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Reactions of 1,1′-Bis(diphenylphosphino)ferrocene with Boranes, Thiaboranes, and Carboranes

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The reactions of 1,1′-bis(diphenylphosphino)ferrocene (dppf) with a variety of boranes, thiaboranes, and carboranes were found to produce a series of acid−base adducts or, in one case, a phosphonium salt. As confirmed by a single-crystal X-ray study, dppf reacted with BH_3·THF or *nido*-B_5H_9 to produce the complex dppf$(BH_3)_2$ (**1**) in which the two borane groups are coordinated directly to the phosphorus atoms of the dppf. Depending upon reaction stoichiometries, the reaction of dppf with *nido*-6-SB_9H_{11} yielded *arachno*-9-(*arachno*-9′-dppf-6′-SB_9H_{11})-6-SB_9H_{11} (**2**) or *arachno*-9-dppf-6-SB_9H_{11} (**3**). Further reaction of **3** with BH_3·THF formed *arachno*-9-dppf-(BH_3)-6-SB_9H_{11} (**4**). The reaction of *nido*-8-Me_2S-7-$CB_{10}H_{12}$ with dppf produced *nido*-8-dppf-7-$CB_{10}H_{12}$ (**5**), but the analogous reaction with *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$ resulted in methyl transfer to dppf to produce the phosphonium salt [dppf-Me^+][*nido*-9-MeS-7,8-$C_2B_9H_{11}^-$] (**6**). Reactions of dppf with $B_{10}H_{14}$ produced both *arachno*-6,9-$(dppf)_2B_{10}H_{12}$ (**7**) and oligomeric [*arachno*-6,9-dppf-$B_{10}H_{12}$]$_n$ (**8**) materials.

Introduction

The extensive recent investigations of the properties of 1,1′-bis(diphenylphosphino)ferrocene (dppf) have now established that it can strongly coordinate as either a mono- or bidentate ligand to numerous transition metals, thus forming a range of mono- and polymetallo complexes and oligomers.[1] In this paper, we report that dppf also forms a wide variety of strongly bonded complexes with Lewis acidic boranes, thiaboranes, and carboranes.

Experimental Section

Materials. [*arachno*-6-$SB_9H_{12}^-$][NMe_4^+],[2] *nido*-8-Me_2S-7-$CB_{10}H_{12}$,[3] and *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$[4] were prepared as previously reported. Pentaborane(9), *nido*-B_5H_9, was obtained from laboratory stock. Decaborane was obtained from Johnson Matthey or Callery Chemical and sublimed before use. dppf was purchased from Aldrich and used as received or flash-chromatographed in 50:50 CH_2Cl_2/hexane and recrystallized from same. All solvents were of reagent grade and were dried according to literature methods. Flash column chromatography was performed as described by Still[5] using Merck 60−200 mesh silica gel and the indicated solvents. Preparative thin-layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck 5744). Analytical TLC was performed on 0.25 mm (2 × 4 cm) silica gel F-254 plates (Merck).

Physical Methods. Proton, phosphorus-31, and boron-11 NMR spectra at 200.1, 80.1, and 64.2 MHz, respectively, were obtained on a Bruker WP-200 spectrometer. Proton, boron-11, and carbon-13 NMR spectra at 500.1, 160.5, and 125.7 MHz, respectively, were obtained on a Bruker AM-500 spectrometer. All boron-11 chemical shifts are referenced to BF_3·OEt_2 (0.00 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to residual protons in the lock solvents and are referenced to tetramethylsilane (0.0 ppm) with positive values indicating downfield shifts. Carbon-13 chemical shifts were measured relative to the carbons in the lock solvents and are referenced to TMS. Phosphorus-31 chemical shifts were measured relative to an external 85% H_3PO_4 standard (0.00 ppm) with negative values indicating upfield shifts. High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer using negative-ion detection. IR spectra were obtained on a Perkin-Elmer 1430 spectrometer. Elemental analyses were performed at Robertson Microlit Laboratories. Molecular weight distribution averages were determined by Dr. E. E. Remsen at Monsanto, using size exclusion chromatography with in-line viscometric detection (SEC/VISC).

dppf$(BH_3)_2$ (1) from BH_3·THF. To a two-neck flask fitted with stirbar, septum, and nitrogen inlet were added 0.60 g (1.08 mmol) of dppf and 25 mL of toluene. Under nitrogen, 5 mL of BH_3·THF (1 M solution in THF) was added via syringe. TLC analysis in 50:50 CH_2Cl_2/hexane indicated all dppf had been consumed after 1 h. The solution was then filtered through a short plug of silica gel and the solvent vacuum-evaporated from the bright orange filtrate. The remaining solid was flash chromatographed using 50:50 CH_2Cl_2/hexane as eluent to afford 0.50 g (0.86 mmol, 80% yield) of bright orange dppf$(BH_3)_2$. Further purification was effected by thin-layer chromatography on silica gel using a 50:50 solution of CH_2Cl_2/hexane (R_f 0.67). For **1**: mp 192−194 °C; IR (CCl_4/NaCl plates) 3160 (w), 3140 (w), 2400 (s), 2360 (s), 2320 (s), 2220 (w), 1490 (m), 1450 (s), 1390 (w), 1380 (w), 1310 (w), 1200 (w), 1190 (m), 1180 (s), 1140 (w), 1110 (s), 1070 (m), 1060 (s), 1030 (s), 840 (s), 780 (m), 730 (s), 700 (s), 640 (s), 615 (s) cm^{-1}. Exact mass measurement for $^{12}C_{34}{}^{1}H_{34}{}^{11}B_2{}^{56}Fe^{31}P_2$, *m/z*: calcd, 582.1671; found, 582.1683. Anal. Calcd for $C_{34}H_{34}B_2FeP_2$: C, 70.16; H, 5.89. Found: C, 69.91; H, 5.83.

dppf$(BH_3)_2$ (1) from B_5H_9. To a one-piece flask fitted with stirbar and Teflon stopcock was added 2.50 g (6.1 mmol) of dppf. THF (25 mL) and 0.39 g (6.1 mmol) of B_5H_9 were then added by vacuum transfer. The orange-yellow solution was stirred at 0 °C for 4 h and then allowed to react at room temperature overnight. Solvent and excess B_5H_9 were vacuum-evaporated, and the resulting yellow glassy solid was recrystallized using CH_2Cl_2/heptane to afford 1.57 g (2.70 mmol, 45% yield) of dppf$(BH_3)_2$ (**1**). The analytical and spectroscopic data for the isolated product were identical to those described above.

***arachno*-9-(*arachno*-9′-dppf-6′-SB_9H_{11})-6-SB_9H_{11} (2).** The literature method[2] was used to prepare *nido*-6-SB_9H_{11} by reaction of 0.86 g (4.0 mmol) of [*arachno*-6-$SB_9H_{12}^-$][NMe_4^+] with 0.51 g (2.0 mmol) of I_2 in 30 mL of toluene at 70 °C. After 2 h at reflux, the resulting solution of *nido*-6-SB_9H_{11} was filtered, and the filtrate was added to a 100 mL two-neck flask fitted with a reflux condenser, nitrogen inlet, and stirbar which had already been charged with 0.55 g (1.0 mmol) of dppf. According to TLC analysis, all dppf was consumed after overnight reflux. The solution was then filtered and the solvent

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Table 1. NMR Data[a]

compound	nucleus	δ (multiplicity, J (Hz), assignment)
dppf(BH$_3$)$_2$ (**1**)	^{11}B{^{1}H}[b]	−38.7 (br s)
	^{1}H[c]	7.45 (m, 20, Ph), 4.53 (s, 4, Cp), 4.25 (s, 4, Cp), 1.12 (d, 3, $^2J_{PH}$ 20,[d] BH)
	^{13}C{^{1}H}[e]	132.5 (d, J_{CP} 10, Ph), 131.1 (s, Ph), 130.9 (d, J_{CP} 55, Ph), 128.5 (d, J_{CP} 10, Ph), 74.5 (d, J_{CP} 7, Cp), 73.9 (d, J_{CP} 9.5, Cp), 70.5 (d, J_{CP} 64.8, Cp)
	^{31}P{^{1}H}[f]	16.5 (br)
arachno-9-(*arachno*-9′-dppf-6′-SB$_9$H$_{11}$)-6-SB$_9$H$_{11}$ (**2**)	^{11}B[g]	6.7 (d, 1, J_{BH} 120), −5.2 (br, 1), −8.3 (br, 2), −25.8 (d of d, 1, J_{BP} 105[h]), −31.0 (d, 2, J_{BH} 117), −36.1 (d, 2, J_{BH} 145)
	^{1}H[i]	7.51 (m, 20, Ph), 4.60 (s, 4, Cp), 4.39 (s, 4, Cp), −1.6 (br, 1, μBHB)
	^{13}C{^{1}H}[e]	133.4 (d, J_{CP} 9, Ph), 132.4 (d, J_{CP} 2, Ph), 128.9 (d, J_{CP} 11, Ph), 127.0 (d, J_{CP} 70, Ph), 74.9 (d, J_{CP} 8, Cp), 74.8 (d, J_{CP} 10, Cp), 70.3 (d, J_{CP} 76, Cp)
	^{31}P{^{1}H}[f]	9.45 (m, J ∼104)
arachno-9-dppf-6-SB$_9$H$_{11}$ (**3**)	^{11}B[g]	6.9 (d, 1, J_{BH} 124), −5.5 (br, 1), −8.2 (br, 2), −25.2 (d of d, 1), −30.9 (d, 2, J_{BH} 113), −36.1 (d, 2, J_{BH} 145)
	^{1}H[i]	7.70−7.30 (m), 7.25 (s, 20, Ph), 4.52 (s, 2, Cp), 4.40 (s, 2, Cp), 4.21 (s, 2, Cp), 4.16 (s, 2, Cp), −1.24 (br, 2, μBHB)
	^{13}C{^{1}H}[e]	138.5 (d, J_{PC} 11, Ph), 133.6 (d, J_{PC} 3, Ph), 133.4 (d, J_{PC} 14, Ph), 132.1 (d, J_{PC} 3, Ph), 128.8 (d, J_{PC} 17, Ph), 128.6 (d, J_{PC} 15, Ph), 128.5 (d, J_{PC} 18, Ph), 128.4 (d, J_{PC} 38, Ph), 127.4 (d, J_{PC} 70, Ph), 78.9 (d, J_{PC} 11, Cp), 74.9 (d, J_{PC} 14, Cp), 74.6 (d, J_{PC} 10, Cp), 74.1 (d, J_{PC} 8, Cp), 72.8 (d, J_{PC} 3.5, Cp), 68.3 (d, J_{PC} 79, Cp)
	^{31}P{^{1}H}[f]	9.4 (br, 1), −18.4 (s, 1)
arachno-9-dppf(BH$_3$)-6-SB$_9$H$_{11}$ (**4**)	^{11}B[g]	6.6 (d, 1, J_{BH} 133), −5.3 (s, 1), −8.4 (br s, 2), −25.7 (d of d, 1, J_{BP} ∼100),[h] −30.1 (d, 2, J_{BH} 128), −36.2 (d, 2, J_{BH} 146), −39.0 (s, 1, BH$_3$)
	^{1}H[i]	7.5 (m, 20, Ph), 4.59 (s, 2, Cp), 4.41 (s, 4, Cp), 4.27 (s, 2, Cp), −1.5 (br, 1, μBHB)
	^{13}C{^{1}H}[e]	133.5 (d, J_{CP} 9, Ph), 132.5 (d, J_{CP} 9, Ph), 132.2 (d, J_{CP} 2, Ph), 131.3 (d, J_{CP} 10, Ph), 130.5 (d, J_{CP} 60, Ph), 128.7 (d, J_{CP} 10, Ph), 128.6 (d, J_{CP} 69.7 Ph), 127.2 (d, J_{CP} 70, Ph), 75.1 (d, J_{CP} 9, Cp), 74.6 (d, J_{CP} 10, Cp), 74.3 (d, J_{CP} 8, Cp), 74.1 (d, J_{CP} 10, Cp), 71.6 (d, J_{CP} 66, Cp), 69.4 (d, J_{CP} 76, Cp)
	^{31}P{^{1}H}[f]	16.7 (br, 1), 10.7 (br m, 1, J_{PB} ∼130)
nido-8-dppf-7-CB$_{10}$H$_{12}$ (**5**)	^{11}B[g]	1.6 (d, 1, J_{BH} 132), −8.5 (d, 1, J_{BH} 143), −11.0 (br, 2), −10.8 (br, 1), −19.6 (d, 1, J_{BH} 110), −24.3 (d, 1, J_{BH} ∼100), −25.1 (d, 1, J_{BH} 139), −27.8 (d, 1, J_{BH} 138), −28.6 (d, 1, J_{BH} 140)
	^{1}H[i]	7.9−7.4 (m, 20, Ph), 4.63 (s, 2, Cp), 4.45 (s, 1, Cp), 4.40 (s, 1, Cp), 4.35 (s, 1, Cp), 4.27 (s, 1, Cp), 4.18 (s, 1, Cp), 4.07 (s, 1, Cp), 1.78 (s, 1, CH), −2.6 (br, 1, μBHB), −3.5 (br, 1, μBHB)
	^{13}C{^{1}H}[e]	138.2 (d, J_{CP} 10, Ph), 137.9 (d, J_{CP} 10, Ph), 133.8 (d, J_{CP} 10, Ph), 133.5 (d, J_{CP} 9, Ph), 133.4 (d, J_{CP} 9, Ph), 133.4 (d, J_{CP} 6, Ph), 133.3 (d, J_{CP} 8, Ph), 133.0 (d, J_{CP} 3, Ph), 132.5 (d, J_{CP} 10, Ph), 129.3 (d, J_{CP} 12, Ph), 129.1 (d, J_{CP} 11, Ph), 128.9 (s, Ph), 128.5 (d, J_{CP} 7, Ph), 128.4 (d, J_{CP} 9, Ph), 128.3 (d, J_{CP} 7, Ph), 124.9 (d, J_{CP} 74, Ph), 123.9 (d, J_{CP} 75, Ph), 75.6 (d, J_{CP} 9, Cp), 75.1 (d, J_{CP} 9, Cp), 74.9 (d, J_{CP} 15, Cp), 74.8 (d, J_{CP} 12, Cp), 74.2 (d, J_{CP} 9, Cp), 73.6 (d, J_{CP} 9, Cp), 73.4 (d, J_{CP} 75, Cp), 65.8 (d, J_{CP} 83, Cp), 38.4 (cage CH)
	^{31}P{^{1}H}[f]	3.9 (m, 1, J_{PB} ∼160 Hz), −17.6 (1)
[dppf-Me$^+$][*nido*-9-SMe-7,8-C$_2$B$_9$H$_{11}^-$] (**6**)	^{11}B[g]	0.54 (s, 1), −10.7 (d, 1, J_{BH} 192), −14.3 (d, 1, J_{BH} 128), −18.6 (d, 1, J_{BH} 176), −21.9 (d, 1, J_{BH} 128), −23.6 (d, 1, J_{BH} 208), −24.7 (d, 1, J_{BH} 144), −32.9 (d, 1, J_{BH} 144), −38.7 (d, 1, J_{BH} 144)
	^{1}H[i]	7.82−7.28 (m, 20, Ph), 4.77 (s, 2, Cp), 4.41 (s, 4, Cp), 4.19 (s, 2, Cp), 2.64 (d, 3, PMe$^+$, J_{PCH} 13), 2.21 (s, 1, CH), 2.07 (s, 3, SMe), 1.71 (s, 1, CH), −2.52 (br, μBHB)
	^{13}C{^{1}H}[e]	137.7 (d, J_{CP} 8, Ph), 135.2 (d, J_{CP} 3, Ph), 133.5 (d, J_{CP} 20, Ph), 132.2 (d, J_{CP} 11, Ph), 130.4 (d, J_{CP} 13, Ph), 129.2 (s), 128.6 (d, J_{CP} 5, Ph), 120.8 (d, J_{CP} 91, Ph), 76.2 (d, J_{CP} 11, Cp), 75.2 (d, J_{CP} 13, Cp), 73.6 (d, J_{CP} 13, Cp), 73.4 (s, Cp), 60.4 (d, J_{CP} 104, Cp), 49.1 (br s, cage CH), 36.5 (br s, cage CH), 16.1 (s, SC), 9.78 (s, J_{CP} 60, PC)
	^{31}P{^{1}H}[f]	23.41(s, 1), −18.31 (br)
arachno-6,9-(dppf)$_2$-B$_{10}$H$_{12}$ (**7**)	^{11}B[b]	−6.0 (d, 2, J_{BH} 141), −12.0 (d, 2, J_{BH} 132), −28.5 (d, 2, J_{BH} 137), −37.3 (br, 2),[j] −51.5 (d, 2, J_{BH} 148)
	^{1}H[c]	7.6−7.4 (m, 40, Ph), 4.65 (s, 1, Cp), 4.63 (s, 1, Cp), 4.40 (s, 2, Cp), 4.39 (s, 1, Cp), 4.28 (s, 2, Cp), 3.97 (s, 1, Cp), −2.5 (br, 2, μBHB)
	^{13}C{^{1}H}[e,k]	Ph region: 133.4, 133.3, 133.2, 133.2, 132.5, 132.5, 132.5, 132.4, 132.4, 132.1, 131.2, 131.1, 131.0, 130.8, 130.3, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1
		Cp region: 75.5, 75.4, 74.7, 74.7, 74.6, 74.5, 74.5, 74.3, 74.3, 74.2, 74.0, 73.9, 73.6, 73.5, 73.2
	^{31}P{^{1}H}[f]	15.2 (br s), −17.7 (s)
[6,9-dppf-B$_{10}$H$_{12}$]$_n$ (**8**)	^{11}B{^{1}H}[b,j]	−3.3, −16.5, −36.8
	^{1}H[c]	7.4 (m, Ph), 4.6 (s, Cp), 4.5 (s, Cp), 4.4 (s, Cp), 4.3 (s, Cp), −3.78 (br, μBHB)
	^{31}P{^{1}H}[f]	∼15, ∼9 (br)

[a] CD$_2$Cl$_2$ solvent. [b] 64.1 MHz. [c] 200.1 MHz. [d] $^2J_{PH}$ was determined in the ^{1}H{^{11}B}NMR spectrum. [e] 125.8 MHz. [f] 80.1 MHz. [g] 160.5 MHz. [h] J_{BP} was determined from ^{11}B{^{1}H} NMR spectra. [i] 500.1 MHz. [j] Broad and unstructured; therefore, J_{BH} values were unobtainable. [k] Due to the extent of overlapping peaks, no J_{CP} values were assignable; peaks were recorded individually.

vacuum-evaporated from the yellow filtrate. The remaining yellow oil was flash-chromatographed using 70:30 CH$_2$Cl$_2$/hexane (TLC R_f 0.60, 70:30 CH$_2$Cl$_2$/hexane) to yield 0.18 g (0.20 mmol, 21% yield based on consumed dppf) of *arachno*-9-(*arachno*-9′-dppf-6′-SB$_9$H$_{11}$)-6-SB$_9$H$_{11}$ (**2**) as a yellow solid. For **2**: mp >300 °C dec; IR (NaCl, CCl$_4$) 2520 (vs), 1480 (m), 1430 (s), 1390 (w), 1370 (w), 1310 (w), 1200 (w), 1180 (m), 1170 (m), 1160 (w), 1100 (m), 1050 (w), 1030 (m), 1005 (m, br), 940 (m), 910 (m), 830 (m), 790 (m), 740 (m), 730 (m), 710 (m), 690 (m), 650 (w), 620 (w), 600 (vw), 550 (w), 510 (w), 495 (m), 480 (m), 470 (m, br), 420 (w), 410 (w) cm^{-1}. Anal. Calcd for C$_{34}$H$_{50}$B$_{18}$FeP$_2$S$_2$·CH$_2$Cl$_2$: Anal. Calcd: C, 45.68; H, 5.70. Found: C, 45.83; H, 5.66.

***arachno*-9-dppf-6-SB$_9$H$_{11}$ (3).** Using the method[2] described above, *nido*-6-SB$_9$H$_{11}$ was prepared by the reaction of 1.8 g (8.3 mmol) of [*arachno*-6-SB$_9$H$_{12}^-$][NMe$_4^+$] with 1.05 g (4.1 mmol) of I$_2$ in 100 mL of toluene at 70 °C. After being heated at reflux for 2 h, the solution was filtered and the filtrate reacted as described above with 2.22 g (4.0 mmol) of dppf for 20 h. Purification by column chromatography on silica gel, using 30:70 CH$_2$Cl$_2$/hexane as eluent (R_f 0.24), produced 2.31 g (3.32 mmol), 44% yield, of *arachno*-9-dppf-6-SB$_9$H$_{11}$ as a yellow solid. For **3**: mp 102−104 °C; IR (KBr pellet) 3010 (w), 2900 (m, sh), 2820 (w), 2520 (s), 1430 (s), 1380 (w), 1200 (vw), 1170 (w), 1100 (m), 1020 (m), 1000 (m), 920 (w), 910 (w), 820 (w), 790 (vw), 730 (s), 690 (s), 530 (w), 480 (m) cm^{-1}. Exact mass measurement for ^{12}C$_{34}$^{1}H$_{38}$^{11}B$_9$^{32}S^{31}P$_2$^{56}Fe, (P − 1), *m/z*: calcd, 695.2356; found, 695.2370. Anal. Calcd for C$_{34}$H$_{39}$B$_9$SP$_2$Fe: C, 58.77; H, 5.66. Found: C, 58.71; H, 5.72.

***arachno*-9-dppf(BH$_3$)-6-SB$_9$H$_{11}$ (4).** A 25 mL two-neck flask fitted with a stirbar, septum, and nitrogen inlet was charged with 0.25 g (0.35 mmol) of **3** and 15 mL of toluene. The reaction mixture was purged with nitrogen, and a 1 mL aliquot of 1 M $BH_3{\cdot}THF$ in THF was added via syringe. According to TLC analysis, all of **3** was consumed after 2 h. The reaction mixture was then filtered in air through silica gel, and the solvent vacuum-evaporated from the filtrate. The resulting oil was flash-chromatographed (50:50 CH_2Cl_2/hexane) to afford 0.25 g (0.35 mmol, >99% yield) of *arachno*-9-dppf(BH_3)-6-SB_9H_{11} as a yellow solid. For **4**: mp 150−151 °C; IR (NaCl, CCl_4) 3050 (w), 2560 (s), 2400 (m), 2330 (w), 1480 (w), 1435 (s), 1390 (w), 1310 (w), 1190 (m, sh), 1170 (m), 1105 (m), 1060 (m), 1030 (m), 1010 (m, sh), 930 (w), 910 (w), 835 (w), 800 (vw), 740 (s), 690 (s), 625 (w), 610 (w), 480 (m) cm^{-1}. Anal. Calcd for $C_{34}H_{42}B_{10}FeP_2S{\cdot}CH_2Cl_2$: C, 52.97; H, 5.59. Found: C, 52.98; H, 5.55.

***nido*-8-dppf-7-$CB_{10}H_{12}$ (5).** A 100 mL one-piece flask fitted with a stirbar and high-vacuum stopcock was charged with 0.50 g (2.5 mmol) of *nido*-8-Me_2S-7-$CB_{10}H_{12}$, 1.50 g (2.7 mmol) of dppf, and 30 mL of dry toluene. The mixture was heated for 12 h at 85 °C with periodic degassing. Following filtration and solvent evaporation, the product was purified by flash chromatography on silica gel using 50:50 CH_2Cl_2/hexane as eluent to provide 0.60 g (0.87 mmol, 35% yield) of the yellow product, **5**. For **5**: mp 201−203 °C; IR (CCl_4, NaCl) 3200 (w), 2980 (w), 2960 (w), 2520 (vs), 1590 (w), 1550 (w), 1470 (m), 1440 (s), 1390 (w), 1360 (w), 1310 (w), 1260 (w), 1200 (w), 1180 (m), 1100 (s), 1040 (m), 1010 (m), 980 (w) cm^{-1}. Exact mass measurement for $^{12}C_{35}{}^{1}H_{38}{}^{11}B_{10}{}^{31}P_2{}^{56}Fe$ (P − 2H), *m/z*: calcd, 686.2729; found, 686.2716. Anal. Calcd for $C_{35}H_{40}B_{10}P_2Fe$: C, 61.23; H, 5.87; Found: C, 63.75, H, 5.94.

[dppf-Me^+][*nido*-9-MeS-7,8-$C_2B_9H_{11}{}^-$] (6). A 100 mL one-piece flask fitted with a stirbar and high-vacuum stopcock was charged with 0.55 g (2.8 mmol) of *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$, 1.50 g (2.80 mmol) of dppf, and ∼20 mL of toluene. The reaction mixture was stirred at 80 °C for 61 h with periodic degassing. Separation of the product mixture by flash chromatography on silica gel using 100% CH_2Cl_2 as eluent gave 1.05 g (1.76 mmol, 52% yield) of a thermally unstable orange oil that was then stored at −78 °C to avoid decomposition. For **6**: IR (KBr Pellet) 3030 (m), 2930 (s, sh), 2840 (s), 2530 (vs), 1780 (w), 1720 (s), 1690 (w), 1590 (w), 1570 (m), 1440 (vs), 1400 (w), 1370 (w), 1310 (w), 1280 (w), 1190 (s, sh), 1170 (s), 1100 (s), 1040 (s), 1010 (s), 1000 (s), 940 (m), 920 (m), 840 (m), 800 (s), 750 (s), 730 (s), 700 (m) cm^{-1}. Although the ^1H, ^{11}B, and ^{13}C NMR spectra (Supporting Information) indicated that **6** could be initially isolated in excellent purity, repeated attempts at microanalysis did not give satisfactory results, with the best analysis being the following. Anal. Calcd for $C_{38}H_{45}B_9P_2FeS$: C, 60.94; H, 6.06. Found: C, 55.63; H, 7.85.

***arachno*-6,9-$(dppf)_2B_{10}H_{12}$ (7).** A 100 mL two-neck flask fitted with a reflux condenser, N_2 inlet, and stirbar was charged with 2.77 g (5.0 mmol) of dppf and 60 mL of CH_2Cl_2. A solution containing 1.00 g (8.0 mmol) of $B_{10}H_{14}$ dissolved in 20 mL of CH_2Cl_2 was added via syringe and the mixture stirred at room temperature. As evidenced by TLC analysis, the reaction was near completion within 2 h. Purification by thin-layer chromatography on silica gel using 50:50 CH_2Cl_2/hexane as eluent (R_f 0.52) gave 0.31 g (0.40 mmol, 5% yield) of *arachno*-6,9-$(dppf)_2B_{10}H_{12}$. Remaining at the baseline of the TLC separation were large amounts of oligomeric materials (see below). For **7**: mp 90−94 °C; IR (KBr pellet) 3200 (w, br), 2510 (s), 2380 (s, sh), 1480 (m), 1430 (s), 1380 (w), 1330 (vw), 1320 (w), 1250 (vw), 1190 (m), 1180 (m), 1100 (s), 1050 (m), 1030 (m), 990 (w), 920 (w), 835 (m), 735 (s) cm^{-1}. Anal. Calcd for $C_{68}H_{68}B_{10}Fe_2P_4$: C, 66.46; H, 5.58. Found: C, 64.50; H, 5.84.

[6,9-dppf-$B_{10}H_{12}$]$_n$ (Oligomer) (8). To a 150 mL, two-neck flask were added 1.00 g (8.06 mmol) of $B_{10}H_{14}$, 4.50 g (8.12 mmol) of dppf, and 75 mL of CH_2Cl_2. The reaction mixture was flushed with N_2 and stirred at ∼50 °C overnight. Following filtration and solvent evaporation, the resulting solid was dissolved in CH_2Cl_2 and the concentrated solution poured into pentane. The cloudy solution was filtered, the precipitate was redissolved in CH_2Cl_2, the resulting solution was poured into pentane. This procedure was repeated twice, and the resulting peach-colored material was dried *in vacuo* to afford 3.58 g (65% yield) of product. For **8**: mp >300 °C; $M_n = 1670$, $M_w = 2660$, $M_z = 6604$; IR (NaCl, CCl_4) 3250 (w), 3090 (w), 2520 (s), 2470 (m), 1500 (m), 1450 (s), 1410 (w), 1330 (w), 1180 (w), 1100 (m), 1050 (m), 1020 (m), 1000 (w), 930 (m), 850 (w), 810 (w), 760 (m), 710 (s), 670 (w), 500 (s), 440 (w) cm^{-1}. Anal. Calcd for $C_{34}H_{40}B_{10}FeP_2$: C, 60.54; H, 5.98. Found: C, 59.49; H, 5.91.

Table 2. Data Collection and Structural Refinement Information for **1** and **3**

formula	$FeC_{34}B_2H_{34}P_2$	$FeC_{35}H_{41}P_2SB_9Cl_2$[a]
fw	582.06	779.76
crystal class	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z	1	4
cell constants		
a (Å)	9.1516(4)	13.0289(5)
b (Å)	10.3214(6)	11.3930(5)
c (Å)	8.7133(4)	26.683(1)
α (deg)	113.481(4)	
β (deg)	90.826(3)	92.061(2)
γ (deg)	86.252(3)	
V (Å^3)	753.21(7)	3958.2(2)
μ (cm^{-1})	6.28	6.75
crystal size, mm	0.47 × 0.12 × 0.060	0.56 × 0.08 × 0.06
D_{calc} (g/cm^3)	1.283	1.308
F(000)	304	401
radiation (λ (Å)	Mo Kα (0.7107)	Mo Kα (0.7107)
θ range (deg)	2.0−25.0	4.0−49.5
h,k,l collected	+10,±12,±10	0,±15,±31
no. of reflns measd	5906	28 259
no. of unique reflns (R_{merge})	2393 (0.033)	6867 (0.0642)
no. of reflns used in refinmt	1884	4392 ($F^2 > 3.0\sigma$)
no. of params	246	401
data/param ratio	7.66	11.0
R_1	0.034	0.115
R_2	0.037	0.1211
GOF	1.74	5.07

[a] The crystals of **3** were found to contain less than equivalent amounts of CH_2Cl_2.

Crystallographic Studies of 1 and 3. Single crystals of **1** and **3** were grown by slow evaporation of CH_2Cl_2/heptane solutions under N_2.

(a) Collection and Reduction of the Data. X-ray intensity data for **1** and **3** were collected on a MSC/RAXIS IIc area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at a temperature of 233−5 K. Indexing was performed from a series of 1° oscillation images with exposures of either 5 min (**1**) or 10 min (**3**) per frame. Data were collected using 6° oscillation angles with exposures of 10 min per frame and a crystal-to-detector distance of 82 mm. Oscillation images were processed using bioteX,[6] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the teXsan[7] program package for further processing and structure solution and refinement on a Silicon Graphics Indigo R4000 computer.

The intensity data were corrected for Lorentz and polarization effects, but not for absorption.

(b) Solution and Refinement of the Structures. The structures were solved by direct methods (SIR92[2]). Refinement was accomplished by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. For **1**, non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. For **3**, CH_2Cl_2 was found to be present in less than stoichiometric amounts. In addition, the SB_9 cage was found to be disordered by a rotation about the P1−B1 bond. A satisfactory disorder model was not devised; thus the S and B atoms were only refined isotropically. All other non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as constant contributions to the structure factors and were not refined.

Results and Discussion

Many boranes, carboranes, and thiaboranes are sufficiently acidic to form strong adducts with Lewis bases, with the simplest examples being the borane adducts of the formula, $BH_3{\cdot}L$.[8]

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(6) Chen, D.; Day, C. L.; Ferrara, J. D.; Higashi, T. L.; Pflugrath, J. W.; Santarsiero, B. D.; Swepston, P. N.; Troup, J. M.; Vincent, B. R.; Xiong, L. *bioteX: A Suite of Programs for the Collection, Reduction and Interpretation of Imaging Plate Data*; Molecular Structure Corp.: The Woodlands, TX 77381, 1995.

(7) *teXsan: Single Crystal Structure Analysis Software*, Version 1.7; Molecular Structure Corp.: The Woodlands, TX 77381, 1995.

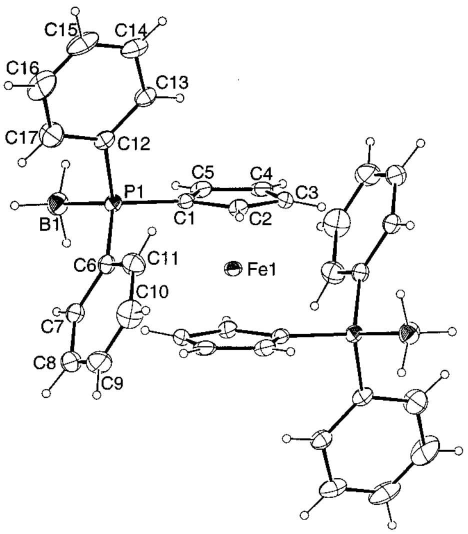

Figure 1. ORTEP plot of the structure of dppf$(BH_3)_2$, **1**.

Table 3. Refined Positional Parameters for dppf$(BH_3)_2$, **1**

atom	*x*	*y*	*z*	B_{eq} (Å^2)
Fe1	$^1/_2$	$^1/_2$	$^1/_2$	2.19(2)
P1	0.26882(7)	0.30187(8)	0.19210(9)	2.30(3)
C1	0.3288(3)	0.4676(3)	0.3371(3)	2.1(1)
C2	0.2805(3)	0.5517(3)	0.5050(4)	2.7(1)
C3	0.3589(4)	0.6766(3)	0.5640(4)	3.3(1)
C4	0.4553(4)	0.6701(3)	0.4367(4)	3.5(1)
C5	0.4373(3)	0.5434(3)	0.2974(4)	2.8(1)
C6	0.2522(3)	0.1895(3)	0.3047(4)	2.6(1)
C7	0.3519(4)	0.0746(3)	0.2728(4)	3.3(1)
C8	0.3473(4)	−0.0100(4)	0.3604(5)	4.2(2)
C9	0.2432(5)	0.0194(4)	0.4828(5)	5.1(2)
C10	0.1420(5)	0.1322(5)	0.5151(5)	5.0(2)
C11	0.1442(4)	0.2172(4)	0.4256(4)	3.8(2)
C12	0.0816(3)	0.3365(3)	0.1413(3)	2.7(1)
C13	0.0128(3)	0.4700(4)	0.1922(4)	2.9(1)
C14	−0.1289(4)	0.4881(5)	0.1406(4)	3.9(2)
C15	−0.2003(4)	0.3740(6)	0.0403(5)	5.0(2)
C16	−0.1345(4)	0.2428(6)	−0.0093(6)	6.0(2)
C17	0.0063(4)	0.2204(4)	0.0396(5)	4.8(2)
B1	0.3917(4)	0.2198(5)	−0.0046(5)	3.5(2)

Accordingly, the reaction of 2 equiv of BH_3·THF with dppf (eq 1) gave the bis(borane) complex dppf$(BH_3)_2$, **1**, which was

$$2BH_3{\cdot}THF + dppf \rightarrow \underset{\mathbf{1}}{dppf(BH_3)_2} + 2THF \qquad (1)$$

isolated as air-stable yellow needles in 80% yield by column and plate chromatography.

As shown in the ORTEP drawing in Figure 1, a single-crystal X-ray determination confirmed the two borane groups are phosphorus-coordinated, with a B−P length of 1.922(4) Å comparable to that found in $PMe_3{\cdot}BH_3$ (1.93(1) Å).[9] The iron atom lies on a crystallographic inversion center; thus the two cyclopentadienyl rings are parallel, with an Fe to ring centroid distance of 1.658 Å. As is found in the structure of the parent dppf complex,[10] the two cyclopentadienyl rings in **1** have a staggered configuration with the substituents oriented in an anti configuration, as shown in Figure 2. The phosphorus atom lies 0.049 Å above the plane of the cyclopentadienyl ring, but the boron atom is displaced 0.25 Å out of this plane toward the iron. Thus, the dihedral angle between the plane of the cyclopentadienyl ring and the C1−P1−B1 plane is 10.6°. The angles around the phosphorus (average C−P−C 105.9°; average C−P−B 112.8°) and boron atoms (average P−B−H 105°; average H−B−H 114°) are approximately tetrahedral. The boron−Fe distance is greater than 5 Å.

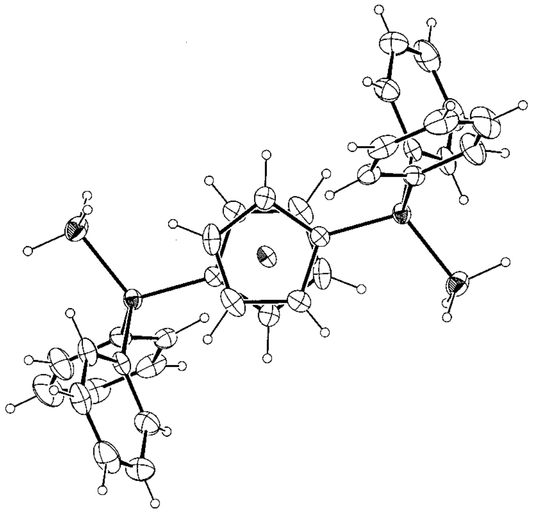

Figure 2. Alternate view of the structure of dppf$(BH_3)_2$, **1**, showing the staggered anti arrangement of the cyclopentadienyl rings.

The NMR data for **1** are consistent with the solid state structure. The ^{11}B NMR spectrum shows one broad resonance at a shift (−38.7 ppm) similar to those of other simple phosphine−borane adducts (e.g., for $PPh_3{\cdot}BH_3$, −37.5 ppm).[11] The ^{1}H NMR spectrum contains a phenyl multiplet and two intensity 4 resonances, at 4.53 and 4.25 ppm, attributed to the two sets of Cp protons. The resonance due to the three BH protons at 1.12 ppm is very broad owing to coupling to both boron and phosphorus but upon boron decoupling sharpens to a doublet with $^2J_{PH} = 20$ Hz. The ^{13}C NMR spectrum shows the phenyl resonances between 132 and 128 ppm and three cyclopentadienyl resonances between 76 and 70 ppm. The carbon resonances exhibit phosphorus coupling with the largest J_{CP} observed for the carbon bound directly to the phosphorus. The J_{CP} values are somewhat larger than those found for the parent dppf, consistent with the four-coordination of the phosphorus in **1**.[12] The ^{31}P NMR spectrum shows only a single broad resonance, consistent with the complexation of both phosphorus atoms, at a shift (16.5 ppm) that is similar to that found for $Ph_3P{\cdot}BH_3$ (20.7 ppm)[11] but downfield from that found for dppf (−17.2 ppm).[1]

Pentaborane, B_5H_9, reacts with many phosphines to yield, depending upon the phosphine and reaction conditions, adducts, *hypho*-$(R_3P)_2B_5H_9$, and/or cleavage products including, $B_3H_5{\cdot}3PR_3$, $B_2H_4{\cdot}2PR_3$, and $R_3P{\cdot}BH_3$.[13] Reactions of B_5H_9 with the diphosphines bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)ethane (dppe) are reported to yield air-stable *hypho*-(dppm)B_5H_9 and *hypho*-(dppe)B_5H_9 adducts in which the diphosphine ligands bridge the apical and basal positions of the *hypho*-pentaborane framework.[13f,g] The reaction (eq 2) of pentaborane with dppf, however, produced only **1**, in 45% yield along with intractable decomposition products. Even when

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(8) See, for example: (a) Coyle, T. D.; Stone, F. G. A. *Prog. Boron Chem.* **1964**, *1*, 83. (b) Parshall, G. W. In *The Chemistry of Boron and its Compounds*; Muetterties, E. L., Ed.; Wiley: New York, 1967; Chapter 9, pp 617−646. (c) Nöth, H. *Prog. Boron Chem.* **1970**, *3*, 213−223.

(9) Huffman, J. C.; Skupinski, W. A.; Caulton, K. G. *Cryst. Struct. Commun.* **1983**, *11*, 1435.

(10) Casellato, U.; Ajó, D.; Valle, G.; Corain, B.; Longato, B.; Graziani, R. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 583−590.

(11) Durand, M.; Jouany, C.; Jugie, G.; Elegant, L.; Gal, J.-F. *J. Chem. Soc., Dalton Trans.* **1977**, 57−60.

(12) (a) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 1, pp 1−60. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 275.

Table 4. Selected Bond Distances (Å) and Angles (deg) for dppf$(BH_3)_2$, **1**

Fe1−C1	2.051(2)	Fe1−C2	2.041(3)	Fe1−C3	2.050(3)
Fe1−C4	2.056(3)	Fe1−C5	2.053(3)	P1−C1	1.790(3)
P1−C6	1.806(3)	P1−C12	1.812(3)	P1−B1	1.922(4)
C1−C2	1.430(4)	C1−C5	1.430(4)	C2−C3	1.422(4)
C3−C4	1.405(5)	C4−C5	1.403(4)	C6−C7	1.385(4)
C6−C11	1.387(4)	C7−C8	1.373(5)	C8−C9	1.368(6)
C9−C10	1.378(6)	C10−C11	1.387(5)	C12−C13	1.378(4)
C12−C17	1.393(4)	C13−C14	1.392(4)	C14−C15	1.357(5)
C15−C16	1.349(6)	C16−C17	1.385(5)	B1−H15	1.117(32)
B1−H16	1.089(32)	B1−H17	1.083(31)		

C1−P1−C6	107.6(1)	C1−P1−C12	106.3(1)	C1−P1−B1	112.5(2)
C6−P1−C12	103.9(1)	C6−P1−B1	114.3(2)	C12−P1−B1	111.7(2)
P1−B1−H15	103.5(17)	P1−B1−H16	106.0(17)	P1−B1−H17	106.2(16)
H15−B1−H16	113.1(24)	H15−B1−H17	114.7(22)	H16−B1−H17	112.3(22)

reactions were monitoried by NMR, there was no evidence of any other soluble products.

$$B_5H_9 + \text{dppf} \rightarrow \text{dppf}(BH_3)_2 + \text{“}B_3H_3\text{”} \qquad (2)$$

1

The polyhedral thiaborane *nido*-6-SB_9H_{11} is strongly Lewis acidic and is known to form strong *arachno*-9-L-6-SB_9H_{11} complexes with many bases.[14] It was likewise found that, depending upon the reaction stoichiometry and conditions, the reaction of *nido*-6-SB_9H_{11} with dppf in refluxing toluene produced the mono- and bisadducts of dppf.

$$2\textit{nido}\text{-6-}SB_9H_{11} + \text{dppf} \rightarrow \textit{arachno}\text{-9-(}\textit{arachno}\text{-9′-dppf-6′-}SB_9H_{11}\text{)-6-}SB_9H_{11} \qquad (3)$$

2

$$\textit{nido}\text{-6-}SB_9H_{11} + \text{dppf} \rightarrow \textit{arachno}\text{-9-dppf-6-}SB_9H_{11} \qquad (4)$$

3

Both compounds were easily purified by flash column chromatography, and their compositions are consistent with their elemental analyses. In agreement with the structure proposed in Figure 3, the 160.5 MHz ^{11}B NMR spectrum of **2** consists of six resonances of relative intensities 1:1:2:1:2:2 at chemical shifts typical of those found for *arachno*-9-L-6-SB_9H_{11} compounds.[14] The intensity 1 resonance (B9) at −25.8 ppm exhibits phosphorus coupling, indicating its attachment to the dppf. The ^1H NMR spectrum shows, in addition to the resonances arising from the phenyl and cyclopentadienyl protons, one bridge hydrogen resonance of intensity 2 at −1.6 ppm. The ^{13}C NMR spectrum of **2** is similar to that of **1**, and its ^{31}P NMR spectrum consists of only one broad resonance at 9.45 ppm, which is again shifted downfield relative to that of the parent dppf.

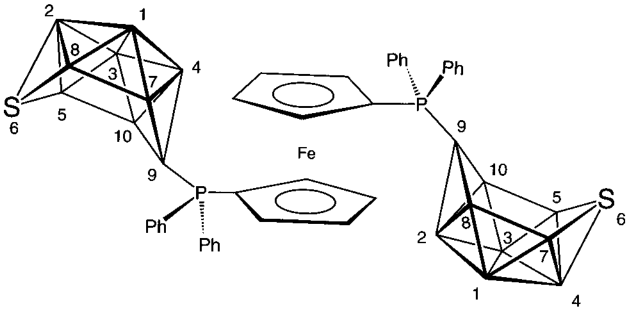

Figure 3. Proposed structure of *arachno*-9-(*arachno*-9′-dppf-6′-SB_9H_{11})-6-SB_9H_{11}, **2**.

The ^{11}B NMR spectrum of **3** is similar to that of **2**, but its ^1H NMR spectrum differs because of its inequivalent cyclopentadienyl groups. Thus, the spectrum contains, in addition to the bridge hydrogen resonance of intensity 2 at −1.24 ppm, a complicated multiplet for the phenyl protons and four separate singlet resonances of intensity 2 arising from the cyclopentadienyl protons. Likewise, its ^{13}C NMR spectrum shows four resonances (two Ph resonances and two Cp resonances) exhibiting the >60 Hz carbon−phosphorus coupling characteristic of direct attachment of the carbon to a phosphorus.[12] The ^{31}P NMR spectrum exhibits a sharp resonance (−18.4 ppm) in the dppf region, indicative of an uncoordinated phosphorus, and one broad resonance (9.4 ppm) near the shift observed for the phosphorus coordinated by the thiaborane cage of **2**.

Although disorder problems prevented a satisfactory refinement, a single crystal X-ray study confirmed the structure proposed for **3**, as shown in the ORTEP drawing given in Figure 4. Unfortunately, the SB_9 cage was found to be disordered by a rotation about the P1−B1 bond. A satisfactory disorder model was not devised; thus the sulfur and boron atoms were only refined isotropically. All other non-hydrogen atoms were refined anisotropically. While the distances and angles from this determination must be considered unreliable, several gross features regarding the structure are evident. In agreement with the spectral data and previous structural studies of *arachno*-9-L-6-SB_9H_{11} complexes,[14c] the dppf is found to be coordinated at the 9-boron position in **3**. The two cyclopentadienyl rings of the dppf have a dihedral angle of only 3.5° and are nearly eclipsed, with the two phosphine substituents oriented such that the P1−C−Fe and P2−C−Fe planes form a dihedral angle of 135° rather than the staggered anti (i.e., 180°) orientation found in **1**.

Compound **3** reacts (eq 5) with $BH_3{\cdot}THF$ to give the mixed adduct *arachno*-9-dppf(BH_3)-6-SB_9H_{11}, **4**, in quantitative yields. The elemental analyses are in excellent agreement with the crystallization of **4** with 1 equiv of the CH_2Cl_2 solvent.

$$\textit{arachno}\text{-9-dppf-6-}SB_9H_{11} + BH_3{\cdot}THF \rightarrow \textit{arachno}\text{-9-dppf(}BH_3\text{)-6-}SB_9H_{11} + THF \qquad (5)$$

4

In agreement with the structure proposed for **4**, its ^{11}B NMR spectrum at 160.5 MHz shows the appropriate peaks for the *arachno*-6-SB_9H_{11} cage, as well as one additional peak at −38.9 ppm for the BH_3 group. The ^1H NMR spectrum shows three singlet resonances of intensities 2:4:2 attributed to the Cp

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(13) (a) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1973**, 179−184. (b) Fratini, A. V.; Sullivan, G. W.; Denniston, M. L.; Hertz, R. K.; Shore, S. G. *J. Am. Chem. Soc.* **1974**, *96*, 3013−3015. (c) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288−2292. (d) Kameda, M.; Kodama, G. *Inorg. Chem.* **1987**, *26*, 2011−2012. (e) Schwarz, A.; Kodama, G. *Inorg. Chem.* **1993**, *32*, 3970−3972. (f) Alcock, N. W.; Colquhoun, H. M.; Haran, G.; Sawyer, J. F.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2243−2255. (g) Alcock, N. W.; Colquhoun, H. M.; Haran, G.; Sawyer, J. F.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1977**, 368−370.

(14) (a) Hertler, W. R.; Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 1696−1706. (b) Siedle, A. R.; McDowell, D.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 2735−2739. (c) Hilty, T. K.; Rudolph, R. W. *Inorg. Chem.* **1979**, *18*, 1106−1109.

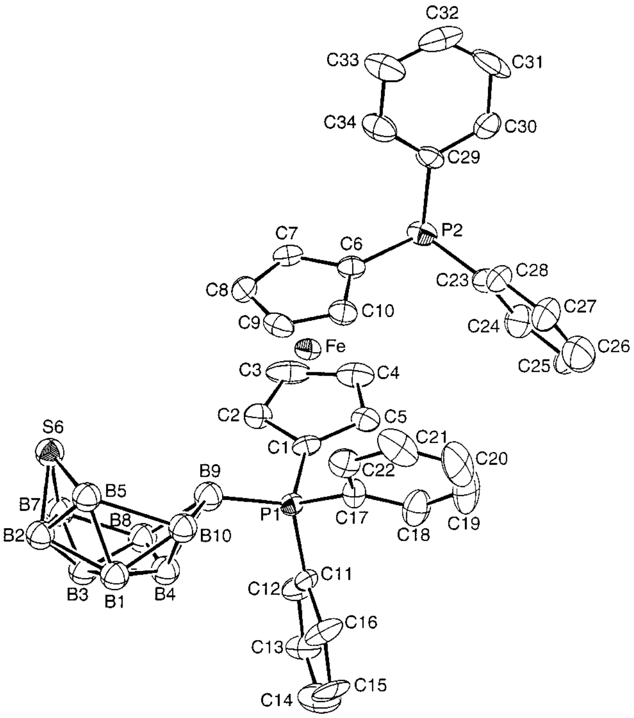

Figure 4. ORTEP plot of the structure of *arachno*-9-dppf-6-SB_9H_{11}, **3**.

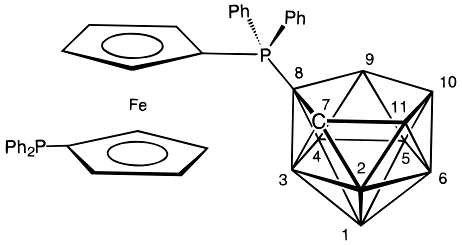

Figure 5. Proposed structure of *nido*-8-dppf-7-$CB_{10}H_{12}$, **5**.

protons. The ^{13}C NMR spectrum is similar to that found for **3**. The ^{31}P NMR spectrum exhibits two broad resonances, one at a shift (16.7 ppm) similar to that found for the borane-substituted phosphorus in **1**, while that assigned to the thiaborane-substituted phosphine is observed at a shift (10.7 ppm) similar to that found for **3**.

The reaction of the monocarbaborane *nido*-8-Me_2S-7-$CB_{10}H_{12}$ with PPh_3 has been shown to result in displacement of the Me_2S and formation of the phosphine adduct in good yields.[3] A similar reaction of *nido*-8-Me_2S-7-$CB_{10}H_{12}$ with dppf (eq 6) resulted in *nido*-8-dppf-7-$CB_{10}H_{12}$ in 35% yield.

$$\textit{nido}\text{-8-Me}_2\text{S-7-CB}_{10}\text{H}_{12} + \text{dppf} \rightarrow \underset{\mathbf{5}}{\textit{nido}\text{-8-dppf-7-CB}_{10}\text{H}_{12}} + \text{Me}_2\text{S} \quad (6)$$

Exact mass measurements and elemental analysis established its composition. Supporting the structure proposed in Figure 5, the ^{11}B NMR spectrum of **5** at 160.5 MHz has nine broad, overlapping resonances in 1:1:2:1:1:1:1:1 ratios at chemical shifts similar to those of *nido*-8-Ph_3P-7-$CB_{10}H_{12}$.[3] Likewise, the ^{1}H NMR spectrum contains two bridge hydrogen resonances, a phenyl multiplet, and the cage CH resonance, at shifts consistent with those found for *nido*-8-Me_2S-7-$CB_{10}H_{12}$ and *nido*-8-Ph_3P-7-$CB_{10}H_{12}$.[3] In agreement with the C_1 symmetry of the complex, the Cp region shows seven resonances, one of intensity 2 and six of intensity 1. The ^{31}P NMR spectrum is similar to that of **3**; the downfield peak at 3.9 ppm is once again broad, indicating coordination to the boron, and the upfield peak at −17.6 ppm occurs in the dppf region, indicating one uncoordinated phosphorus.

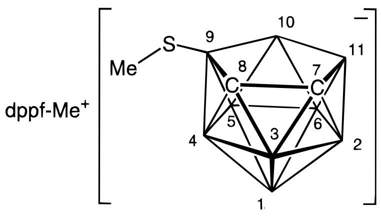

Figure 6. Proposed structure of [dppf-Me^+][*nido*-9-MeS-7,8-$C_2B_9H_{11}^-$], **6**.

Attempts to prepare the dppf analog of the dicarbaborane *nido*-9-Ph_3P-7,8-$C_2B_9H_{11}$[15] by the reaction of *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$ with dppf in refluxing toluene (eq 7) did not yield the expected ligand substitution product, 9-dppf-7,8-$C_2B_9H_{11}$, but gave instead the methylphosphonium salt of 9-MeS-7,8-$C_2B_9H_{11}^-$.

$$\textit{nido}\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11} + \text{dppf} \rightarrow \underset{\mathbf{6}}{[\text{dppf-Me}^+][\text{9-MeS-7,8-C}_2\text{B}_9\text{H}_{11}{}^-]} \quad (7)$$

NMR spectra of the reaction mixture indicated that, even after reflux for 4 days, the reaction did not go to completion. Although the product could be separated by flash column chromatography, it was necessary that it be stored at −78 °C to prevent the re-formation of *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$.

The ^{11}B NMR spectrum of **6** at 160.5 MHz consists of eight doublets and one singlet of equal intensities, similar to that of *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$, but with the singlet shifted upfield. The singlet does not show phosphorus coupling, thus supporting the retention of a sulfur−boron bond. The ^{13}C and ^{1}H NMR spectra strongly support the structure shown in Figure 6, in which one of the Me_2S methyl groups has been transferred to a dppf phosphorus, producing the phosphonium complex [dppf-Me^+][9-MeS-7,8-$C_2B_9H_{11}^-$], **6**. Thus, both the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra show phenyl and cyclopentadienyl resonances, indicating C_1 symmetry, with one set of both the phenyl and cyclopentadienyl carbons showing large J_{CP} couplings that are characteristic of organophosphoniums.[12,16] The ^{1}H NMR spectrum also shows the two cage CH peaks and methyl resonances arising from the MeS− (2.07 ppm) and MeP^+ (2.64 ppm, $^{2}J_{HP}$ 13 Hz) groups. Likewise, in the $^{13}C\{^{1}H\}$ NMR spectrum, the resonance assigned to the PMe^+ carbon (9.78 ppm) shows coupling to phosphorus (J_{CP} 60 Hz), while that of the SMe is a singlet at 16.1 ppm. The ^{31}P NMR spectrum is also consistent, showing two resonances, with one in the normal dppf region and the other at a chemical shift (23.41 ppm) characteristic of a phosphonium.[12]

The polyhedral cage systems discussed above were found to form only monobase adducts; however, other polyhedral boranes, such as decaborane(14), $B_{10}H_{14}$, are capable of forming dibase adducts. Thus, *arachno*-6,9-$L_2B_{10}H_{12}$ complexes are readily produced upon reaction of decaborane with 2 equiv of many Lewis bases,[17] including triphenylphosphine.[17c] The reactions of decaborane(14) with bidentate organophosphine bases, such as Ph_2POPPh_2, have also been found to produce

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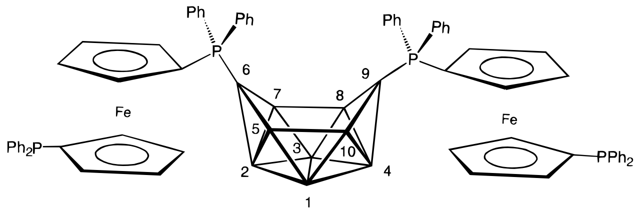

Figure 7. Possible structure of *arachno*-6,9-(dppf)$_2$B$_{10}$H$_{12}$, **7**.

polymeric materials of composition [Ph$_2$POPPh$_2$B$_{10}$H$_{12}$]$_n$.[18] The corresponding reaction of decaborane with dppf produced both *arachno*-6,9-(dppf)$_2$B$_{10}$H$_{12}$, **7**, and oligomeric materials of formula [*arachno*-6,9-dppf-B$_{10}$H$_{12}$]$_n$, **8**, as shown in eq 8.

$$\mathrm{B_{10}H_{14}} + \text{dppf} \rightarrow \underset{\mathbf{7}}{\textit{arachno}\text{-6,9-(dppf)}_2\mathrm{B_{10}H_{12}}} + \underset{\mathbf{8}}{[\textit{arachno}\text{-6,9-dppf-}\mathrm{B_{10}H_{12}}]_n} \quad (8)$$

Oligomer **8** was isolated as a solid by its repeated precipitation from pentane/methylene chloride solutions. Remaining in the solution was **7** which was then chromatographically purified to also give a solid. Both materials appear air and water stable. The relative amounts of **7** and **8** varied with the reaction conditions, with the formation of **7** favored by lower temperatures and shorter reaction times.

According to elemental analysis, **7** contains two dppf units coordinated to a single B$_{10}$H$_{12}$ fragment. A possible structure for this compound based on those previously observed for *arachno*-6,9-L$_2$B$_{10}$H$_{12}$ compounds[19] is shown in Figure 7. The ^{11}B NMR spectrum of **7** exhibits five resonances (four doublets and one broad multiplet) of equal intensity. The broad resonance at −37.2 ppm has a shift characteristic of the 6,9-borons in *arachno*-6,9-L$_2$B$_{10}$H$_{12}$ compounds[20] and its multiplet structure strongly suggests attachment of these borons to the dppf phosphorus atoms. Normal 6,9-substituted decaborane structures have C_{2v} symmetry and thus exhibit only four resonances in 2:4:2:2 ratios,[20] instead of the five resonances found for **7**. It is possible, however, that, because of their large size, the two 6,9-coordinated dppf units in **7** must be oriented in such a fashion that the normal degeneracy of the B5, B7, B8, and B10 atoms is broken into two sets, and indeed, the doublets at −12.0 and −28.5 ppm fall on either side of the shift of the single resonance normally expected for these borons. The remaining two resonances at −6.0 and −51.5 ppm are near the normal shifts expected for the 2,4- and 1,3-borons, respectively, in *arachno*-6,9-L$_2$B$_{10}$H$_{12}$ compounds.[20] The ^{1}H NMR spectrum shows one broad resonance of intensity 2 at −2.5 ppm arising from the bridging hydrogens expected at the B5−B10 and B4−B7 edges of the decaborane fragment.[19] The remainder of the spectrum is similar to that of **3**, showing sets of resonances characteristic of inequivalent phenyl and cyclopentadienyl groups, thus indicating the coordination of only one of the phosphines in each of the dppf units. Consistent with this conclusion, the ^{31}P NMR spectrum shows two peaks with chemical shifts and line widths characteristic of the coordinated (15.2 ppm, broad) and uncoordinated (−17.7 ppm, sharp) phosphines.

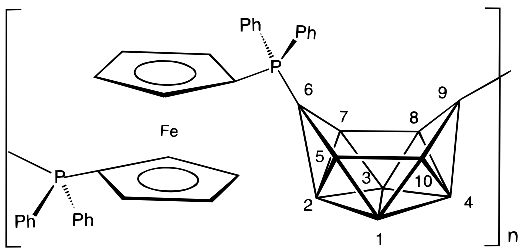

Figure 8. Possible structure of [*arachno*-6,9-dppf-B$_{10}$H$_{12}$]$_n$, **8**.

The major product of the reaction in eq 8, was the solid oligomeric material **8** which elemental analysis indicated had a repeating unit containing one dppf and one decaborane fragment, i.e. [dppf-B$_{10}$H$_{12}$]$_n$. The ^{11}B NMR spectrum of **8** consists of three very broad unresolvable resonances, spanning the shift ranges found for *arachno*-6,9-L$_2$B$_{10}$H$_{12}$ compounds[20] and the [Ph$_2$POPPh$_2$B$_{10}$H$_{12}$]$_n$ polymer,[18] suggesting the [*arachno*-6,9-dppf-B$_{10}$H$_{12}$]$_n$ structure depicted in Figure 8. Its ^{1}H NMR spectrum contains a resonance at −3.78 ppm again consistent with the bridging hydrogens on the B$_{10}$H$_{12}$ fragment, but the remainder of the spectrum is complex with numerous broad resonances for the phenyl and cyclopentadienyl protons. Likewise, the ^{31}P NMR spectrum shows only broad peaks in the region expected for coordinated phosphines. Preliminary SEC molecular weight studies of this material show M_n of 1670 and M_w of 2660, which would correspond to approximately three dppf−decaborane units. This is perhaps surprising in light of the much higher molecular weights attained by the [Ph$_2$POPPh$_2$B$_{10}$H$_{12}$]$_n$ polymers (27 000),[18] but with more forcing conditions and with solvents that prevent polymer precipitation, it may be possible to substantially increase the degree of polymerization.

In summary, the results described above have demonstrated that dppf can form strong molecular and polymeric adducts with a variety of boranes, thiaboranes, and carboranes.[21] Because of the increased air and water stabilities of these adducts compared to their unsubstituted boron starting materials, such complexes may now find a variety of uses. One potential application that takes advantage of the established bioactivity of dppf[1] is as boron-delivery agents in boron neutron capture therapy (BNCT).[22] In another area, the [Ph$_2$POPPh$_2$B$_{10}$H$_{12}$]$_n$[18] and silylferrocene polymers[23] were recently shown to serve as precursors to BCP and SiCFe ceramic materials, suggesting that boron−dppf polymers can have similar uses as precursors to complex BCPFe ceramics. We are presently exploring such properties, and these results will be reported in subsequent publications.

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Supporting Information Available: Listings of atomic coordinates, bond distances and angles, and thermal parameters for **1** and **3** and figures showing NMR spectra (^{11}B, ^{11}B{^{1}H}, ^{1}H, and ^{13}C) for compound **6** (14 pages). Ordering information is given on any current masthead page.

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