹H NMR (ppm, CD₂Cl₂): 3.14 (br s, 2 H, carboranyl C-H), 2.29 (s, 3 H, NC-CH₃). ¹¹B{¹H} NMR (ppm, THF): 7.0, -3.3, -6.2, -8.2, -15.1, -17.1 (1:2:2:1:2:1).

An alternate route to 5 consisted of photolyzing (using the light source described above) a yellow solution of 8 (100 mg, 0.38 mmol) in 40 mL of acetonitrile for 17.5 h. The resulting orange solution was reduced in volume, and the resultant reddish brown precipitate was recrystallized from CH₂Cl₂/heptane to produce 85 mg of 5 (81% yield).

[*closo*-3,3-(CO)₂-3-P(OCH₃)₃-3,1,2-FeC₂B₉H₁₁] (6). To a red solution of [(CH₃)₄N]₂[2] (1.30 g, 2.0 mmol) in 60 mL of THF was added a beige solution generated by stirring a slurry of anhydrous CuCl (400 mg, 4.0 mmol) and trimethyl phosphite (1.40 mL, 12 mmol) in 50 mL of THF for 1 h at room temperature. Stirring of the resulting pink slurry for 4 h at room temperature was followed by removal of a pink solid and shiny Cu metal by filtration over a Celite pad. Solvent was removed from the filtrate, and the resulting brownish yellow residue was placed atop a 4 × 30 cm silica gel chromatography column prepared in CH₂Cl₂. Elution with CH₂Cl₂ developed a large yellow band, which upon rotary evaporation of solvent produced a yellow oil. The oil was washed three times with 100 mL of diethyl ether. The Et₂O washings were combined and solvent was removed by using a rotary evaporator to isolate a greenish yellow solid. Recrystallization from CH₂Cl₂/heptane afforded analytically pure product in a yield of 7.8% (120 mg). Anal. Calcd for C₇H₂₀B₉O₅PF₆: C, 22.82; H, 5.48; B, 26.41; P, 8.41; Fe, 15.16. Found: C, 22.99; H, 5.33; B, 26.40; P, 8.25; Fe, 15.05. IR (cm⁻¹): 2555, 2533 (B-H), 2053, 2000 (MC=O). ¹H NMR (ppm, CD₂Cl₂): 3.84 (d, 9 H, OCH₃, J_{P-H} = 11 Hz), 2.97 (br s, 2 H, carboranyl C-H). ¹¹B{¹H} NMR (ppm, THF): 5.4, -2.5, -5.7, -9.6, -17.1, -20.6 (1:1:2:2:2:1).

[*closo*-3-CO-3,3-[P(OCH₃)₃]₂-3,1,2-FeC₂B₉H₁₁] (7). After the isolation of 6, the ether-insoluble residue was recrystallized from CH₂Cl₂/Et₂O to afford analytically pure golden yellow crystals in a yield of 13.5% (260 mg). Anal. Calcd for C₉H₂₈B₉O₅P₂Fe: C, 23.27; H, 6.31; B, 20.95; Fe, 12.02. Found: C, 23.48; H, 6.11; B, 20.73; Fe, 12.05. IR (cm⁻¹): 2563, 2527 (B-H), 1974 (MC=O). ¹H NMR (ppm, CD₂Cl₂): 3.76 (t, 18 H, OCH₃, J_{P-H} = 5.5 Hz), 2.87 (br s, 2 H, carboranyl C-H). ¹¹B{¹H} NMR (ppm, THF): 1.4, -5.2, -7.7, -11.0, -19.3, -21.4 (1:1:2:2:1).

[*closo*-3,3,3-(CO)₃-3,1,2-FeC₂B₉H₁₁] (8). A nitrogen-flushed three-necked 250-mL round-bottomed flask was fitted with a reflux condenser having a gas outlet, a glass tube that introduced carbon monoxide, and a gas inlet that was connected to a nitrogen

Table V. Details of the Crystallographic Data Collection^a

	3	4	7	8
cryst size/mm	0.13 × 0.29 × 0.45	0.19 × 0.3	0.08 × 0.16 × 0.32	0.05 × 0.25 × 0.20
normal to faces	011, 0,1,-2, 100	100, -1,0,2 ^b	001, 010, 100	010, 001, 101
appearance	yellow parallelepiped	red triangular plate	yellow parallelepiped	amber platelet
space group	A2/a	C2/c	Pbnm ^c	P2 ₁ /n
a/Å	18.384 (3)	28.050 (2)	10.397 (2)	6.971 (4)
b/Å	12.762 (2)	11.5715 (9)	14.419 (3)	15.900 (9)
c/Å	23.059 (3)	19.042 (2)	15.092 (3)	11.237 (7)
β/deg	104.081 (4)	116.846 (2)		91.42 (2)
V/Å ³	5229	5499	2262	1245
Z	8	8	4 ^d	4
ρ(calcd)/g cm ⁻³	1.28	1.25	1.36	1.45
μ/cm ⁻¹	6.5	6.2	2.4 (not applied)	11.91
range of transm factors	0.95-0.91	0.951-0.939		
av	0.93	0.946		
scan width				
below Kα ₁	1.3	1.2	1.3	1.3
above Kα ₂	1.6	1.6	1.6	1.6
scan rate/deg min ⁻¹	6.0	6.0	3.0	3.0
no. of unique reflns	3423	3609	1541	1628
no. of obsd (I > 3σ(I)) reflns	1780	1702	1051	1108
no. of params refined	190	199	120	108
R	0.074	0.065	0.071	0.062
R _w	0.088	0.077	0.089	0.074
GOF	2.25	2.24	2.65	2.04

^a Conditions: T/K, 298; radiation (graphite monochromator), Mo Kα; wavelength, 0.7107 Å; 2θ max/deg, 45; data collected, +h, +k, ±l. ^b Other faces 1,-1,-1, -1,0,0, 1,1,-1. ^c Standard setting Pnma. ^d Eight half-molecules related by mirror at z = 1/4.

manifold. To the flask was added 4.7 g (5.8 mmol) of Cs₂[2]-CH₃CN·H₂O, anhydrous CuCl (1.23 g, 12.4 mmol), and 150 mL of THF. Carbon monoxide was bubbled into the solution for 24 h at room temperature and pressure. A pink solid and shiny Cu metal were removed by filtration over a Celite pad. Solvent was removed, and the residue was washed three times with 100 mL of diethyl ether. The Et₂O washings were combined, and rotary evaporation of solvent produced a greenish yellow solid. This solid was placed atop a 4 × 30 cm silica gel chromatography column prepared in pentane. Elution with pentane produced a green band containing Fe₃(CO)₁₂. Elution with 25% CH₂Cl₂/pentane developed a large yellow band, which, upon rotary evaporation of solvent, produced golden yellow microcrystals. Recrystallization from THF/hexane afforded analytically pure product in a yield of 39% (1.22 g). Anal. Calcd for C₅H₁₁B₉O₃Fe: C, 22.05; H, 4.08; B, 35.73; Fe, 20.51. Found: C, 21.89; H, 3.94; B, 35.67; Fe, 20.30. IR (cm⁻¹): 2562, 2539 (B-H), 2103, 2042 (MC≡O). ¹H NMR (ppm, CD₂Cl₂): 3.38 (br s, 2 H, carboranyl C-H). ¹¹B{¹H} NMR (ppm, THF): 11.2, -0.3, -3.4, -7.7, -14.6, -18.8 (1:1:2:2:2:1).

Collection and Reduction of X-ray Data for 3. A yellow air-stable crystal, obtained from THF/heptane solution, was mounted on a thin glass fiber on a diffractometer constructed by Professor C. E. Strouse of this department. Systematic absences were found for hkl reflections for which k + l ≠ 2n, and for h0l reflections for which h ≠ 2n. Unit cell parameters were determined from a least-squares fit of 23 accurately centered reflections (9.6° < 2θ < 20.3°). These dimensions and other parameters, including conditions of data collection, are summarized in Table V. Data were collected at 25 °C in the θ-2θ scan mode. Three intense reflections, (411), (0,0,10), and (1,-5,-1), were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated ca. ±5% during the course of the experiment (70.7 h). Of the 3423 unique reflections measured, 1780 were considered observed (I > 3σ(I)) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. No decay corrections were applied. Programs used in this work include locally modified versions of crystallographic programs listed in ref 24.

Solution and Refinement of the Structure of 3. Atoms in 3 and also for the three compounds that follow were located by

(24) CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; MULTANSO (Main et al.), statistical methods; SHELX76 (Sheldrick), structure solution package; ABSORB (Coppens, Edwards, and Hamilton), absorption correction calculation; ORTEP (Johnson).

Table VI. Positional and Equivalent Isotropic Thermal Parameters for 3^a

atom	x	y	z	10 ⁴ U
Fe(3)	0.3907 (1)	0.0408 (1)	0.2452 (1)	614 (12)
P(1)	0.4251 (1)	0.0234 (2)	0.3472 (1)	550 (20)
C(01)	0.4960 (6)	0.0148 (9)	0.2269 (4)	701 (88)
O(04)	0.3719 (5)	0.2659 (6)	0.2536 (4)	1104 (85)
O(03)	0.2339 (5)	0.0117 (8)	0.2448 (4)	1080 (83)
B(10)	0.4295 (8)	0.0278 (12)	0.1074 (6)	867 (118)
B(11)	0.4783 (8)	-0.0935 (12)	0.1201 (6)	817 (117)
B(06)	0.5263 (8)	-0.1003 (13)	0.1967 (6)	854 (126)
B(08)	0.3632 (8)	-0.0964 (11)	0.1879 (5)	753 (107)
C(02)	0.4520 (6)	-0.0935 (8)	0.2322 (4)	679 (88)
O(03)	0.2962 (7)	0.0219 (9)	0.2466 (5)	773 (97)
B(05)	0.5175 (8)	0.0208 (12)	0.1596 (6)	877 (125)
B(04)	0.4435 (7)	0.0959 (10)	0.1762 (5)	731 (106)
B(07)	0.4388 (9)	-0.1672 (11)	0.1705 (6)	919 (136)
B(12)	0.3815 (8)	-0.0906 (12)	0.1146 (6)	816 (117)
B(09)	0.3545 (7)	0.0277 (10)	0.1464 (5)	641 (94)
C(04)	0.3823 (7)	0.1768 (10)	0.2526 (5)	857 (108)

$${}^a U_{eq} = [1/(6\pi^2)] \sum \sum \beta_{ij} a_i a_j (\text{\AA}^2).$$

use of the heavy-atom method. All calculations for 3, 4, 7, and 8 were performed on the VAX 11/750 crystallographic computer. For all four compounds, scattering factors for hydrogen were obtained from Stewart et al.²⁵ and for other atoms were taken from ref 26.

All hydrogens on the carborane icosahedron in 3 were kept in located positions. All hydrogens had an assigned value of B = 8.0 Å². All phenyls were treated as rigid C₆H₅ groups with C-C = 1.4 Å, C-H = 0.95 Å, and angles = 120°. Anisotropic thermal parameters were refined for all non-hydrogen atoms with the exception of phenyl carbon atoms. No hydrogen parameters were refined. Anomalous dispersion terms were applied to the scattering of Fe and P. The largest peak on a final difference electron density map was 0.3 e Å⁻³. Final positional and thermal parameters for non-hydrogen atoms are given in Table VI.

Collection and Reduction of X-ray Data for 4. A red air-stable crystal, obtained from THF/heptane solution, was mounted on a thin glass fiber on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Sys-

(25) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.

(26) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table VII. Positional and Equivalent Isotropic Thermal Parameters for 4^a

atom	x	y	z	10 ⁴ U
Fe(3)	0.2154 (1)	0.1147 (1)	0.0863 (1)	688 (14)
P(1)	0.1288 (1)	0.0623 (2)	0.0420 (2)	721 (28)
O(07)	0.2107 (3)	0.0793 (6)	-0.0674 (4)	908 (82)
C(04)	0.1747 (4)	0.3614 (9)	0.0480 (5)	682 (106)
B(04)	0.3009 (4)	0.1179 (11)	0.1266 (7)	783 (128)
C(06)	0.2119 (8)	0.0965 (9)	-0.0071 (6)	751 (113)
C(02)	0.2413 (4)	0.1044 (8)	0.2084 (5)	695 (98)
B(07)	0.2310 (5)	-0.0295 (9)	0.1624 (6)	722 (118)
B(12)	0.2962 (5)	-0.0937 (10)	0.2073 (7)	774 (130)
C(01)	0.2802 (4)	0.1834 (8)	0.1875 (5)	716 (99)
B(10)	0.3412 (5)	0.0029 (11)	0.2790 (7)	874 (140)
B(05)	0.3450 (5)	0.1322 (11)	0.2314 (6)	774 (127)
B(06)	0.3061 (5)	0.1263 (11)	0.2826 (6)	787 (124)
B(09)	0.3396 (5)	-0.0041 (11)	0.1828 (7)	816 (136)
B(08)	0.2716 (4)	-0.0281 (10)	0.1102 (6)	705 (119)
B(11)	0.2751 (5)	-0.0107 (11)	0.2674 (7)	802 (129)
N(03)	0.1897 (3)	0.2723 (7)	0.0663 (4)	700 (83)
C(05)	0.1532 (4)	0.4779 (10)	0.0196 (6)	991 (128)

$${}^a U_{\text{eq}} = [1/(6\pi^2)] \sum \beta_{ij} a_i a_j (\text{\AA}^2).$$

tematic absences were found for hkl reflections for which $h + k \neq 2n$, and for $h0l$ reflections for which $l \neq 2n$. Unit cell parameters were determined from a least-squares fit of 33 accurately centered reflections ($9.6^\circ < 2\theta < 20.2^\circ$). These and other parameters, including conditions of data collection, are summarized in Table V. Data were collected at 25 °C in the θ - 2θ scan mode. Three intense reflections, $(-8,2,1)$, (441) , and $(5,1,-4)$, were monitored every 97 reflections to check stability. Intensities of these reflections decayed less than 2% during the course of the experiment (37.0 h). A total of 3609 unique reflections were measured. Of these, 1702 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Other conditions for collection and reduction were the same as those that were applied to 3.

Solution and Refinement of the Structure of 4. All hydrogens on the carborane icosahedron and on methyl groups were kept in located positions with an assigned value of $B = 7.0 \text{ \AA}^2$. All phenyls were treated as rigid C_6H_5 groups with $\text{C}-\text{C} = 1.4 \text{ \AA}$, $\text{C}-\text{H} = 0.95 \text{ \AA}$, and angles = 120° . Hydrogens of phenyl groups had an assigned value of $B = 9.0 \text{ \AA}^2$. Anisotropic thermal parameters were refined for all non-hydrogen atoms with the exception of phenyl carbon atoms. No hydrogen parameters were refined. Anomalous dispersion terms were applied to the scattering of Fe and P. Final positional and thermal parameters for non-hydrogen atoms are given in Table VII. A final difference electron density map was essentially featureless, the maximum and minimum peaks being about $\pm 0.3 \text{ e \AA}^{-3}$.

Collection and Reduction of X-ray Data for 7. A yellow air-stable crystal, obtained from THF/heptane solution, was mounted on a thin glass fiber on a Picker FACS-1 diffractometer. Systematic absences were found for $h0l$ reflections for which $h + l \neq 2n$, and for $0kl$ reflections for which $k \neq 2n$. Unit cell parameters were determined from a least-squares fit of 34 accurately centered reflections ($9.8^\circ < 2\theta < 20.3^\circ$). These dimensions and other parameters, including conditions of data collection, are summarized in Table V. Data were collected at 25 °C in the θ - 2θ scan mode. Three intense reflections, (023) , $(0,-2,3)$, and $(-3,0,1)$, were monitored every 97 reflections to check stability. Intensities of these reflections decayed less than 7% during the course of the experiment (30.8 h). Of the 1541 unique reflections measured, 1051 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Other conditions for data collection and reduction were the same as those applied to 3.

Solution and Refinement of the Structure of 7. Positional parameters for all hydrogens on the carborane icosahedron were refined. All methyls were treated as rigid CH_3 groups with $\text{C}-\text{H} = 1.00 \text{ \AA}$ and $\text{H}-\text{C}-\text{H} = 109.5^\circ$. Isotropic u for carboranyl and methyl hydrogens were assigned to be 0.12 and 0.14 or 0.16 \AA^2 , respectively. Anisotropic thermal parameters were refined for Fe, P, and O. Anomalous dispersion terms were applied to the scattering of Fe and P. The largest peak on a final difference electron density map was 0.6 e \AA^{-3} . Final positional and thermal parameters for non-hydrogen atoms are given in Table VIII.

Table VIII. Positional and Equivalent Isotropic Thermal Parameters for 7^a

atom	x	y	z	$\langle U^2 \rangle$
Fe(03)	0.5323 (17)	0.1582 (11)	0.2500	0.054
P(01)	0.6232 (25)	0.2431 (19)	0.3519 (16)	0.072
O(04)	0.7472 (97)	0.0302 (75)	0.2500	0.118
O(11)	0.6166 (75)	0.2145 (54)	0.4519 (43)	0.112
O(12)	0.7670 (82)	0.2563 (87)	0.3379 (53)	0.175
O(13)	0.5581 (11)	0.3428 (50)	0.3581 (53)	0.160
C(04)	0.6647 (14)	0.0811 (10)	0.2500	0.077 (4)*
C(01)	0.3463 (13)	0.2144 (10)	0.2500	0.079 (4)*
B(02)	0.3751 (10)	0.1535 (8)	0.3396 (8)	0.080 (3)*
C(02)	0.3751 (10)	0.1535 (8)	0.3396 (8)	0.080 (3)*
B(05)	0.2138 (13)	0.1716 (9)	0.3079 (9)	0.095 (4)*
B(07)	0.4267 (12)	0.0437 (8)	0.3094 (8)	0.085 (4)*
B(09)	0.2641 (13)	0.0616 (10)	0.3423 (10)	0.099 (4)*
B(10)	0.1621 (21)	0.0738 (15)	0.2500	0.100 (6)*
B(12)	0.2979 (21)	-0.0053 (15)	0.2500	0.104 (6)*
C(11)	0.6595 (12)	0.1286 (8)	0.4842 (9)	0.120 (4)*
C(12)	0.8579 (17)	0.2930 (12)	0.3776 (11)	0.183 (7)*
C(13)	0.5565 (14)	0.4080 (9)	0.4166 (9)	0.144 (5)*

^aUnits of $\langle U^2 \rangle$ are \AA^2 . Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. Asterisks denote values for atoms refined isotropically. Isotropic values are $[1/(8\pi^2)] B_{\text{eq}}$.²⁷

Table IX. Positional and Equivalent Isotropic Thermal Parameters for 8^a

atom	x	y	z	10 ⁴ U
Fe(3)	0.1237 (2)	0.1238 (1)	0.2313 (1)	433 (7)
C(01)	0.0050 (11)	0.2227 (5)	0.3313 (7)	461 (21)
C(02)	0.2218 (11)	0.2428 (5)	0.2882 (6)	461 (21)
C(03)	0.3193 (12)	0.0755 (6)	0.1566 (7)	539 (57)
C(04)	-0.0323 (13)	0.0435 (5)	0.1767 (8)	602 (62)
C(05)	0.1796 (14)	0.0655 (6)	0.3697 (9)	655 (66)
O(03)	0.4420 (10)	0.0440 (4)	0.1099 (6)	772 (48)
O(04)	-0.1285 (9)	-0.0073 (4)	0.1349 (7)	882 (52)
O(05)	0.2118 (12)	0.0296 (4)	0.4534 (6)	963 (58)
B(04)	-0.1422 (13)	0.1942 (6)	0.2163 (8)	457 (23)
B(05)	-0.1537 (13)	0.2974 (6)	0.2800 (8)	473 (25)
B(06)	0.0758 (14)	0.3275 (7)	0.3312 (9)	473 (25)
B(07)	0.2436 (13)	0.2303 (6)	0.1399 (8)	473 (25)
B(08)	0.0079 (14)	0.2001 (6)	0.0860 (8)	473 (25)
B(09)	-0.1512 (13)	0.2846 (6)	0.1226 (8)	473 (25)
B(10)	-0.0153 (13)	0.3673 (6)	0.1931 (8)	458 (23)
B(11)	0.2304 (14)	0.3314 (7)	0.2044 (8)	511 (25)
B(12)	0.0840 (14)	0.3063 (6)	0.0767 (8)	490 (25)

$${}^a U_{\text{eq}} = [1/(6\pi^2)] \sum \beta_{ij} a_i a_j (\text{\AA}^2).$$

Collection and Reduction of X-ray Data for 8. A pale amber air-stable crystal, obtained from THF/heptane solution, was mounted on a thin glass fiber on a diffractometer constructed by Professor C. E. Strouse of this department. Systematic absences were found for $h0l$ reflections for which $h + l \neq 2n$, and for $0k0$ reflections for which $k \neq 2n$. Unit cell parameters were determined from a least-squares fit of 15 accurately centered reflections ($11.8^\circ < 2\theta < 19.7^\circ$). These dimensions and other parameters, including conditions of data collection, are summarized in Table V. Data were collected at 25 °C in the θ - 2θ scan mode. Three intense reflections, (132) , $(1,-6,-2)$, and $(1,4,-1)$, were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated ca. $\pm 5\%$, during the course of the experiment (33.7 h). Of the 1628 unique reflections measured, 1108 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Other conditions for collection and reduction were the same as those applied to 3.

Solution and Refinement of the Structure of 8. All hydrogens were kept in located positions with an assigned value of $B = 5.0 \text{ \AA}^2$. Anisotropic thermal parameters were refined for Fe and for C and O of the carbonyl groups. No hydrogen parameters were refined. Anomalous dispersion terms were applied to the scattering of Fe. The largest peak on a final difference electron density map was 0.7 e \AA^{-3} . Final positional and thermal parameters for non-hydrogen atoms are given in Table VIII.

(27) Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 609.

eters for non-hydrogen atoms are given in Table IX.

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Supplementary Material Available: Tables of crystal data, positional and thermal parameters, anisotropic thermal parameters, and interatomic distances and angles (20 pages); listings of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

New Cyclic Phosphazenes with (Trimethylsilyl)methyl Side Groups: X-ray Crystal Structure of $[\text{NP}(\text{CH}_2\text{SiMe}_3)_2]_3$ and Its Conversion to $(\text{NPMe}_2)_3^1$

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The synthesis of $[\text{NP}(\text{CH}_2\text{SiMe}_3)_2]_3$ has been achieved in almost quantitative yield via the reaction of $\text{Me}_3\text{SiCH}_2\text{Li}$ with $(\text{NPF}_2)_3$ in tetrahydrofuran at 40 °C, followed by addition of a proton source. Treatment of $[\text{NP}(\text{CH}_2\text{SiMe}_3)_2]_3$ with ${}^n\text{Bu}_4\text{N}^+\text{F}^-$ gave $(\text{NPMe}_2)_3$ in 60% yield. Partially substituted trimers of the formula $\text{N}_3\text{P}_3\text{F}_2(\text{CH}_2\text{SiMe}_3)_{6-x}$, where $x = 2$ and 4, were also prepared. The interaction of $(\text{NPF}_2)_3$ with $\text{Me}_3\text{SiCH}_2\text{Li}$ involves a metal-hydrogen exchange side reaction to generate species such as $\text{N}_3\text{P}_3(\text{CH}_2\text{SiMe}_3)_5(\text{CHSiMe}_3)^-\text{Li}^+$, hence the need for subsequent protonation. Attempts to replace the fluorine atoms in *gem*- $\text{N}_3\text{P}_3\text{F}_4(\text{CH}_2\text{SiMe}_3)_2$ by treatment with $\text{NaOCH}_2\text{CF}_3$ led also to C-Si bond cleavage to generate *gem*- $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4\text{Me}_2$. No C-Si bond cleavage occurred during the attempted preparation of *gem*- $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_2(\text{CH}_2\text{SiMe}_3)_4$, and none was detected when $[\text{NP}(\text{CH}_2\text{SiMe}_3)_2]_3$ was treated with $\text{NaOCH}_2\text{CF}_3$. The structure of $[\text{NP}(\text{CH}_2\text{SiMe}_3)_2]_3$ has been determined by single-crystal X-ray diffraction methods. Crystals were monoclinic with a $P2_1/n$ space group, with $a = 11.012$ (2) Å, $b = 19.851$ (5) Å, $c = 19.554$ (8) Å, $\beta = 90.51$ (2)°, $V = 4309.3$ Å³, and $Z = 4$. A comparison is made with other alkyl- and (alkylsilyl)cyclo-triphosphazenes.

The synthesis of phosphazene ring systems that bear organosilicon side groups is of interest from both mechanistic and practical points of view.²⁻¹⁴ From a fundamental viewpoint a major problem is the development of reaction routes for the linkage of organosilicon units to the phosphorus atoms of phosphazene rings or chains. In our laboratory this has involved the study of a variety of reactions, including the interactions of chlorophosphazenes with aminosiloxane reagents⁹ or Grignard reagents^{4,5} or the reactions of phosphazenes having pendent organometallic sites with chloroorganosilanes.⁸ Neilson and Wisian-Neilson¹³⁻¹⁵ have also investigated a variant of this last route.

Our earlier work indicated that reactions of organosilyl

Grignard reagents, such as $\text{Me}_3\text{SiCH}_2\text{MgCl}$, with chlorophosphazenes⁴⁻⁷ provided an effective route for the replacement of *some* but not all of the chlorine atoms by organosilicon units. This method did not allow the preparation of species in which *all* the side groups were organosilicon units, because of interference by side reactions such as phosphorus-nitrogen bond cleavage.¹⁶

It is known from earlier studies¹⁷⁻¹⁹ that the reactions between fluorophosphazenes and organolithium reagents are cleaner than their counterpart reactions that utilize chlorophosphazenes. Side reactions such as phosphorus-nitrogen bond cleavage, metal-halogen exchange, or metal coordination to the skeletal nitrogen atoms play a smaller role in the chemistry of fluorophosphazenes. The fact that fluorine replacement is favored over side reactions in fluorophosphazene chemistry is attributed to the high electronegativity of the fluorine atoms.¹⁷ For these reasons the present work involves an investigation of the reactions of hexafluorocyclotriphosphazene, $(\text{NPF}_2)_3$, with ((trimethylsilyl)methyl)lithium, $\text{Me}_3\text{SiCH}_2\text{Li}$. A major objective was the replacement of all six of the fluorine atoms by organosilicon units, together with an attempt to understand the mechanism of the substitution reaction.

(1) This paper is the ninth from our laboratory on organosilicon derivatives of phosphazenes. For previous papers in this series see ref 2-9.

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(16) Attempted reaction between excess $\text{ClMgCH}_2\text{SiMe}_3$ and $\text{N}_3\text{P}_3\text{Cl}_6$ at 66 °C for extended periods of time resulted in degradation of the phosphorus-nitrogen skeleton.^{4,7} Attempts made in this work to react $\text{Me}_3\text{SiCH}_2\text{MgCl}$ with $(\text{NPF}_2)_3$ did not result in any replacement of the fluorine atoms after refluxing for 24 h at 66 °C.

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