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Organotransition-Metal Metallacarboranes. 59.[1] Synthesis and Linkage of Boron-Functionalized Ferracarborane Clusters

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Negishi cross-coupling has been applied to B−I and B−Br bonds in small *closo*-ferracarboranes as a means of effecting controlled substitution at boron, with subsequent linkage to form polymetallacarborane systems. Reaction of (η^6-C_6H_6)Fe(2,3-$Et_2C_2B_4H_3$-5-I) (**2**) with vinyl−, butyl−, (trimethylsilyl)ethynyl−, and phenyl−organozinc reagents (RZnCl) in the presence of catalytic amounts of palladium(0) catalyst produced the corresponding B-functionalized derivatives (**3**−**5** and **8**, respectively) in moderate to good yields. Similarly, (η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-7-C≡CSiMe$_3$) (**12**) was prepared from the B(7)−Br (**11a**) or B(7)−I derivative (**11b**). A second alkynyl fragment was introduced at B(5) on **12** to yield the B(5,7)-diethynyl-substituted compound **16**. Treatment of (η^6-C_6H_6)Fe(2,3-$Et_2C_2B_4H_3$-5-Ph) (**8**) with $Cr(CO)_6$ in refluxing *n*-butyl ether gave the heterodimetallic complex (η^6-C_6H_6)Fe[$Et_2C_2B_4H_3$-5-{(η^6-C_6H_5)Cr(CO)$_3$}] (**9**). A series of diferracarboranes bridged by thiophene (**18**), dihydrophenanthrene (**19**), or mono-, di-, or triphenylene (**22**−**24**) linking groups was generated via reaction of **2** with bis(chlorozinc) reagents and palladium(0) catalyst, as were B(5)−ferrocenyl derivatives (**20**, **21**). Reaction of the known complex (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) with **8** at 180 °C formed (η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-5-Ph)Fe($Et_2C_2B_4H_4$) (**25**) via displacement of cyclooctatriene. Electrophilic B-iodination on the unsubstituted C_2B_4 cage of **25** afforded a dark red air-stable crystalline B(5)−iodo complex (**26**). Pd-catalyzed cross-coupling of **26** with PhZnCl, followed by cyclooctatriene displacement from (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$), produced the triferracarborane-linked oligomer (η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-5-Ph)Fe($Et_2C_2B_4H_3$-5′-Ph)Fe($Et_2C_2B_4H_4$) (**28**) in an overall yield from **8** of 40% in this four-step sequence. Deprotection of **5** and **12** with fluoride gave the B(5)− and B(7)−C≡CH derivatives **6** and **13**, respectively. Homocoupling of these terminal alkynes with Pd/Cu catalyst afforded the linked isomers [(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-*n*-C≡C)]$_2$ (**29**, $n = 5$; **31**, $n = 7$). Alternatively, **6** and **13** were treated with 1,3,5-$C_6H_3I_3$ under similar conditions to form the benzene-centered triferracarborane complexes [(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-*n*-C≡C)]$_3C_6H_3$ (**30,** $n = 5$; **32,** $n = 7$). X-ray diffraction analyses confirmed the structures of **9**, **18**, **24**, and **26**.

Introduction

Pentagonal-pyramidal *nido*-RR′$C_2B_4H_4^{2-}$ and *nido*-RR′$C_2B_4H_5^-$ anions (R, R′ = H, silyl, organic substituents) are versatile metal-binding ligands that are related to both dicarbollide (RR′$C_2B_9H_9^{2-}$) and cyclopentadienide ions yet exhibit a notably different chemistry.[2,3] The ability of these small carborane ligands to form strong covalent bonds with a broad spectrum of main-group and transition-metal ions—in general, much stronger than is achievable in metal−Cp or metal−arene systems—has been exploited to stabilize unusual metal−ligand molecular architectures: e.g., covalently bonded multidecker[4] and oligodecker[5] sandwiches and fused-cage systems.[2,3] A special advantage afforded by many, though not all, metal−C_2B_4 complexes (seven-vertex MC_2B_4 clusters) is that they are amenable to replacement of the apex boron by metal−ligand or B−X units;[6] this property furnishes a powerful synthetic tool for the construction of target systems having useful electronic, catalytic, or other properties.[7]

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(1) Part 58: Malaba, D.; Sabat, M.; Grimes, R. N. *Eur. J. Inorg. Chem.* **2001**, 2557.

(2) For example, a property of M(C_2B_4)$_2$ complexes that has no counterpart in either metal−dicarbollide or metal−hydrocarbon sandwich chemistry is the facile, low-energy, face-to-face fusion of the carborane ligands with expulsion of the metal. See: Grimes, R. N. *Coord. Chem. Rev.* **1995**, *143*, 71.

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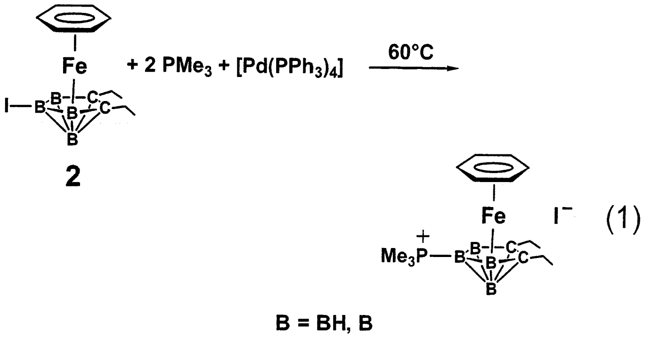
Previously, directed B-substitution on *closo*-LMC_2B_4 metallacarboranes was limited to electrophilic halogenation,[8] and the only means of introducing organic groups at boron involved the "recapitation" of *nido*-$Cp^*CoR_2C_2B_3H_5^{2-}$ anions with organoboryl reagents[6] to afford B(7)-substituted products. To develop controlled syntheses of small carborane-based polycluster systems for nanostructured materials or other applications, one clearly requires more direct and versatile routes. Work in other laboratories on larger, 12-vertex *closo*-carboranes has demonstrated the indispensability of metal-catalyzed cross-coupling for the introduction of sp-, sp^2-, and sp^3-hybridized groups at boron.[9] Most of these studies employed Kumada-type coupling with Grignard reagents, but Suzuki[9j] (boronic acids) and Negishi conditions[9c] have also been utilized.

Much of the small-carborane chemistry emanating from our laboratory in recent years has involved cobalt systems,[3c,d,4–6,8] although (ligand)MC_2B_4 clusters involving group 4 and 5 metals, some of them catalytically active, have been studied in detail.[7c,10] Formal replacement of the ubiquitous $CpCo^{III}$ (or Cp*Co) units with isoelectronic (arene)Fe^{II} or $CpFe^{II}H$ groups generates ferracarboranes[11,12] whose chemistry and redox properties differ significantly from those of their CoC_2B_4 analogues. In this paper we report metal-facilitated syntheses of B-functionalized FeC_2B_4 and FeC_2B_3 derivatives that can, in turn, be coupled to generate poly(ferracarborane) target complexes; other studies based on CoC_2B_4 clusters will be reported separately.

Results and Discussion

Mechanistic Aspects. Grignard reagents, alkyllithiums, boronic acids, and organostannanes were found to be ineffective in coupling to the B(5)−iodo species (η^6-C_6H_6)Fe(2,3-$Et_2C_2B_4H_3$-5-I) (**2**, described below); only Negishi-type coupling[13] was sufficiently reactive to effect B−C bond formation. The Pd-catalyzed coupling of **2** under Negishi conditions probably follows a mechanistic pathway similar to that reported earlier for 1,7-$C_2B_{10}H_{11}$-9-I (9-iodo-*m*-carborane).[14] As in that study, we found no NMR-observable reaction between **2** and the Pd catalyst under the same conditions. Furthermore, reaction of **2** with tetrakis(triphenylphosphine)palladium in the presence of $[Bu_4N]Br$ gave evidence of B−I activation with the formation of the B−Br derivative.[15] However, in contrast to 9-iodo-*m*-carborane,[14] the presumed (η^6-C_6H_6)Fe($Et_2C_2B_4H_3$)-Pd(I)$(PPh_3)_2$ intermediate that is generated from **2** undergoes B−P elimination rather than B−I reduction at elevated temperatures. Thus, reaction of **2** with a stoichiometric amount of palladium complex in the presence of 2 molar equiv of trimethylphosphine resulted in immediate formation of the trimethylphosphonium salt as a brown insoluble solid (eq 1). Structural assignment of the salt is based on the ^1H NMR spectrum, which establishes the presence of one PMe_3 molecule per ferracarborane unit, and the $^{11}B\{^1H\}$ NMR spectrum, which reveals a clear doublet at δ −3.3 with $J = 166$ Hz, consistent with typical $J(^{11}B,^{31}P)$ values.[16] In addition, the $^{31}P\{^1H\}$ NMR spectrum shows a quartet with the same coupling constant, indicative of phosphorus in close proximity to boron (^{11}B, $I = {}^3/_2$).



(1)

B(5)-Organosubstitution on (η^6-C_6H_6)Fe(2,3-$Et_2C_2B_4H_4$) (1). The parent ferracarborane **1**[17] was treated with *N*-iodosuccinimide to give **2** in high yield, in a procedure analogous to the B-halogenation of (η^5-C_5R_5)-Co(2,3-$Et_2C_2B_4H_4$) cobaltacarboranes (R = H, Me)[8] (Scheme 1). Compound **2** is a versatile starting reagent for a variety of B(5)-organosubstituted species; thus, treatment of **2** with vinylzinc chloride in the presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium afforded the B−vinyl complex **3** as an air-stable brown solid, while reaction of **2** with *n*-butylzinc chloride gave the brown B(5)−butyl derivative **4**.

Introduction of an alkynyl group at B(5) was achieved via reaction of **2** with ((trimethylsilyl)ethynyl)zinc chloride (TMSZ), generating yellow-brown (η^6-C_6H_6)Fe(2,3-$Et_2C_2B_4H_3$-5-C≡$CSiMe_3$) (**5**) in quantitative yield (Scheme 1). Removal of the TMS group with fluoride afforded the B(5)−ethynyl species **6**, a brown air-stable solid, in 80% yield. Complex **6** is a particularly versatile synthon: as will be shown, it can serve as a direct precursor to linked systems containing two or more Fe centers and can also be converted to its *nido*-FeC_2B_3 form, which can be recapped to yield B(7)-functionalized

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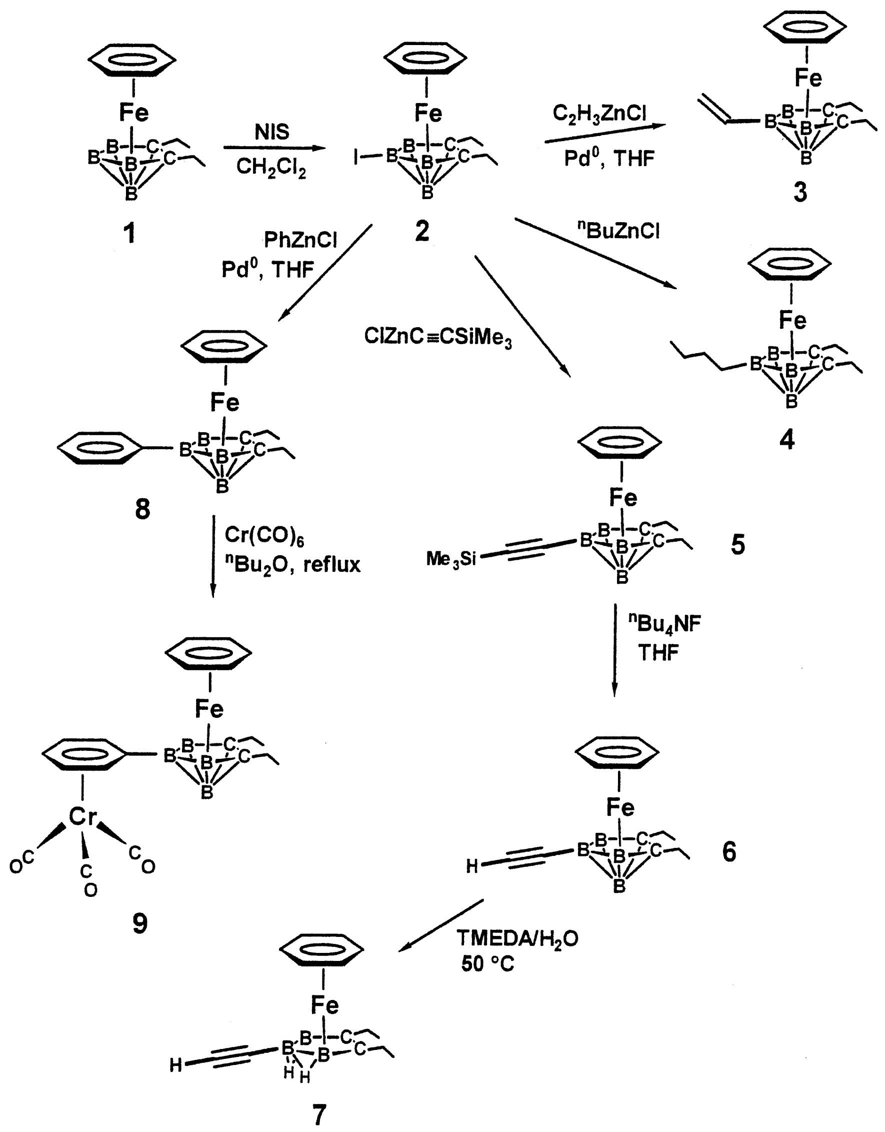
Scheme 1[a]



[a] B = BH, B.

derivatives. Thus, treatment of **6** with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) afforded yellow *nido*-(η^6-C_6H_6)Fe(2,3-$Et_2C_2B_3H_4$-5-C≡CH) (**7**). The proton NMR spectrum of the nido complex **7** displays significant (~0.3 ppm) shielding of the acetylenic hydrogen relative to **6**.

Reaction of **2** with phenylzinc chloride and palladium(0) catalyst in THF afforded in 77% yield the B(5)−phenyl derivative **8**, an air-stable, oily solid. Reaction of this compound with chromium hexacarbonyl in refluxing *n*-butyl ether (Scheme 1) gave the dimetallic complex (η^6-C_6H_6)Fe(2,3-$Et_2C_2B_4H_3$)-5-(η^6-C_6H_5)Cr(CO)$_3$ (**9**) as an air-sensitive yellow solid that was characterized via spectroscopic data and X-ray crystallography. Complexation to the Cr(CO)$_3$ moiety produced, as expected, a substantial high-field shift (>2 ppm) in the phenyl proton NMR resonances, and the molecular structure of **9** (Figure 1) confirms the substitution at B(5). Table 1 lists experimental X-ray data and data collection parameters, while selected distances and angles are summarized in Table 2. The B(5)−C(7) distance and the smaller C(8)−C(7)−C(12) angle of 116.7° are comparable to B-aryl values previously reported.[6,18] The C_6H_6 and C_2B_3 rings are mutually tilted by only 3.8°, and their distances to Fe (1.54 and 1.61 Å, respectively) are normal; however, torsional strain forces the C_6H_5 and C_2B_3 rings out of coplanarity by 17.4°. The closer proximity of B(4) to the Cr(CO)$_3$ group causes the C(7)−B(5)−B(4) angle to be 4.4° larger than the corresponding angle C(7)−B(5)−B(6).

B(7)-Organosubstituted (η^6-C_6H_6)Fe($Et_2C_2B_4H_4$) Derivatives. Recent work in our laboratory,[6] partially in collaboration with Siebert and co-workers,[6b] showed that recapping of *nido*-CoC_2B_3 complexes with monoboron reagents furnishes a useful route to apically (B(7)) functionalized CoC_2B_4−X species. In the present study we found that this approach can also be applied to ferracarboranes. Scheme 2 summarizes the conversion of *nido*-(η^6-C_6H_6)Fe($Et_2C_2B_3H_5$) (**10**)[19] to a B(7)−alkynyl derivative via three different routes. In the first two approaches, deprotonation of **10** with *tert*-butyllithium to generate the **10**$^{2-}$ dianion, followed by reaction with

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Table 1. Experimental X-ray Diffraction Parameters and Crystal Data

	9	**18**	**23**	**25**
empirical formula	$C_{21}H_{24}B_4O_3FeCr$	$C_{28}H_{50}B_8Fe_2S$	$C_{42.5}H_{51}B_8ClFe_2$	$C_{24}H_{37}B_8Fe_2I$
fw	475.50	616.92	795.46	650.62
cryst dimens (mm)	0.41 × 0.32 × 0.18	0.38 × 0.27 × 0.20	0.31 × 0.17 × 0.11	0.38 × 0.17 × 0.16
space group	*Pbca* (No. 61)	$P3_1$ (No. 144)	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)
a, Å	21.091(5)	18.6124(5)	21.275(2)	7.6421(5)
b, Å	23.371(6)	18.6124(5)	14.187(1)	15.801(1)
c, Å	8.772(3)	7.8924(3)	14.480 (1)	22.503(2)
β, deg			106.776(2)	91.606(2)
V, $Å^3$	4323(1)	2367.8(1)	4184.5(7)	2716.2(3)
Z	8	3	4	4
D(calcd), g cm^{-3}	1.461	1.298	1.263	1.591
μ(Mo Kα), mm^{-1}	1.193	1.003	0.85	2.218
diffractometer	Rigaku AFC6S	Bruker SMART APEX CCD	Bruker SMART APEX CCD	Bruker SMART APEX CCD
temp, K	193(2)	153(2)	153(2)	153(2)
$2\theta_{max}$	46	65	65	65
transmissn factors	0.62−1.00	0.41−1.00	0.68−0.80	0.63−0.80
no. of rflns collected	3432	32 826	28 652	37 080
no. of obsd rflns ($I > n\sigma(I)$)	2184 ($n = 3$)	10 713 ($n = 2$)	7608 ($n = 2$)	9822 ($n = 2$)
no. of params refined	272	442	259	464
R	0.046	0.0301	0.0747	0.0360
R_w	0.065	0.0721	0.2162	0.0690
largest peak in final diff map, e/$Å^3$	0.34	0.65	0.64	1.30
goodness of fit	1.91	0.98	1.026	0.867
abs structure param		0.003(8)		

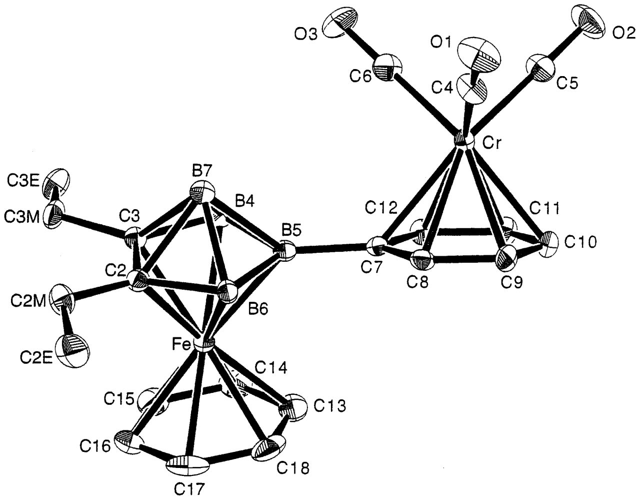


Figure 1. Molecular structure of **9** with 30% thermal ellipsoids (hydrogen atoms omitted for clarity).

Table 2. Selected Distances and Angles for 9

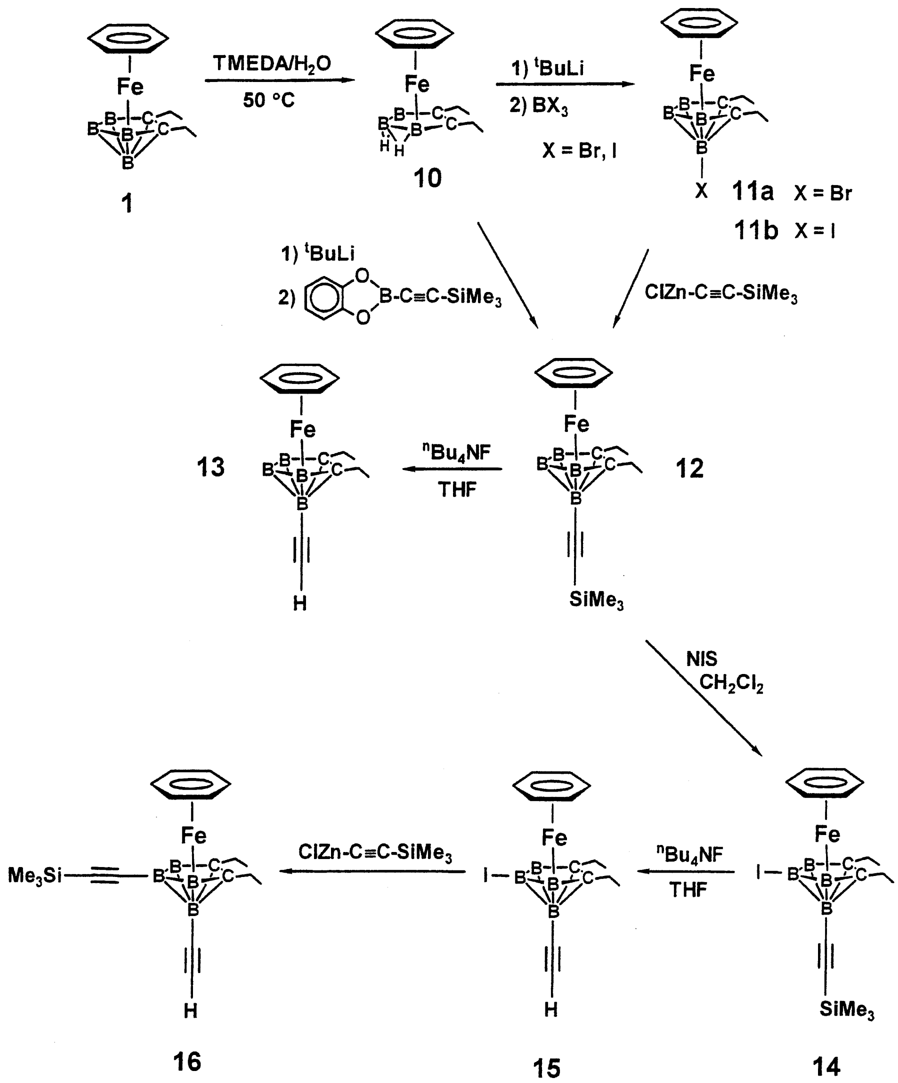
Distances, Å			
Fe−C(2)	2.060(5)	C(3)−C(3M)	1.524(7)
Fe−C(3)	2.061(5)	C(3)−B(4)	1.564(8)
Fe−B(4)	2.142(6)	C(3)−B(7)	1.772(8)
Fe−B(5)	2.136(6)	B(4)−B(5)	1.674(8)
Fe−B(6)	2.126(6)	B(4)−B(7)	1.804(8)
⟨Fe−C(C_6H_6 ring)⟩	2.078(15)	B(5)−B(6)	1.682(8)
C(2)−C(3)	1.471(7)	B(5)−B(7)	1.772(9)
C(2)−B(6)	1.569(8)	B(6)−B(7)	1.785(8)
C(2)−C(2M)	1.504(8)	B(5)−C(7)	1.568(8)
C(2)−B(7)	1.777(8)	⟨Cr−C(C_6H_5 ring)⟩	2.225(13)
C(2M)−C(2E)	1.505(9)	⟨Cr−C(CO)⟩	1.838(10)
C(3M)−C(3E)	1.490(7)	⟨C−O⟩	1.157(12)
Angles, deg			
C(3)−C(2)−B(6)	111.8(5)	C(8)−C(7)−C(12)	116.7(5)
C(2)−C(3)−B(4)	113.3(4)	C(4)−Cr−C(6)	89.9(3)
C(3)−B(4)−B(5)	104.4(4)	C(4)−Cr−C(5)	86.1(3)
C(2)−B(6)−B(5)	104.9(4)	C(5)−Cr−C(6)	88.9(3)
B(4)−B(5)−B(6)	105.6(4)	Cr−C(5)−O(2)	179.3(5)
C(7)−B(5)−B(4)	129.4(5)	Cr−C(4)−O(1)	177.3(5)
C(7)−B(5)−B(6)	125.0(5)	Cr−C(6)−O(3)	177.8(6)

boron tribromide or boron triiodide, afforded (η^6-C_6H_6)-Fe(2,3-$Et_2C_2B_4H_3$)-7-X (**11a**, X = Br; **11b**, X = I); these complexes were then treated with TMSZ to afford the B(7)−(trimethylsilyl)ethynyl derivative **12** in yields of 85% (from **11b**) or 98% (from **11a** consumed). An alternative synthesis of **12** involved direct reaction of the dianion with 2-((trimethylsilyl)ethynyl)-1,3,2-benzodioxaborole, as shown (yield 94% based on **10** consumed). While each of these methods gave **12** in high yield, the reaction of **11b** proceeded much more readily (higher conversion rate) and, hence, is the preferred synthesis. Interestingly, the B(7)−I ^{11}B NMR resonance in **11b** is shifted upfield by 27 ppm relative to the B(5)−I resonance in **2**.

Removal of the TMS group from **12** with fluoride proceeded easily to give the B(7)−ethynyl species **13**, which can be dimerized (vide infra). Comparison of the proton NMR spectra of **12** and **13** with those of their B(5) (equatorially) substituted isomers (**5** and **6**) reveals that the acetylenic and trimethylsilyl protons in the latter species are significantly deshielded (by 1.6 and 0.3 ppm, respectively). The introduction of a second alkynyl group at B(5)—an important synthetic objective—was achieved via reaction of **12** with NIS to generate the B(5)−iodo derivative **14**, which in turn was disilylated to give **15** and the iodo substituent replaced with TMSZ to produce the B(5,7)−dialkynyl complex **16** (Scheme 2). The individual steps in this sequence each proceeded essentially quantitatively, except for the conversion of **15** to **16** (ca. 70%).

Synthesis of B(5)−X−B(5) Connected Bis(ferracarborane) Systems. The B(5)−iodo derivative **2** was shown to be a useful precursor to several types of linked systems. Direct B−B coupling was accomplished by a Wurtz-type reaction of **2** with a dispersion of potassium on silica gel, affording in low yield the brown air-stable dimer [(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$)-5-]$_2$ (**17**; Scheme 3). The CpCo analogue of **17** was similarly prepared earlier and characterized by X-ray diffraction.[4d] Palladium-promoted coupling of **2** proved especially versatile, for example allowing the syntheses of the thiophene- and dihydrophenanthrene-bridged bis(ferracarboranes) **18**

Scheme 2[a]



[a] B = BH, B.

and **19**, respectively, via reaction with the corresponding bis(chlorozinc) reagents (Scheme 3). Both **18** and **19** were isolated as air-stable red crystalline solids in ca. 30% yield.

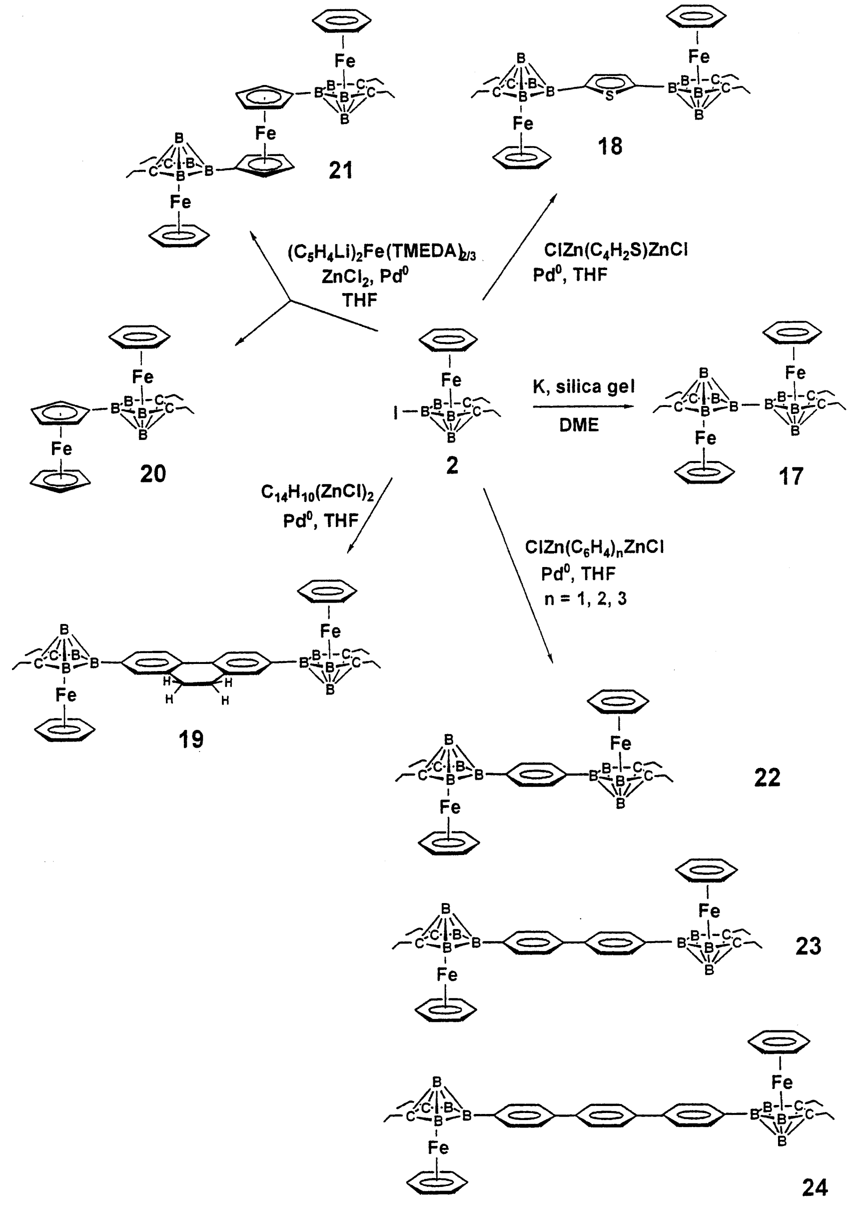
Red hexagonal crystals of **18**, grown from chloroform and hexane and subjected to X-ray structural analysis, adopt a noncentrosymmetric, enantiomorphic $P3_1$ space group. Although not dictated by the space group, the ORTEP representation (Figure 2) reveals an approximate 2-fold symmetry axis which passes through S and bisects the C(19)−C(20) bond. Disorder also occurs in the molecular structure with two equally populated orientations of the ethyl groups connected to C(2) and C(4)—one as depicted in the figure, and another with one ethyl group on each cage rotated out of the C_2B_3 ring plane. The selected distances and angles in Table 3 are consistent with the other structures in this paper. The benzene and C_2B_3 rings are parallel (0.9°), while the C_2B_3 and thiophene planes subtend an angle of 52°.

Table 3. Selected Distances and Angles for 18

	Distances, Å		
Fe(1)−C(2)	2.049(2)	B(4)−B(7)	1.780(3)
Fe(1)−C(3)	2.050(2)	B(5)−B(6)	1.666(3)
Fe(1)−B(4)	2.123(2)	B(5)−B(7)	1.752(3)
Fe(1)−B(5)	2.157(2)	B(6)−B(7)	1.791(3)
Fe(1)−B(6)	2.135(2)	B(5)−C(18)	1.561(2)
⟨Fe(1)−C(C_6H_6 ring)⟩	2.067(5)	B(9)−C(21)	1.564(2)
C(2)−C(3)	1.472(2)	S−C(18)	1.730(2)
C(2)−B(6)	1.559(3)	S−C(21)	1.729(2)
C(2)−B(7)	1.767(3)	C(18)−C(19)	1.370(2)
C(3)−B(4)	1.563(3)	C(19)−C(20)	1.422(2)
C(3)−B(7)	1.760(2)	C(20)−C(21)	1.372(2)
B(4)−B(5)	1.682(3)		
	Angles, deg		
C(3)−C(2)−B(6)	112.7(1)	C(18)−B(5)−B(6)	129.3(2)
C(2)−C(3)−B(4)	112.2(1)	C(19)−C(18)−B(5)	127.5(1)
C(3)−B(4)−B(5)	104.7(2)	B(5)−C(18)−S	124.1(2)
C(2)−B(6)−B(5)	105.0(1)	C(19)−C(18)−S	108.3(1)
B(4)−B(5)−B(6)	105.4(2)	C(21)−S−C(18)	94.91(7)
C(18)−B(5)−B(4)	124.6(2)	C(18)−C(19)−C(20)	114.2(2)

Treatment of **2** with a ferrocenylzinc reagent and a palladium catalyst gave the mono- and bis(ferracarboranyl)ferrocene derivatives (η^6-C_6H_6)Fe(2,3-$Et_2C_2B_4H_3$)-5-(C_5H_4)FeCp (**20**) and [(C_6H_6)Fe($Et_2C_2B_4H_3$)-5-C_5H_4]$_2$-Fe (**21**) as red air-sensitive compounds (Scheme 3), but the relative yields of these products were strongly dependent on the proportion of $ZnCl_2$ employed. When 1 equiv of *rigorously dried* $ZnCl_2$/equiv of dilithioferrocene was used, the yields of **20** and **21** were 21% and 30%, respectively, based on **2** consumed; when the $ZnCl_2$/dilithioferrocene ratio was 2.0, the yields of both products were lower, with **20** predominating ca. 2/1.

Scheme 3[a]



[a] B = BH, B.

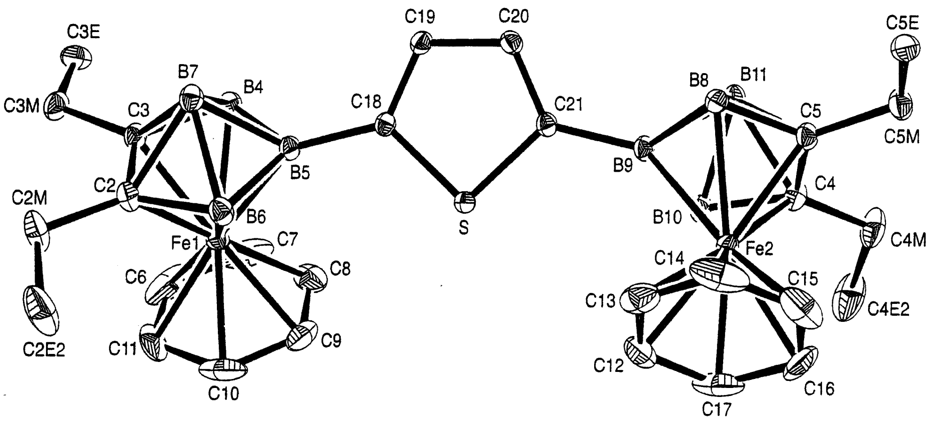


Figure 2. Molecular structure of **18** with 30% thermal ellipsoids (hydrogen atoms omitted for clarity).

These seemingly counterintuitive findings are reminiscent of the observations of Rosenblum et al. on reactions of zincated metallocenes with 1,8-diiodonaphthalene, where a 1/1 $ZnCl_2$/dilithioferrocene mixture led to polymer formation, whereas a 2/1 ratio favored monomeric bis(ferrocenyl)naphthalene products.[20] As in the Rosenblum study, the precise composition of the zincated metallocene has not been established, but it is

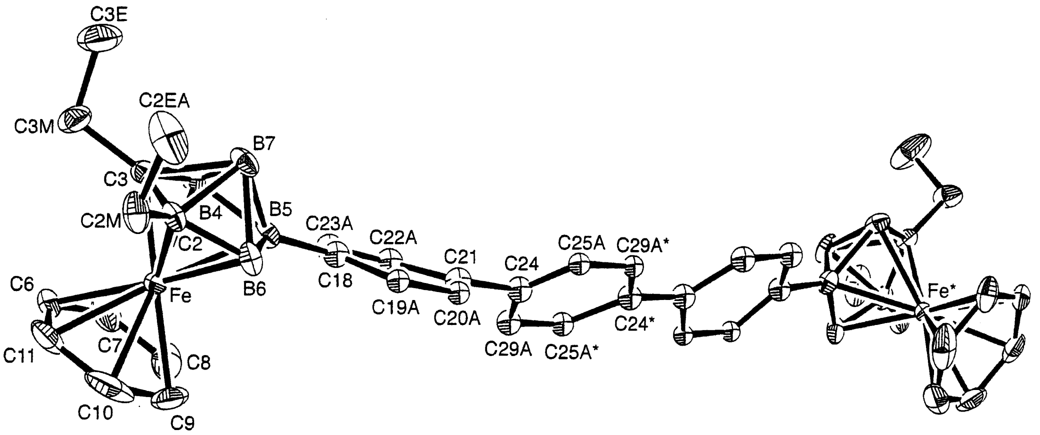


Figure 3. Molecular structure of **24** with 30% thermal ellipsoids (hydrogen atoms and solvent molecule omitted for clarity). One of two observed orientations of the triphenylene group is depicted.

Table 4. Selected Distances and Angles for 24

	Distances, Å		
Fe–C(2)	2.045(3)	C(3)–B(4)	1.547(5)
Fe–C(3)	2.036(3)	C(3)–B(7)	1.762(5)
Fe–B(4)	2.104(3)	B(4)–B(5)	1.656(5)
Fe–B(5)	2.163(4)	B(4)–B(7)	1.758(6)
Fe–B(6)	2.133(4)	B(5)–B(6)	1.690(5)
C(2)–C(3)	1.461(4)	B(5)–B(7)	1.754(5)
C(2)–B(6)	1.549(5)	B(6)–B(7)	1.773(6)
C(2)–B(7)	1.765(4)	B(5)–C(18)	1.568(5)
	Angles, deg		
C(3)–C(2)–B(6)	112.5(3)	B(4)–B(5)–B(6)	103.7(3)
C(2)–C(3)–B(4)	111.9(3)	C(18)–B(5)–B(4)	128.9(3)
C(3)–B(4)–B(5)	106.6(3)	C(18)–B(5)–B(6)	127.1(3)
C(2)–B(6)–B(5)	105.3(3)		

assumed to consist of both diferrocenylzinc and chlorozinc ferrocene; moreover, as before,[20] this mixture is likely to undergo continuous change during the reaction.

In an analogous procedure, *p*-bis(chlorozinc) mono-, di-, and triphenyl reagents were prepared in situ and reacted with **2** to generate the phenylene-linked bis(ferracarboranes) $[(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3)\text{-}5\text{-}]_2(C_6H_4)_n$ (**22**, $n = 1$; **23**, $n = 2$; **24**, $n = 3$) (Scheme 3). The three products were isolated in 20–30% yields as air-stable red or brown solids, and the multinuclear NMR and mass spectroscopic characterization of the structure of **24** was augmented by X-ray crystallographic data (Figure 3).

The solid-state structure of **24** is dimorphic. Crystals grown from a chloroform/hexanes solution have a very large unit cell containing three independent molecules of **24**, each having a seemingly random orientation in its individual phenylene rings. In contrast, crystals grown from dichloromethane/hexanes solution exhibit a higher, 2-fold axis of symmetry through the central ring of the triphenylene linker. The molecular structure is still not free of crystallographic problems, in that one of the ethyl groups and each of the C_6H_4 rings are disordered with two possible orientations, only one of which is shown in Figure 3. In addition, the structure contains 0.5 disordered dichloromethane molecule per molecule of **24**, located at an inversion center. Selected distances and angles (Table 4) are normal for small metallacarboranes, and **24** has a metal–metal separation of 18.2 Å.

Synthesis of B(5)–Aryl–Fe Connected Bis(ferracarborane) Systems. In an alternative approach to intermolecular linkage, we utilized the facile arene displacement of cyclooctatriene from $(\eta^6\text{-}C_8H_{10})$ferracarboranes as in earlier studies.[3c,4a,21] As illustrated in Scheme 4, $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ was thermolyzed with **8** at 180 °C in the absence of solvent to give the brown, air-stable solid $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}Ph)Fe(Et_2C_2B_4H_4)$ (**25**) in 84% yield. Complete conversion to **25** is evident from the disappearance of resonances at 7.49 ppm and a high-field shift of 2 ppm. Complex **25** can be rendered multifunctional; for example, it can be derivatized at B(5) on one cage and can be decapped/recapped (see above) to achieve B(7) substitution on either cage. Thus, iodination of **25** gave the B(5)–I derivative **26** quantitatively as dark red, air-stable crystals.

Single crystals of **25** and **26** were grown, but only **26** yielded a satisfactory molecular structure free from disorder. The crystals of **25** obtained from ethyl acetate/hexanes revealed a $P2_12_12_1$ space group, with two independent molecules in the asymmetric unit having parallel C_6H_6 and C_6H_5 rings, as illustrated in Scheme 4. The solid-state structure of **26** (shown in Figure 4 with selected distances and angles summarized in Table 5) demonstrates the rotational freedom about the B(5)–C(6) bond, as the phenyl group is rotated out of the C_2B_3 plane by ~120°. The B(9)–I distance is similar to that observed in *p*-carboranes,[22] and the long Fe(2)–C(6) bond length approximates that reported for the Fe–bridgehead carbon distance in $(\eta^6\text{-}C_{10}H_8)Fe(Et_2C_2B_4H_4)$.[23] Apparently as a consequence of the close proximity of B(4) to C(5M), the C(6)–B(5)–B(4) angle is 6.1° larger than the corresponding C(6)–B(5)–B(6) angle. Within each ferracarborane unit the C_6 and C_2B_3 ring planes are essentially parallel, exhibiting very small dihedral angles of 0.5 and 1.6°.

Replacement of the iodo substituent by phenyl via treatment with phenylzinc and palladium(0) complexes afforded the brown air-stable compound $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}Ph)Fe(Et_2C_2B_4H_3\text{-}5'\text{-}Ph)$ (**27**) in 68% yield.

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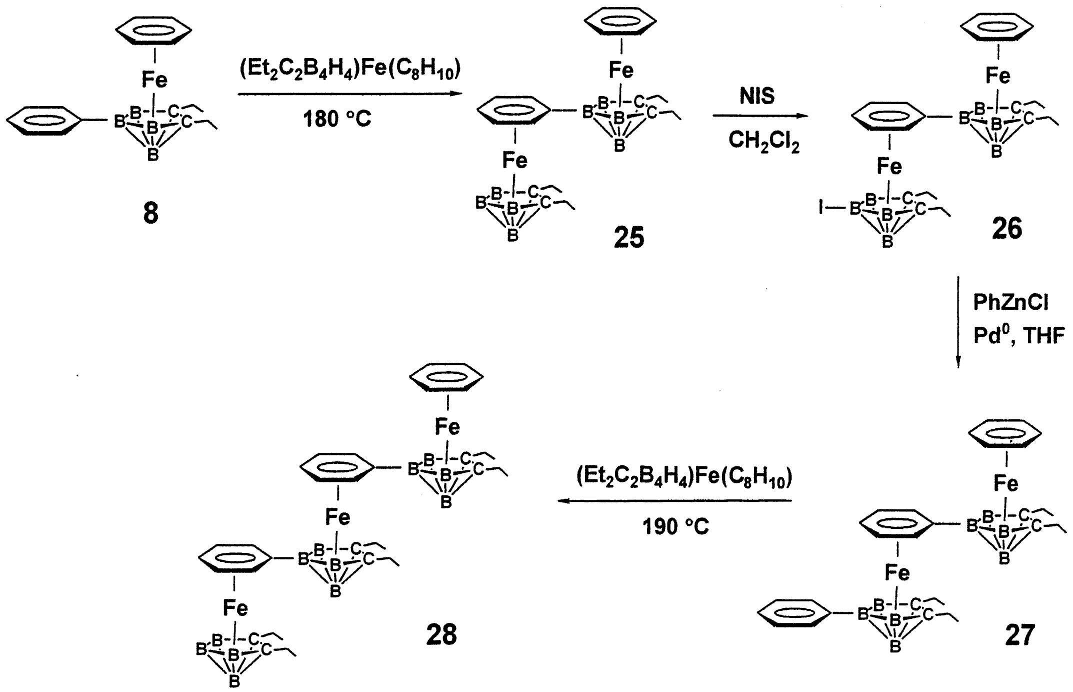
(20) (a) Arnold, R.; Matchett, S. A.; Rosenblum, M. *Organometallics* **1988**, *7*, 2261. (b) Arnold, R.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1988**, *7*, 1253.

(21) Swisher, R. G.; Sinn, E.; Butcher, R. J.; Grimes, R. N. *Organometallics* **1983**, *2*, 506.

(22) Jiang, W.; Knobler, C. B.; Curtis, C. E.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 3491.

(23) Swisher, R. G.; Sinn, E.; Grimes, R. N *Organometallics* **1985**, *4*, 896.

Scheme 4[a]



[a] B = BH, B.

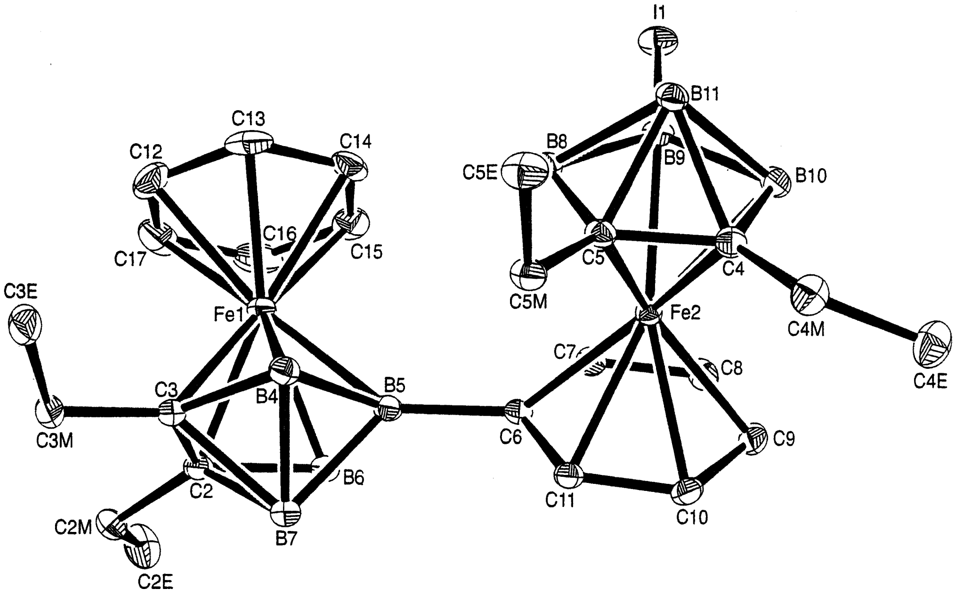


Figure 4. Molecular structure of **26** with 30% thermal ellipsoids (hydrogen atoms omitted for clarity).

As shown in Scheme 4, this complex was employed to generate a trimetallic species via thermolysis with (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) at 190 °C. The product, (η^6-C_6H_6)-Fe($Et_2C_2B_4H_3$-5-Ph)Fe($Et_2C_2B_4H_3$-5′-Ph)Fe($Et_2C_2B_4$-H_4) (**28**), was isolated in 73% yield as a red air-stable solid.

Synthesis of Alkynyl-Linked Bis- and Tris(ferracarborane) Systems. A recent publication[1] from our laboratory described the synthesis and characterization of a series of alkyne-connected bis(cobaltacarborane) complexes, of interest as potential models for electron transport over acetylenic chains between metal centers ("molecular wires"[24]). Accordingly, we investigated metal-promoted coupling reactions of the B−alkynyl synthons **6** and **13**, whose synthesis is described above. Reaction of **6** with $PdCl_2(PPh_3)_2$, CuI, I_2, and triethylamine gave the target compound [(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-5-C≡C)]$_2$ (**29**) in 55% yield as a (surprisingly) very insoluble orange solid, as depicted in Scheme 5.

Similar treatment of **6** using the Sonogashira conditions with 1,3,5-triiodobenzene in place of I_2 gave the benzene-centered tris(ferracarboranyl-5-ethynyl) species 1,3,5-[(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-5-C≡C)]$_3C_6H_3$ (**30**), which was isolated as an air-stable yellow solid in low (19%) yield (Scheme 5). This compound is structurally related to our recently reported[18] tris(cobaltacarboranyl)benzene complex 1,3,5-[Cp*Co($Et_2C_2B_4H_3$-7-)]$_3C_6H_3$ but differs in the metal, the connectors to benzene, and the

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[24] For a list of leading references in this general area, see ref 1, footnote 7.

Scheme 5

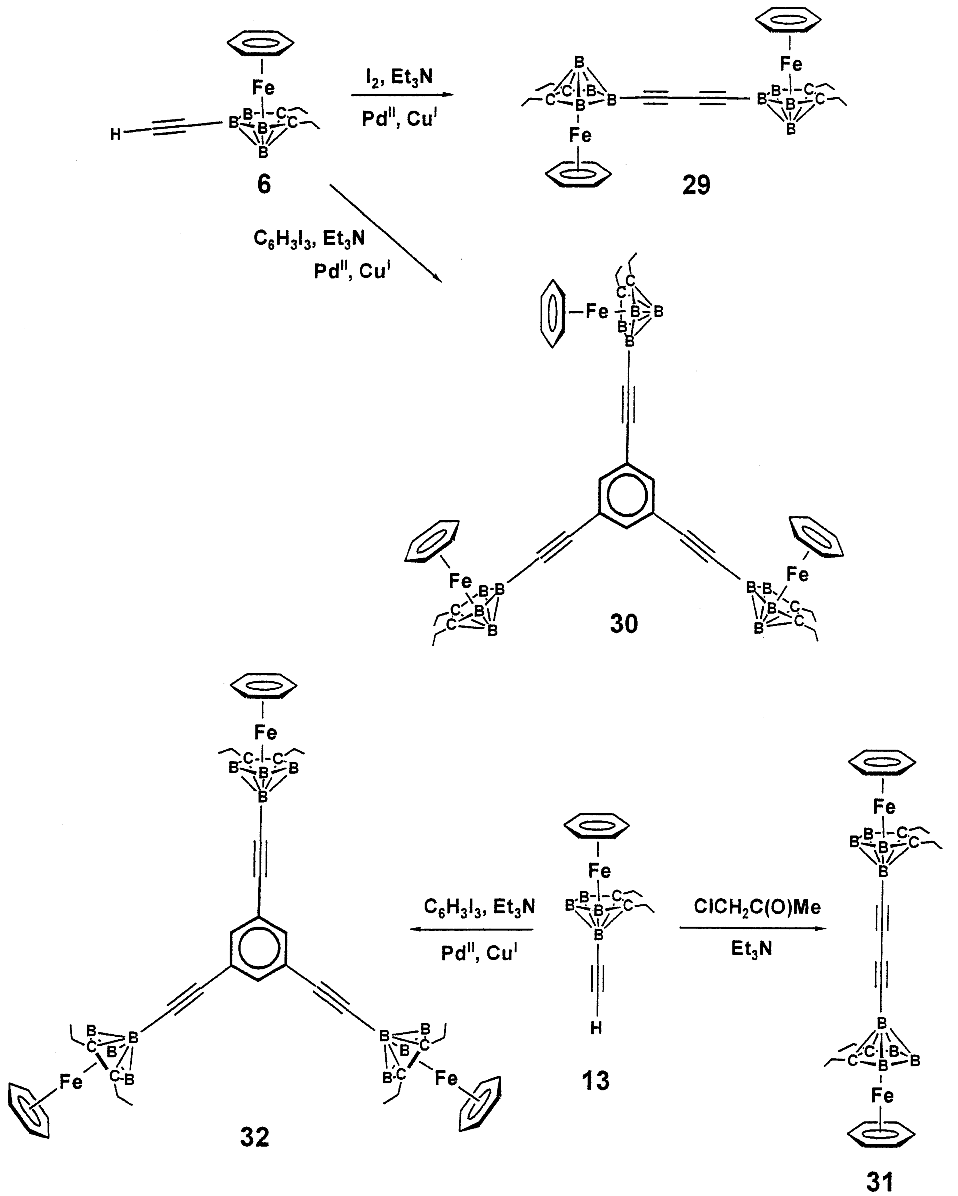

Table 5. Selected Distances and Angles for 26

	Distances, Å		
Fe(1)−C(2)	2.053(2)	B(4)−B(5)	1.671(3)
Fe(1)−C(3)	2.052(2)	B(4)−B(7)	1.787(3)
Fe(1)−B(4)	2.142(2)	B(5)−B(6)	1.676(3)
Fe(1)−B(5)	2.155(2)	B(5)−B(7)	1.758(3)
Fe(1)−B(6)	2.119(2)	B(6)−B(7)	1.796(3)
⟨Fe(1)−C(C_6H_6 ring)⟩	2.085(6)	Fe(2)−B(9)	2.127(2)
C(2)−C(3)	1.473(3)	Fe(2)−C(6)	2.149(2)
C(2)−B(6)	1.558(3)	⟨Fe(2)−C(C_6H_5 ring)⟩	2.095(5)
C(2)−B(7)	1.760(3)	I(1)−B(9)	2.170(2)
C(3)−B(4)	1.565(3)	B(5)−C(6)	1.574(3)
C(3)−B(7)	1.764(3)		
	Angles, deg		
C(3)−C(2)−B(6)	112.5(2)	C(4)−B(10)−B(9)	103.7(2)
C(2)−C(3)−B(4)	112.5(2)	B(8)−B(9)−B(10)	107.3(2)
C(3)−B(4)−B(5)	104.60(2)	C(6)−B(5)−B(4)	129.6(2)
C(2)−B(6)−B(5)	104.7(2)	C(6)−B(5)−B(6)	123.5(2)
B(4)−B(5)−B(6)	105.7(2)	C(11)−C(6)−C(7)	116.1(2)
C(5)−C(4)−B(10)	112.4(2)	B(8)−B(9)−I(1)	127.8(2)
C(4)−C(5)−B(8)	112.9(2)	B(10)−B(9)−I(1)	124.7(2)
C(5)−B(8)−B(9)	103.7(2)		

point of attachment of the connectors on the carborane ligand.

The apically substituted complex **13** was similarly linked to generate the B(7)-connected dimer [(η^6-C_6H_6)-Fe($Et_2C_2B_4H_3$-7-C≡C)]$_2$ (**31**), obtained via reaction with chloroacetone and triethylamine in the presence of palladium/copper catalyst. Palladium-catalyzed coupling of **13** with triiodobenzene generated in 37% yield the B(7)-linked air-stable yellow complex 1,3,5-[(η^6-C_6H_6)-Fe($Et_2C_2B_4H_3$-7-C≡C)]$_3C_6H_3$ (**32**).

Conclusions

Metal-assisted cross-coupling has been employed to synthesize several families of mono-, di-, and tri-*closo*-ferracarborane derivatives possessing a variety of boron-connected multicage architectures that were previously inaccessible. The di- and triferracarboranes produced are prime candidates for mixed-valence and electron delocalization studies of their oxidized products, as reported in the accompanying paper.[25] Work is currently

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[25] Fabrizi de Biani, F.; Fontani, M.; Ruiz, E.; Zanello, P.; Russell, J. M.; Grimes, R. N. *Organometallics* **2002**, *21*, 4129.

underway to apply these useful synthetic techniques to new families of seven-vertex metallacarborane sandwich complexes.

Experimental Section

Instrumentation. ^{1}H (500 MHz (where noted), 300 MHz), ^{11}B (160.4 MHz (where noted), 96.4 MHz), ^{13}C (125.8 MHz (where noted), 75.4 MHz), and ^{31}P (121.7 MHz) NMR spectra were recorded on GE GN-300/44 and Varian Unity/Inova 500/51 or 300/51 instruments. ^{1}H and ^{13}C shifts are referenced to residual ^{1}H and ^{13}C signals in the deuterated solvent. ^{11}B and ^{31}P NMR resonances are referenced to the external standards $BF_3{\cdot}OEt_2$ and H_3PO_4, respectively. Unit resolution mass spectra were acquired on a Finnigan (Model LCQ Classic) quadrupole ion trap mass spectrometer using an atmospheric pressure chemical ionization interface. Infrared spectra were obtained on a Nicolet Impact-400 spectrophotometer as either thin films or pressed pellets. Ultraviolet−visible spectra were recorded on a HP 8452A diode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab in Norcross, GA. Owing to incomplete combustion (not uncommon in polyhedral boron clusters), the carbon analyses for **3** and 1**9** were slightly outside normal limits. For all new compounds, the compound purity and identity were established from multinuclear NMR spectra supplemented by mass spectrometry, showing the expected isotopic envelopes. X-ray crystallography provided unambiguous structural assignments for **9**, **18**, **24**, and **26**.

Materials and Procedures. All reactions were carried out in oven-dried glassware under a dinitrogen atmosphere using conventional glovebox or Schlenk techniques, and the products were worked up in air unless otherwise noted. Anhydrous zinc chloride was purchased from Aldrich Chemical Co. and used as received, with the exception that extra-dry $ZnCl_2$ (prepared by treatment under refluxing oxalyl chloride for 2 h) was used in the preparation of **20** and **21**. All other commercial reagents were used as received without further purification. THF, diethyl ether, 1,2-dimethoxyethane, di-*n*-butyl ether, and toluene were distilled from sodium benzophenone ketyl prior to use. When anhydrous dichloromethane was required, the solvent was distilled from P_2O_5 under N_2. Triethylamine was distilled from CaH_2 under an inert atmosphere. 2-((Trimethylsilyl)ethynyl)-1,3,2-benzodioxaborole, not previously reported in the literature, was prepared by the reaction of commercially available *B*-chlorocatecholborane (Aldrich) with $Me_3SiC{\equiv}CSnMe_3$.[26] Potassium metal dispersion on silica gel,[27] $[(C_5H_4Li)_2Fe](TMEDA)_{2/3}$,[28] 2,7-dibromo-9,10-dihydrophenanthrene,[29] 4,4″-dibromo-*p*-terphenyl,[30] $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$,[31] and 1,3,5-triiodobenzene[32] were prepared according to published procedures. Periodically the organolithium reagents were titrated with 2,2-diphenylacetic acid to determine the active organometallic content.

$(C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}I)$ (2). This synthesis was carried out in air. A 1.000 g portion of $(C_6H_6)Fe(Et_2C_2B_4H_4)$ (**1**; 3.797 mmol) was dissolved in 50 mL of dichloromethane and cooled to 0 °C. To this solution was added 854 mg of *N*-iodosuccinimide (3.80 mmol), with a subsequent darkening in color. After 0.5 h the mixture was warmed to room temperature and was stirred for an additional 1.5 h. The solvent was removed, and the resulting residue was purified on a 15 cm column of silica gel using a 1/2 dichloromethane/hexanes solution to afford 1.437 g of **2** as an air-stable brown solid (97% yield). ^{1}H NMR ($CDCl_3$): δ 5.45 (s, 6H, C_6H_6), 2.60, 2.31 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.24 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 93.7 (C_2B_4), 85.6 (C_6H_6), 24.2 (ethyl CH_2), 14.9 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 4.2 (s, 1B, *B*−I), 2.1 (d, 2B, $J = 186$ Hz), −0.3 (d, 1B, $J = 122$ Hz). IR (KBr pellet, cm^{-1}): 3075 (w), 2965 (s), 2931 (s), 2906 (m), 2870 (m), 2834 (w), 2558 (s), 1443 (s), 1061 (m), 1048 (m), 1012 (m), 981 (m), 897 (m), 861 (m), 835 (s), 819 (s), 746 (m), 687 (w), 637 (w), 582 (m), 532 (m), 481 (m), 423 (m). CI^{+}-MS: *m*/*z* (%) 390 ([M^{+}], 70). Anal. Calcd for $C_{12}H_{19}B_4FeI$: C, 37.03; H, 4.92. Found: C, 37.27; H, 4.74.

Reaction of 2 with PMe_3 and $Pd(PPh_3)_4$. In a 25 mL Schlenk flask under dinitrogen, 90 mg of $Pd(PPh_3)_4$ (0.078 mmol) and 32 mg of **2** (0.082 mmol) were dissolved in 5 mL of dry, degassed benzene. A 0.17 mL portion of a 1.0 M PMe_3 solution in toluene (0.17 mmol) was added via syringe, and the solution was heated to 60 °C. Immediate precipitate formation occurred, and the reaction was continued for 10 min until precipitate formation had ceased. The mixture was cooled to room temperature and the solid filtered off under anaerobic conditions. The solid was then washed with three 5 mL portions of benzene and dried in vacuo to give 30.6 mg of the trimethylphosphonium salt $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}PMe_3I)$ in 84% yield. ^{1}H NMR ($CDCl_3$): δ 5.82 (s, 6H, C_6H_6), 2.69, 2.31 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.83 (d, 9H, $J = 13$ Hz, P−CH_3), 1.23 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 92.7 (s br, C_2B_4), 24.9 (ethyl CH_2), 14.9 (ethyl CH_3), 12.7 (d, $J = 47$ Hz, P−CH_3). ^{11}B NMR (CD_2Cl_2): δ 14.3 (d, 3B, $J = 110$ Hz), −3.3 (d, 1B, $J = 166$ Hz, *B*−P(CH_3)$_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ −7.1 (quartet, 1P, $J = 165$ Hz, B−*P*). IR (KBr pellet, cm^{-1}): 3039 (m), 2963 (s), 2933 (s), 2897 (s), 2872 (m), 2548 (s), 1443 (s), 1376 (m), 1340 (w), 1298 (m), 1292 (m), 1145 (w), 1114 (w), 1066 (m), 974 (s), 894 (w), 866 (m), 837 (m), 761 (m), 675 (m), 547 (w), 479 (m), 420 (m).

$(C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-vinyl})$ (3). Into a 50 mL Schlenk flask under dinitrogen, 10 mL of dry, degassed THF and 0.83 mL of a 1.40 M solution of methyllithium in diethyl ether (1.2 mmol) were transferred. A 65.6 mg portion of tetravinylstannane (0.289 mmol) was added via a microliter syringe, and the contents were stirred for 2 h. The solvent was removed in vacuo, and 15 mL of fresh THF was added. To the brownish yellow solution was added 158 mg of anhydrous $ZnCl_2$ (1.16 mmol) all at once, and the mixture was stirred. After 0.5 h, 150 mg of **2** (0.385 mmol) and 22 mg of $Pd(PPh_3)_4$ (0.019 mmol) were added and the contents were stirred overnight. Following solvent removal, the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/3 CH_2Cl_2/hexanes solution, affording 92 mg of **3** (82% yield) as an air-stable brown solid. ^{1}H NMR ($CDCl_3$): δ 6.69 (dd, 1H, $J = 13$, 19 Hz, $CH{=}CH_2$), 5.55 (dd, 1H, $J = 4$, 19 Hz, CH=*trans*-CH_2), 5.59 (1H obscured, CH=*cis*-CH_2), 5.34 (s, 6H, C_6H_6), 2.61, 2.34 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.25 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 143.4 (v br, B−$CHCH_2$), 123.4 (B−$CHCH_2$), 93.2 (C_2B_4), 84.4 (C_6H_6), 24.4 (ethyl CH_2), 14.9 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 14.3 (s, 1B, *B*−vinyl), 5.3 (d, 1B, $J = 148$ Hz), 0.2 (d, 2B, $J = 144$ Hz). IR (KBr pellet, cm^{-1}): 3045 (m), 2967 (s), 2924 (m), 2870 (m), 2535 (vs), 1442 (s), 1374 (m), 1011 (m), 921 (m), 887 (m), 862 (m), 813 (m), 791 (w), 622 (m), 486 (m), 421 (m). UV−vis (CH_2Cl_2, nm (%)): 230 (100), 273 (93), 418 (5) $\epsilon_{max} = 10\,900$ cm^{-1} M^{-1}. CI^{+}-MS: *m*/*z* (%)

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290 ([M$^+$], 93), 263 ([M$^+$ − CH═CH$_2$], 31). Anal. Calcd for $C_{14}H_{22}B_4Fe$: C, 58.10; H, 7.66. Found: C, 57.45; H, 7.50.

(C_6H_6)Fe($Et_2C_2B_4H_3$-5-Bu) (4). Into a 50 mL Schlenk flask under dinitrogen, 10 mL of dry, degassed THF and 0.74 mL of a 1.57 M solution of *n*-butyllithium in hexanes (1.2 mmol) were transferred. To this solution at −78 °C was added 158 mg of anhydrous $ZnCl_2$ (1.16 mmol) in 1 mL of THF, and the contents were stirred. After 1 h the mixture was warmed to room temperature and stirred for an additional 1 h. A 150 mg portion of **2** (0.385 mmol) and 23 mg of $Pd(PPh_3)_4$ (0.020 mmol) were added, and the contents were stirred overnight. Following solvent removal, the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/5 CH_2Cl_2/hexanes solution, producing two bands. The first band afforded 61 mg of **4** as a brown oil, and the second yielded 23 mg of recovered **2** (50% yield; 59% based on **2** consumed). ^{1}H NMR ($CDCl_3$): δ 5.29 (s, 6H, C_6H_6), 2.60, 2.33 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.43 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.23 (t, 6H, J = 7 Hz, ethyl CH_3), 1.14 (t, 2H, J = 7 Hz, $CH_2CH_2CH_2CH_3$), 0.92 (t, 3H, J = 7 Hz, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 92.8 (C_2B_4), 83.9 (C_6H_6), 34.1 ($CH_2CH_2CH_2CH_3$), 26.1 ($CH_2CH_2CH_2CH_3$), 24.4 (ethyl CH_2), 16.5 (v br, CH_2CH_2-CH_2CH_3), 14.9 (ethyl CH_3), 14.3 ($CH_2CH_2CH_2CH_3$). ^{11}B NMR ($CDCl_3$): δ 19.3 (s, 1B, *B*−Bu), 5.7 (d, 1B, J = 144 Hz), −0.5 (d, 2B, J = 146 Hz). IR (NaCl plate, cm^{-1}): 3073 (w), 2964 (s), 2929 (s), 2869 (s), 2808 (m), 2528 (s), 1442 (s), 1376 (m), 1225 (w), 1147 (m), 1122 (w), 1063 (w), 1008 (w), 980 (m), 883 (m), 863 (m), 807 (s), 710 (m). UV−vis (CH_2Cl_2, nm (%)): 231 (86), 276 (100), 335 (sh, 13), 422 (3) ϵ_{max} = 10 700 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 320 ([M$^+$], 31), 262 ([M$^+$ − C_4H_9], 100). Anal. Calcd for $C_{16}H_{28}B_4Fe$: C, 60.15; H, 8.83. Found: C, 59.89; H, 8.96.

(C_6H_6)Fe($Et_2C_2B_4H_3$-5-C≡CSiMe$_3$) (5). In a 50 mL Schlenk flask under dinitrogen, a solution of 152 mg of (trimethylsilyl)acetylene (1.55 mmol) and 10 mL of dry, degassed THF at 0 °C was treated dropwise with 0.98 mL of a 1.57 M *n*-butyllithium solution in hexanes (1.5 mmol). After 15 min the mixture was warmed to room temperature and stirred for 1.7 h. To the resulting solution was added 213 mg of anhydrous $ZnCl_2$ (1.56 mmol) all at once, and the mixture was stirred. After an additional 1 h, 300 mg of **2** (0.771 mmol) and 44 mg of $Pd(PPh_3)_4$ (0.04 mmol) were added and the contents were stirred overnight. The THF was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then column chromatographed on silica in 1/1 CH_2Cl_2/hexanes, affording a major yellow-brown band that was characterized as **5** (261 mg, 94% yield). ^{1}H NMR ($CDCl_3$): δ 5.42 (s, 6H, C_6H_6), 2.59, 2.31 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.22 (t, 6H, J = 7 Hz, ethyl CH_3), 0.23 (s, 9H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 115.2 (BC≡*C*SiMe$_3$), 92.6 (C_2B_4), 84.9 (C_6H_6): 24.2 (ethyl CH_2), 14.8 (ethyl CH_3), 0.8 (Si*Me*$_3$). ^{11}B NMR ($CDCl_3$): δ 5.1 (d, 1B, B−H unresolved), 3.8 (s, 1B, *B*C≡CSiMe$_3$), 1.5 (d, 2B, J = 188 Hz). IR (KBr pellet, cm^{-1}): 3079 (w), 2965 (s), 2932 (s), 2871 (m), 2542 (s), 2525 (s), 2102 (s), 1443 (s), 1375 (m), 1245 (s), 1179 (m), 905 (s), 837 (s), 755 (s), 690 (m), 558 (m), 485 (m), 445 (m). UV−vis (CH_2Cl_2, nm (%)): 229 (96), 270 (100), 291 (sh, 82), 420 (7) ϵ_{max} = 8400 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 360 ([M$^+$], 70).

(C_6H_6)Fe($Et_2C_2B_4H_3$-5-C≡CH) (6). In a 50 mL Schlenk flask under dinitrogen, 265 mg of **5** (0.737 mmol) was dissolved in 10 mL of dry, degassed THF and the solution cooled to 0 °C. To this with stirring was added 0.75 mL of 1.0 M tetrabutylammonium fluoride (TBAF) solution in THF (0.75 mmol) with an immediate red color formation. After 1.5 h the mixture was warmed to room temperature and stirred for an additional 2 h. The solvent was removed in vacuo, and the remaining crude material was flash chromatographed through a 3 cm plug of silica gel with dichloromethane. The crude material was then placed atop a 20 cm silica gel column and eluted with a 1/1 dichloromethane/hexanes solution to afford 169 mg of **6** (80% yield) as an air-stable brown solid. ^{1}H NMR ($CDCl_3$): δ 5.45 (s, 6H, C_6H_6), 3.21 (s, 1H, BC≡C*H*), 2.60, 2.32 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.24 (t, 6H, J = 7 Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 95.9 (BC≡*C*H), 92.8 (C_2B_4), 84.9 (C_6H_6), 24.3 (ethyl CH_2), 14.9 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 5.2 (s, 1B, *B*C≡CH), 3.4 (d, 1B, J = 37 Hz), 1.6 (d, 2B, J = 198 Hz). IR (KBr pellet, cm^{-1}): 3296 (s), 3080 (m), 2969 (s), 2933 (m), 2873 (m), 2536 (s), 2046 (vw), 1441 (s), 1378 (w), 1237 (w), 900 (m), 881 (w), 859 (m), 819 (m), 634 (s), 614 (m), 550 (w), 484 (m), 455 (m). CI$^+$-MS: *m/z* (%) 288 ([M$^+$], 50), 264 ([M$^+$ − C≡CH], 80). Anal. Calcd for $C_{14}H_{20}B_4Fe$: C, 58.51; H, 7.01. Found: C, 58.64; H, 6.96.

(C_6H_6)Fe($Et_2C_2B_3H_4$-5-C≡CH) (7). In a separate flask a mixture of 2 mL of TMEDA and 10 drops of water was degassed by N_2 bubbling for 5 min and then transferred to a Pyrex tube equipped with a Teflon stopcock and a stir bar that contained 29.8 mg of **6** (0.104 mmol). The stopcock was closed, and the yellow solution was warmed to 50 °C. After 1 h the reaction mixture, which had darkened, was cooled and the solvent was removed in vacuo. The remaining crude material was dissolved and the solution passed through a 3 cm column of silica gel with dichloromethane to give a yellow solution which provided 27.3 mg of **7** (95% yield) as a yellow, air-stable solid. ^{1}H NMR ($CDCl_3$): δ 5.33 (s, 6H, C_6H_6), 2.91 (s, 1H, BC≡C*H*), 2.08, 2.00 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.10 (t, 6H, J = 7 Hz, ethyl CH_3), −5.71 (br s, 2H, B*H*B). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 109.8 (C_2B_4), 94.6 (BC≡*C*H), 87.8 (C_6H_6), 25.3 (ethyl CH_2), 16.4 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 2.9 (s, 1B, *B*C≡CH), −2.1 (d, 2B, J = 134 Hz). IR (KBr pellet, cm^{-1}): 3254 (s), 3082 (w), 2962 (s), 2931 (m), 2902 (m), 2874 (m), 2825 (w), 2519 (s), 2054 (w), 1571 (m), 1487 (m), 1456 (s), 1442 (s), 1431 (m), 1372 (m), 1286 (m), 1079 (w), 1010 (m), 963 (m), 889 (s), 814 (m), 768 (s), 708 (m), 686 (s), 648 (m), 534 (s), 485 (m), 460 (s). CI$^+$-MS: *m/z* (%) 279 ([M$^+$ + H], 100). Anal. Calcd for $C_{14}H_{21}B_3Fe$: C, 60.57; H, 7.63. Found: C, 60.81; H, 7.90.

(C_6H_6)Fe($Et_2C_2B_4H_3$-5-Ph) (8). Into a 50 mL Schlenk flask under dinitrogen, 25 mL of dry, degassed THF and 1.97 mL of a 1.63 M solution of phenyllithium in hexanes (3.21 mmol) were transferred. To this solution was added 438 mg of anhydrous $ZnCl_2$ (3.21 mmol) all at once, and the mixture was stirred. After 0.5 h, 250 mg of **2** (0.642 mmol) and 37 mg of $Pd(PPh_3)_4$ (0.032 mmol) were added and the contents were stirred overnight. Following solvent removal, the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then flash chromatographed through a second 3 cm plug of silica gel with a 1/5 CH_2Cl_2/hexanes solution, affording 167 mg of **8** (77% yield) as an air-stable, oily brown solid. ^{1}H NMR ($CDCl_3$): δ 7.74 (d, 2H, J = 7 Hz, *o*-C_6H_5), 7.30 (t, 2H, J = 7 Hz, *m*-C_6H_5), 7.21 (t, 1H, J = 7 Hz, *p*-C_6H_5), 5.30 (s, 6H, C_6H_6), 2.67, 2.39 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.30 (t, 6H, J = 7 Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.6 (v br, *i*-C_6H_5), 135.2 (*o*-C_6H_5), 127.2 (*m*-C_6H_5), 125.6 (*p*-C_6H_5), 93.8 (C_2B_4), 84.5 (C_6H_6), 24.5 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 16.5 (s, 1B, *B*−Ph), 5.9 (d, 1B, J = 135 Hz), 0.3 (d, 2B, J = 154 Hz). IR (NaCl plate, cm^{-1}): 3051 (m), 2970 (s), 2934 (m), 2874 (m), 2536 (s), 1443 (m), 1430 (m), 1378 (w), 1265 (s), 1065 (w), 981 (w), 894 (w), 887 (w), 865 (w), 852 (w), 810 (m), 739 (s), 704 (s), 604 (w). UV−vis (CH_2Cl_2, nm (%)): 238 (100), 271 (78), 418 (4) ϵ_{max} = 10 800 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 340 ([M$^+$], 100).

(C_6H_6)Fe{$Et_2C_2B_4H_3$-5-[(C_6H_5)Cr(CO)$_3$]} (9). A 15 mL round-bottom flask was charged with 162 mg of $Cr(CO)_6$ (0.736 mmol), 50 mg of **8** (0.15 mmol), and a solution of 0.4 mL of THF in 5 mL of dry, degassed di-*n*-butyl ether. The flask was equipped with a reflux condenser and a N_2 inlet and setup for reflux. After 27 h the now black mixture was cooled to −20 °C and filtered to yield an orange solution. The solvent was removed in vacuo to yield 55 mg of pure **9** (79% yield) as an air-sensitive yellow-brown solid. ^{1}H NMR (C_6D_6): δ 5.63 (d, 2H, $J = 7$ Hz, *o*-C_6H_5), 4.73 (t, 1H, $J = 7$ Hz, *p*-C_6H_5), 4.66 (t, 2H, $J = 7$ Hz, *m*-C_6H_5), 4.86 (s, 6H, C_6H_6), 2.20, 1.94 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.15 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 235.8 (*C*O), 102.5 (*o*-C_6H_5), 93.8 (*p*-C_6H_5), 93.0 (C_2B_4), 92.4 (*m*-C_6H_5), 84.7 (C_6H_6), 24.5 (ethyl CH_2), 15.1 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 13.4 (s, 1B, *B*−Ph), 5.3 (d, 1B, $J = 126$ Hz), 0.5 (d, 2B, $J = 126$ Hz). IR (KBr pellet, cm^{-1}): 3083 (w), 3051 (w), 2977 (m), 2966 (m), 2932 (w), 2908 (w), 2872 (w), 2560 (s), 2543 (s), 1958 (vs), 1895 (vs), 1857 (vs), 1448 (m), 1442 (s), 1378 (m), 815 (m), 665 (s), 634 (s), 535 (s). UV−vis (CH_2Cl_2, nm (%)): 234 (100), 265 (73), 312 (37), 413 (7) $\epsilon_{max} = 20\,100$ cm^{-1} M^{-1}. CI^+-MS: *m*/*z* (%) 476 ([M^-], 23), 339 ([$M^- - Cr(CO)_3$], 100). Anal. Calcd for $C_{21}H_{24}B_4CrFeO_3$: C, 53.05; H, 5.09. Found: C, 53.16; H, 4.97.

$(C_6H_6)Fe(Et_2C_2B_4H_3$-7-Br) (11a). In a 100 mL Schlenk flask under dinitrogen, a solution of 462 mg of $(C_6H_6)Fe(Et_2C_2B_3H_5)$ (**10**; 1.82 mmol) and 45 mL of dry, degassed toluene at 0 °C was treated dropwise with 1.88 mL of a 1.94 M *tert*-butyllithium solution in pentane (3.65 mmol). After 1 h the mixture was warmed to room temperature and stirred for an additional 6 h. The now dark brown solution was cooled to −78 °C, and 2.80 mL of a 1.0 M BBr_3 solution in hexanes (2.8 mmol) was added with immediate precipitation of LiBr. Over a period of 16 h the flask was slowly warmed to room temperature and its contents were stirred overnight. A 1 mL portion of degassed water was added to the light brown solution, and the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and washed first with hexanes to recover 120 mg of **10** and then with dichloromethane. The dichloromethane wash was column chromatographed (15 cm) on silica gel and eluted with a 1:1 CH_2Cl_2/hexanes solution to afford 300 mg of pure **11a** as a brown, air-stable solid (46% yield; 62% based on **10** consumed). ^1H NMR (500 MHz, CD_2Cl_2): δ 5.46 (s, 6H, C_6H_6), 2.44, 2.08 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.40 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ 91.8 (C_2B_4), 85.1 (C_6H_6), 23.9 (ethyl CH_2), 14.4 (ethyl CH_3). ^{11}B NMR ($CDCl_3$, 50 °C): δ 4.0 (d, 1B, $J = 144$ Hz), −0.5 (d, 2B, $J = 156$ Hz), −9.8 (s, 1B, *B*−Br). IR (KBr pellet, cm^{-1}): 3078 (w), 2971 (m), 2931 (w), 2917 (w), 2543 (s), 1454 (m), 1441 (m), 1431 (m), 1382 (w), 1109 (w), 1008 (w), 980 (w), 916 (m), 814 (m), 756 (s), 627 (w), 512 (m), 482 (w). CI^+-MS: *m*/*z* (%) 343 ([$M^+ + 1$], 100). Anal. Calcd for $C_{12}H_{19}B_4BrFe$: C, 42.11; H, 5.60. Found: C, 41.61; H, 5.45.

$(C_6H_6)Fe(Et_2C_2B_4H_3$-7-I) (11b). In a 100 mL Schlenk flask under dinitrogen, a solution of 420 mg of **10** (1.66 mmol) and 45 mL of dry, degassed toluene at 0 °C was treated dropwise with 1.71 mL of a 1.94 M *tert*-butyllithium solution in pentane (3.32 mmol). After 15 min the mixture was warmed to room temperature and was stirred for an additional 6 h. The now dark brown solution was cooled to −78 °C, and 713 mg of BI_3 in 5 mL of toluene (1.82 mmol) was added with immediate precipitation of LiI. Over a period of 20 h the flask was slowly warmed to room temperature and its contents were stirred overnight. A 1 mL portion of degassed water was added to the light brown solution, and the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and washed first with hexanes to recover 53 mg of **10** and then with dichloromethane. The dichloromethane wash was column chromatographed (15 cm) on silica gel and eluted with a 2/3 ethyl acetate/hexanes solution to afford 37 mg of pure **11b** as a brownish yellow, air-stable solid (6% yield; 7% based on **10** consumed). ^1H NMR (500 MHz, $CDCl_3$): δ 5.45 (s, 6H, C_6H_6), 2.42, 2.02 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.44 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 91.0 (C_2B_4), 84.6 (C_6H_6), 24.2 (ethyl CH_2), 14.2 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 4.7 (d, 1B, $J = 151$ Hz), −0.4 (d, 2B, $J = 144$ Hz), −22.7 (s, 1B, *B*−I). IR (KBr pellet, cm^{-1}): 3078 (w), 2966 (m), 2929 (m), 2913 (w), 2541 (s), 1452 (m), 1441 (m), 1380 (w), 1107 (w), 980 (w), 813 (w), 746 (s), 625 (w), 506 (m), 478 (w), 427 (w). CI^+-MS: *m*/*z* (%) 390 ([M^+], 100).

$(C_6H_6)Fe(Et_2C_2B_4H_3$-7-C≡CSiMe$_3$) (12). Method A. In a 100 mL Schlenk flask under dinitrogen, a solution of 441 mg of **10** (1.74 mmol) and 30 mL of dry, degassed toluene at 0 °C was treated dropwise with 1.65 mL of a 2.11 M *tert*-butyllithium solution in pentane (3.48 mmol). After 1 h the mixture was warmed to room temperature and stirred for an additional 6 h. The now dark brown solution was cooled to 0 °C, and 760 mg of $[(C_6H_4O_2)B]C{\equiv}CSiMe_3$ (3.52 mmol) dissolved in 3 mL of toluene was added. Over a period of 5 h the flask was warmed to room temperature and its contents were stirred overnight. A 5 mL portion of degassed water was added to the cloudy solution, and the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and washed first with hexanes to recover 345 mg of **10** and then with dichloromethane. The dichloromethane wash was column chromatographed (15 cm) on silica gel and eluted with a 1:1 CH_2Cl_2/hexanes solution to afford 128 mg of pure **12** as a brown, air-stable crystalline solid (20% yield; 94% based on **10** consumed).

Method B. In a 50 mL Schlenk flask under dinitrogen, a solution of 35 mg of (trimethylsilyl)acetylene (0.36 mmol) and 3 mL of dry, degassed THF at 0 °C was treated dropwise with 0.20 mL of a 1.53 M *n*-butyllithium solution in hexanes (0.31 mmol). After 0.5 h 43 mg of anhydrous $ZnCl_2$ (0.32 mmol) was added all at once and the mixture was stirred for an additional 0.5 h at room temperature. To the resulting solution were added 40 mg of **11b** (0.10 mmol) and 6 mg of $Pd(PPh_3)_4$ (0.005 mmol), and the contents were stirred for 17 h. The THF was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/2 CH_2Cl_2/hexanes solution, affording 31.4 mg of **12** (85% yield).

Method C. In a 5 mL Schlenk flask under dinitrogen, a solution of 126 mg of (trimethylsilyl)acetylene (1.28 mmol) and 1 mL of dry, degassed THF at 0 °C was treated dropwise with 0.76 mL of a 1.53 M *n*-butyllithium solution in hexanes (1.2 mmol). After 0.5 h 164 mg of anhydrous $ZnCl_2$ (1.20 mmol) was added all at once, and the mixture was stirred for an additional 0.5 h at room temperature. The solvent was removed with a stream of dry dinitrogen and the residue resuspended in 1 mL of fresh THF. The contents of the flask were transferred to a Pyrex tube equipped with a Teflon stopcock that contained 133 mg of **11a** (0.389 mmol) and 35 mg of $Pd(PPh_3)_4$ (0.030 mmol). The stopcock was closed, and the mixture was stirred for 87 h at 55 °C. The mixture was quenched with 1 mL of water, and the solvent was removed in vacuo. The residue was washed through 3 cm of silica with dichloromethane, and the crude material was then extracted with 1/5 CH_2Cl_2/hexanes solution to recover **11a**. The remaining solid was chromatographed on silica gel TLC plates with a 2/3 ethyl acetate/hexanes solution, affording 33 mg of **12** as the first major band (24% yield; 98% based on **11a** consumed). ^1H NMR ($CDCl_3$): δ 5.40 (s, 6H, C_6H_6), 2.58, 2.33 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.39 (t, 6H, $J = 7$ Hz, ethyl CH_3), −0.05 (s, 9H, SiMe_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 94.3 (C_2B_4), 94.6 (BC≡*C*SiMe$_3$), 84.2 (C_6H_6), 24.3 (ethyl CH_2), 14.3 (ethyl CH_3), −0.4 (SiMe_3). ^{11}B NMR ($CDCl_3$): δ 5.5 (d, 1B, $J = 103$ Hz), 0.6 (d, 2B, $J = 142$ Hz), −1.2 (s, 1B, *B*C≡CSiMe$_3$). IR (KBr pellet, cm^{-1}): 3069 (w), 2972 (s), 2933 (m), 2896 (w), 2874 (w), 2530 (s), 2512 (m), 2501 (s), 2125 (vw), 1444 (m), 1377 (w), 1248 (s), 1170 (m), 1142 (s), 1116 (m), 1064 (w), 893 (m), 860 (s), 806 (s), 760 (m). UV−vis (CH_2Cl_2, nm (%)): 230 (61), 272 (100) $\epsilon_{max} = 20\,000$ cm^{-1} M^{-1}. CI^+-MS: *m*/*z* (%) 359 ([$M^+ - 1$], 80). Anal. Calcd for $C_{17}H_{28}B_4FeSi$: C, 56.78; H, 7.85. Found: C, 56.75; H, 7.69.

$(C_6H_6)Fe(Et_2C_2B_4H_3$-7-C≡CH) (13). In a 50 mL Schlenk flask under dinitrogen, 90 mg of **12** (0.25 mmol) was dissolved in 10 mL of dry, degassed THF and cooled to 0 °C. To this with stirring was added 0.26 mL of a 1.0 M of TBAF solution (0.26 mmol) with an immediate red color formation. After 1.5 h the mixture was warmed to room temperature and stirred for an additional 2 h. The solvent was removed in vacuo, and the remaining crude material was flash chromatographed through a 3 cm plug of silica gel with dichloromethane to afford 68 mg of pure **13** (95% yield) as an air-stable, red-brown crystalline solid. ^1H NMR ($CDCl_3$): δ 5.42 (s, 6H, C_6H_6), 2.57, 2.31 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.61 (s, 1H, $C\equiv CH$), 1.41 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 93.8 (C_2B_4), 84.3 (C_6H_6), 76.1 ($BC\equiv CH$), 24.2 (ethyl CH_2), 14.4 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 5.5 (d, 1B, $J =$ 146 Hz), 0.4 (d, 2B, $J = 154$ Hz), -1.7 (s, 1B, $BC\equiv CH$). IR (KBr pellet, cm^{-1}): 3256 (s), 3076 (w), 2971 (m), 2933 (m), 2874 (w), 2539 (s), 2509 (s), 2055 (m), 1444 (s), 1382 (w), 1154 (w), 1126 (w), 1068 (w), 980 (w), 893 (w), 789 (s), 699 (m), 681 (m). CI^+-MS: m/z (%) 288 ([M^+], 95).

$(C_6H_6)Fe(Et_2C_2B_4H_3\text{-5-I-7-}C\equiv CSiMe_3)$ (14). In a 50 mL Schlenk flask under dinitrogen, 74 mg of **12** (0.21 mmol) was dissolved in 10 mL of dry dichloromethane and the solution cooled to 0 °C. To this solution was added, with rapid stirring, 47 mg of *N*-iodosuccinimide (0.21 mmol) dissolved in 4 mL of dichloromethane dropwise over a period of 15 min. After 1 h the mixture was warmed to room temperature and stirred for an additional 1 h. The resulting solution was then passed through a 3 cm column of silica gel with dichloromethane to give 102 mg of crude material. Chromatography on silica gel TLC plates developed with a 1:1 dichloromethane/hexanes solution afforded 94 mg of **14** (94% yield) as an air-stable red-brown solid. ^1H NMR (500 MHz, $CDCl_3$): δ 5.45 (s, 6H, C_6H_6), 2.54, 2.28 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.37 (t, 6H, $J =$ 7 Hz, ethyl CH_3), -0.03 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 96.5 ($BC\equiv CSiMe_3$), 95.2 (C_2B_4), 85.7 (C_6H_6), 23.9 (ethyl CH_2), 14.2 (ethyl CH_3), -0.5 ($BC\equiv CSiMe_3$). ^{11}B NMR ($CDCl_3$): δ 2.2 (d, 2B, $J = 137$ Hz), -0.6 (s, 1B, $BC\equiv CSiMe_3$), -2.0 (s, 1B, $B-I$). IR (KBr pellet, cm^{-1}): 3074 (w), 2973 (m), 2931 (w), 2564 (m), 1459 (w), 1443 (m), 1246 (m), 1154 (m), 1118 (w), 1028 (w), 896 (w), 861 (s), 841 (s), 811 (m), 761 (m), 623 (w). CI^+-MS: m/z (%) 486 ([M^+], 100).

$(C_6H_6)Fe(Et_2C_2B_4H_2\text{-5-I-7-}C\equiv CH)$ (15). Using a procedure analogous to that described above for $(C_6H_6)Fe(Et_2C_2B_4H_3\text{-5-}C\equiv CH)$, 94 mg of **14** (0.19 mmol) was desilylated with 0.21 mL of 1.0 M TBAF solution (0.21 mmol). After flash chromatography with dichloromethane the crude material was chromatographed on silica gel TLC plates developed with a 1:1 dichloromethane/hexanes solution to afford 77 mg of **15** (96% yield) as an air-stable, red-brown solid. ^1H NMR ($CDCl_3$): δ 5.48 (s, 6H, C_6H_6), 2.54, 2.28 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.71 (s, 1H, $C\equiv CH$), 1.39 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 95.2 (C_2B_4), 86.3 (C_6H_6), 77.9 ($BC\equiv CH$), 24.2 (ethyl CH_2), 14.5 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 2.0 (d, 2B, $J = 156$ Hz), -0.6 (s, 1B, $BC\equiv CH$), -2.6 (s, 1B, $B-I$). IR (KBr pellet, cm^{-1}): 3287 (s), 3067 (w), 2970 (s), 2931 (m), 2870 (m), 2579 (m), 2546 (s), 2060 (w), 1442 (s), 1376 (m), 1348 (w), 1295 (w), 1139 (m), 1113 (m), 1004 (s), 981 (m), 897 (m), 847 (m), 807 (s), 790 (m), 679 (s), 649 (s), 612 (m). CI^+-MS: m/z (%) 415 ([$M^+ + H$], 100).

$(C_6H_6)Fe(Et_2C_2B_4H_2\text{-7-}C\equiv CH\text{-5-}C\equiv CSiMe_3)$ (16). Using a procedure analogous to that described above for $(C_6H_6)Fe(Et_2C_2B_4H_3\text{-7-}C\equiv CSiMe_3)$ (method B), 61 mg of (trimethylsilyl)acetylene (0.62 mmol) was deprotonated with 0.37 mL of a 1.53 M *n*-butyllithium solution in hexanes (0.57 mmol). After 0.5 h 79 mg of anhydrous $ZnCl_2$ (0.58 mmol) was added and the mixture was stirred. Following an additional 0.5 h, 77 mg of **15** (0.19 mmol) and 11 mg of $Pd(PPh_3)_4$ (0.0095 mmol) were added and the contents were stirred for 17 h. The THF was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/2 CH_2Cl_2/hexanes solution, affording 49 mg of **16** (69% yield). ^1H NMR ($CDCl_3$): δ 5.45 (s, 6H, C_6H_6), 2.52, 2.26 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.63 (s, 1H, $C\equiv CH$), 1.38 (t, 6H, $J = 7$ Hz, ethyl CH_3), 0.23 (s, 9H, $C\equiv CSiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.6 ($BC\equiv CSiMe_3$), 93.9 (C_2B_4), 85.2 (C_6H_6), 76.8 ($BC\equiv CH$), 23.9 (ethyl CH_2), 14.4 (ethyl CH_3), 0.8 ($BC\equiv CSiMe_3$). ^{11}B NMR ($CDCl_3$): δ 4.0 (s, 1B, $BC\equiv CSiMe_3$), 0.9 (d, 2B, $J = 120$ Hz), -1.8 (s, 1B, $BC\equiv CH$). IR (KBr pellet, cm^{-1}): 3270 (w), 3078 (w), 2966 (s), 2933 (m), 2553 (s), 2106 (m), 2061 (w), 1443 (m), 1379 (w), 1246 (s), 1189 (m), 1127 (w), 1058 (m), 981 (w), 901 (s), 854 (vs), 840 (vs), 806 (s), 758 (s), 701 (m), 652 (m). CI^+-MS: m/z (%) 457 ([$M^+ + SiMe_3$], 35), 444 ([$M^+ + SiMe_2$], 100), 387 ([$M^+ + H$], 20).

$[(C_6H_6)Fe(Et_2C_2B_4H_3)\text{-5-}]_2$ (17). In a 50 mL Schlenk flask under dinitrogen, 100 mg of **2** (0.257 mmol) was dissolved in 10 mL of dry, degassed 1,2-dimethoxyethane and 147 mg of a dispersion of K on silica gel was added (1.29 mmol). After 4 h, 2 mL of distilled water was added to the now dark brown solution and the contents were washed through 3 cm of silica gel with dichloromethane. Following solvent removal, the residue was exposed to the air for 5 h and then was washed through an additional 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/5 CH_2Cl_2/hexanes solution, affording 9 mg of **17** as an air-stable brown solid. ^1H NMR ($CDCl_3$): δ 5.32 (s, 12H, C_6H_6), 2.66, 2.38 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 1.32 (t, 12H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 92.2 (C_2B_4), 84.0 (C_6H_6), 24.7 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 17.0 (s, 2B, $B-B$), 6.0 (d, 2B, $J = 129$ Hz), 1.3 (d, 4B, $J = 134$ Hz). IR (KBr pellet, cm^{-1}): 3072 (w), 2963 (s), 2929 (m), 2870 (m), 2833 (w), 2535 (s), 2519 (s), 2484 (s), 1453 (m), 1439 (m), 1373 (m), 1008 (m), 977 (m), 881 (m), 861 (m), 805 (s), 506 (m), 485 (m), 423 (m). UV−vis (CH_2Cl_2, nm (%)): 260 (100), 317 (60), 423 (13) $\epsilon_{max} = 15\,600$ cm^{-1} M^{-1}. CI^+-MS: m/z (%) 526 ([M^+], 100). Anal. Calcd for $C_{24}H_{38}B_8Fe_2$: C, 54.93; H, 7.30. Found: C, 54.74; H, 7.44.

$[(C_6H_6)Fe(Et_2C_2B_4H_3)\text{-5-}]_2C_4H_2S$ (18). In a 50 mL Schlenk flask under dinitrogen, a solution of 47 mg of 2,5-dibromothiophene (0.19 mmol) and 10 mL of dry, degassed THF at -78 °C was treated dropwise with 0.37 mL of a 1.57 M *n*-butyllithium solution in hexanes (0.58 mmol). After 2 h, 53 mg of anhydrous $ZnCl_2$ (0.39 mmol) in 1 mL of THF was added. After 1 h the mixture was warmed to room temperature and stirred for an additional 1 h. To the now cloudy mixture were transferred 150 mg of **2** (0.385 mmol) and 23 mg of $Pd(PPh_3)_4$ (0.020 mmol), and the contents were stirred overnight. The solvent was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1:1 CH_2Cl_2/hexanes solution, producing four bands. The last band afforded 35 mg of **18** as an air-stable, red crystalline solid (30% yield). ^1H NMR ($CDCl_3$): δ 7.27 (s, 2H, C_4H_2S), 5.32 (s, 12H, C_6H_6), 2.67, 2.39 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 1.30 (t, 12H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.0 (3,4-C_4H_2S), 93.3 (C_2B_4), 84.8 (C_6H_6), 24.5 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 12.5 (s, 2B, $B-C_4H_2S-B$), 5.8 (2B, BH unresolved), 0.2 (d, 4B, $J = 110$ Hz). IR (KBr pellet, cm^{-1}): 3065 (w), 2967 (m), 2931 (m), 2872 (w), 2535 (vs), 1441 (m), 1378 (w), 1236 (m), 979 (w), 891 (w), 862 (w), 828 (w), 813 (m), 484 (m), 418 (w). UV−vis (CH_2Cl_2, nm (%)): 270 (100), 337 (40), 375 (36), 421 (sh, 15) $\epsilon_{max} = 21\,000$ cm^{-1} M^{-1}. CI^+-MS: m/z (%) 608 ([M^+], 100). Anal. Calcd for $C_{28}H_{40}B_8Fe_2S$: C, 55.42; H, 6.64. Found: C, 56.14; H, 6.90.

$[(C_6H_6)Fe(Et_2C_2B_4H_3)\text{-5-}]_2C_{14}H_{10}$ (19). In a 50 mL Schlenk flask under dinitrogen, a solution of 65 mg of 2,7-dibromo-9,-10-dihydrophenanthrene (0.19 mmol) and 10 mL of dry, degassed THF at -78 °C was treated dropwise with 0.37 mL of a 1.57 M *n*-butyllithium solution in hexanes (0.58 mmol). After 1 h, 53 mg of anhydrous $ZnCl_2$ (0.39 mmol) in 1 mL of THF was added. After 1 h the mixture was warmed to room temperature and stirred for an additional 1 h. To the now cloudy mixture 150 mg of **2** (0.385 mmol) and 22 mg of $Pd(PPh_3)_4$ (0.019 mmol) were transferred, and the contents were stirred overnight. The solvent was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1:1 CH_2Cl_2/hexanes solution, producing four bands. The last two bands afforded 35 mg of **2** and 43 mg of **19**, respectively. **19** is an air-stable red crystalline solid (32% yield; 41% based on **2** consumed). ^1H NMR ($CDCl_3$): δ 7.73 (d, 2H, $J = 8$ Hz, 3,6-$C_{14}H_{10}$), 7.65 (d, 2H, $J = 8$ Hz, 4,5-$C_{14}H_{10}$), 7.56 (s, 2H, 1,8-$C_{14}H_{10}$), 5.34 (s, 12H, C_6H_6), 2.94 (s, 4H, 9,10-$C_{14}H_{10}$), 2.69, 2.40 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 1.31 (t, 12H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.7, 133.7 (*o*-C_6H_3), 122.3 (*m*-C_6H_3), 135.9, 133.0 (quat C's), 93.9 (C_2B_4), 84.5 (C_6H_6), 29.6 (C_2H_4), 24.6 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 16.9 (s, 2B, $B{-}C_{14}H_{10}{-}B$), 5.8 (2B, BH unresolved), 0.4 (4B, BH unresolved). IR (KBr pellet, cm^{-1}): 3073 (w), 2963 (s), 2930 (m), 2870 (m), 2832 (w), 2534 (vs), 1474 (w), 1442 (m), 1376 (w), 1287 (w), 1259 (m), 981 (w), 885 (w), 862 (w), 824 (m), 808 (m), 792 (w), 486 (m), 427 (w). UV−vis (CH_2Cl_2, nm (%)): 229 (100), 279 (87), 331 (79), 422 (9) $\epsilon_{max} = 29\,700$ cm^{-1} M^{-1}. CI^+-MS: *m*/*z* (%) 703 ([$M^+ - H$], 3), 441 ([$M^+ - (Et_2C_2B_4H_3)FeC_6H_6$], 100). Anal. Calcd for $C_{38}H_{48}B_8Fe_2$: C, 64.93; H, 6.88. Found: C, 64.09; H, 6.84.

$(C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}Fc)$ (20) and $[(C_6H_6)Fe(Et_2C_2B_4H_3)\text{-}5\text{-}C_5H_4]_2Fe$ (21). In a 50 mL Schlenk flask under dinitrogen, 32 mg of $[(C_5H_4Li)_2Fe](TMEDA)_{2/3}$ (0.12 mmol) was dissolved in 7 mL of dry, degassed THF and 16 mg of extra-dry $ZnCl_2$ (0.12 mmol) was added. After 0.5 h, 92 mg of **2** (0.24 mmol) and 14 mg of $Pd(PPh_3)_4$ (0.012 mmol) were added. After the mixture was stirred for 16 h, the solvent was removed in vacuo and the crude material was then chromatographed in a drybox on silica gel TLC plates with a 1/1 toluene/hexanes solution, producing four bands. The last three bands afforded 14 mg of **20** (21% based on **2** consumed) as an air-sensitive red oil, 31 mg of **21** (30% based on **2** consumed) as a air-sensitive red solid, and 35 mg of **2**, respectively. Data for **20** are as follows. ^1H NMR ($CDCl_3$): δ 5.22 (s, 6H, C_6H_6), 4.27, 4.24 (t, 2H, $J = 2$ Hz, C_5H_4), 3.98 (s, 5H, C_5H_5), 2.65, 2.39 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 1.31 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 93.0 (C_2B_4), 84.2 (C_6H_6), 68.3 ($C_5H_5FeC_5H_4$), 74.3, 69.2 ($C_5H_5FeC_5H_4$), 24.5 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 16.3 (s, 1B, $B{-}Fc$), 5.4 (d, 1B, $J = 145$ Hz), −0.4 (d, 2B, $J = 140$ Hz). IR (NaCl plate, cm^{-1}): 3080 (m), 3066 (m), 2967 (s), 2932 (m), 2909 (m), 2873 (m), 2537 (vs), 1441 (s), 1380 (m), 1265 (s), 1104 (s), 1019 (s), 1000 (m), 979 (m), 887 (m), 863 (m), 828 (m), 810 (vs), 739 (s). UV−vis (CH_2Cl_2, nm (%)): 229 (100), 269 (78), 413 (8), 481 (5). CI^+-MS: *m*/*z* (%) 448 ([M^+], 100). Anal. Calcd for $C_{22}H_{28}B_4Fe_2$: C, 59.06; H, 6.31. Found: C, 59.32; H, 5.94. Data for **21** are as follows. ^1H NMR (d_8-THF, 500 MHz): δ 5.23 (s, 12H, C_6H_6), 4.04, 3.90 (t, 4H, $J = 2$ Hz, C_5H_4), 2.71, 2.41 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 1.33 (t, 12H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR (d_8-THF): δ 93.5 (C_2B_4), 85.3 (C_6H_6), 74.7, 71.2 ($C_5H_4FeC_5H_4$), 25.2 (ethyl CH_2), 15.4 (ethyl CH_3). ^{11}B NMR (d_8-THF): δ 17.0 (s, 2B, $B{-}Fc{-}B$), 4.8 (d, 2B, $J = 129$ Hz), −0.8 (d, 4B, $J = 93$ Hz). IR (KBr pellet, cm^{-1}): 3091 (m), 2963 (s), 2931 (s), 2869 (s), 2527 (s), 1732 (s), 1442 (s), 1375 (m), 1253 (s), 1151 (m), 1073 (m), 1063 (m), 1013 (s), 981 (m), 886 (m), 875 (m), 859 (m), 810 (s), 691 (m), 650 (m), 542 (m), 483 (s), 424 (m). UV−vis (Et_2O, nm (%)): 229 (100), 267 (95), sh 305 (58), 465 (14) $\epsilon_{max} = 20\,000$ cm^{-1} M^{-1}. CI^+-MS: *m*/*z* (%) 710 ([M^+], 100).

$[(C_6H_6)Fe(Et_2C_2B_4H_3)\text{-}5\text{-}]_2C_6H_4$ (22). In a 50 mL Schlenk flask under dinitrogen, a solution of 38 mg of 1,4-dibromobenzene (0.16 mmol) and 10 mL of dry, degassed diethyl ether at −78 °C was treated dropwise with 0.33 mL of a 1.93 M *n*-butyllithium solution in hexanes (0.64 mmol). After 10 min the mixture was warmed to room temperature and stirred for an additional 2 h. Following solvent removal, the residue was redissolved in 10 mL of THF and 44 mg of anhydrous $ZnCl_2$ (0.32 mmol) was added. After 1 h, into the now cloudy mixture 125 mg of **2** (0.321 mmol) and 19 mg of $Pd(PPh_3)_4$ (0.016 mmol) were transferred, and the contents were stirred overnight. The solvent was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 22% CH_2Cl_2/88% hexanes solution, producing five bands. The last two bands afforded 35 mg of **2** and 24 mg of **22**, respectively. **22** is an air-stable red crystalline solid (25% yield; 35% based on **2** consumed). ^1H NMR ($CDCl_3$): δ 7.67 (s, 4H, C_6H_4), 5.29 (s, 12H, C_6H_6), 2.68, 2.40 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 1.31 (t, 12H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.5 (2,3,5,6-C_6H_4), 93.7 (C_2B_4), 84.5 (C_6H_6), 24.6 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 17.5 (s, 2B, $B{-}C_6H_4{-}B$), 6.2 (2B, BH unresolved), 0.3 (d, 4B, $J = 135$ Hz). IR (KBr pellet, cm^{-1}): 3082 (w), 3035 (w), 2985 (m), 2962 (s), 2929 (m), 2870 (m), 2540 (vs), 2521(vs), 1441 (s), 1378 (w), 1006 (m), 866 (m), 847 (m), 819 (s), 807 (s), 601 (w), 486 (m), 424 (m), 407 (m). UV−vis (CH_2Cl_2, nm (%)): 249 (96), 257 (100), 324 (44), 354 (sh, 29), 418 (8) $\epsilon_{max} = 25\,800$ cm^{-1} M^{-1}. CI^+-MS: *m*/*z* (%) 601 ([$M^- - H$], 3), 339 ([$M^- - (Et_2C_2B_4H_3)FeC_6H_6$], 100). Anal. Calcd for $C_{30}H_{42}B_8Fe_2$: C, 59.97; H, 7.05. Found: C, 59.72; H, 6.89.

$[(C_6H_6)Fe(Et_2C_2B_4H_3)\text{-}5\text{-}]_2(C_6H_4)_2$ (23). In a 50 mL Schlenk flask under dinitrogen, a solution of 60 mg of 4,4′-dibromobiphenyl (0.19 mmol) and 10 mL of dry, degassed THF at −78 °C was treated dropwise with 0.37 mL of a 1.57 M *n*-butyllithium solution in hexanes (0.58 mmol). After 1 h, 53 mg of anhydrous $ZnCl_2$ (0.39 mmol) in 1 mL of THF was added. After 1 h the mixture was warmed to room temperature and stirred for an additional 1 h. To the now cloudy mixture were transferred 150 mg of **2** (0.385 mmol) and 22 mg of $Pd(PPh_3)_4$ (0.019 mmol), and the contents were stirred overnight. The solvent was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/2 CH_2Cl_2/hexanes solution, producing four bands. The last two bands afforded 39 mg of **2** and 29 mg of air-stable red crystalline **23** (22% yield; 30% based on **2** consumed). ^1H NMR ($CDCl_3$): δ 7.79 (d, 4H, $J = 8$ Hz, 3,5,3′,5′-C_6H_4), 7.60 (d, 4H, $J = 8$ Hz, 2,6,2′,6′-C_6H_4), 5.34 (s, 12H, C_6H_6), 2.69, 2.40 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 1.31 (t, 12H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.5 (3,5,3′,5′-C_6H_4), 125.8 (2,6,2′,6′-C_6H_4), 139.3 (1,1′-C_6H_4), 93.9 (C_2B_4), 84.5 (C_6H_6), 24.6 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 16.4 (s, 2B, $BC_{12}H_8B$), 5.4 (2B, BH unresolved), 0.1 (4B, BH unresolved). IR (KBr pellet, cm^{-1}): 3059 (w), 3008 (w), 2964 (s), 2929 (m), 2869 (m), 2530 (vs), 1486 (w), 1442 (s), 1376 (m), 1260 (m), 1064 (m), 1005 (m), 980 (m), 885 (w), 851 (m), 817 (s), 603 (w), 557 (w), 486 (w). UV−vis (CH_2Cl_2; nm (%)): 275 (100), 319 (sh, 69), 422 (6) $\epsilon_{max} = 26\,600$ cm^{-1} M^{-1}. CI^+-MS: *m*/*z* (%) 678 ([M^-], 43), 416 ([$MH^- - (Et_2C_2B_4H_3)FeC_6H_6$], 100).

$[(C_6H_6)Fe(Et_2C_2B_4H_3)\text{-}5\text{-}]_2(C_6H_4)_3$ (24). In a 50 mL Schlenk flask under dinitrogen, a slurry of 75 mg of 4,4″-dibromo-*p*-terphenyl (0.19 mmol) and 10 mL of dry, degassed THF at −78 °C was treated dropwise with 0.37 mL of a 1.57 M *n*-butyllithium solution in hexanes (0.58 mmol). After 1 h the mixture was warmed to room temperature and stirred for an additional 0.5 h. The flask was then recooled to −78 °C, and 53 mg of anhydrous $ZnCl_2$ (0.39 mmol) in 1 mL THF was added. After 1 h the mixture was warmed to room temperature and stirred for an additional 0.75 h. To the cloudy mixture were added 150 mg of **2** (0.385 mmol) and 22 mg of $Pd(PPh_3)_4$ (0.019 mmol), and the contents were stirred overnight. The solvent was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/2 CH_2Cl_2/hexanes solution, producing three bands. The last two bands afforded 65 mg of **2** and 25 mg of **24**, respectively. **24** is an air-stable brown crystalline solid (17% yield; 30% based on **2** consumed). ^1H NMR ($CDCl_3$): δ 7.81 (d, 4H, $J = 8$ Hz, 3,5,3″,5″-C_6H_4), 7.60 (d, 4H, $J = 8$ Hz, 2,6,2″,6″-C_6H_4), 7.74 (s, 4H, 2′,3′,5′,6′-C_6H_4), 5.35 (s, 12H, C_6H_6), 2.69, 2.41 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 1.31 (t, 12H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.6 (3,5,3″,5″-C_6H_4), 127.1 (2,6,2″,6″-C_6H_4), 125.9 (2′,3′,5′,6′-C_6H_4), 140.3, 138.1

(1,1′,4′,1′′-C_6H_4), 94.0 (C_2B_4), 84.5 (C_6H_6), 24.6 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 16.4 (s, 2B, $BC_{18}H_{12}B$), 5.4 (2B, BH unresolved), 0.5 (4B, BH unresolved). IR (KBr pellet, cm^{-1}): 3066 (w), 3010 (w), 2965 (s), 2930 (m), 2870 (m), 2531 (vs), 1485 (m), 1442 (m), 1377 (w), 1256 (w), 1004 (m), 980 (w), 886 (w), 854 (m), 814 (vs), 551 (w), 486 (m), 425 (w). UV−vis (CH_2Cl_2, nm (%)): 230 (68), 278 (72), 318 (100), 422 (4) ϵ_{max} = 34 000 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 753 ([M$^+$ − H], 74), 676 ([M$^+$ − C_6H_6], 100), 597 ([M$^+$ − H(C_6H_6)$_2$], 72).

$(C_6H_6)Fe(Et_2C_2B_4H_3$-5-Ph$)Fe(Et_2C_2B_4H_4)$ (25). Into a 2 mL sealed-end Pyrex tube, 50 mg of $(C_6H_6)Fe(Et_2C_2B_4H_3$-5-Ph) (**8**; 0.15 mmol) and 200 mg of $(C_8H_{10})Fe(Et_2C_2B_4H_4)$ (0.686 mmol) were placed. The tube was sealed with a torch in vacuo and immersed in a 180 °C oil bath for 20 min. After it was cooled, the tube was opened, and its contents were extracted with CH_2Cl_2. The extract was then column chromatographed (15 cm) on silica gel using a 1/1 CH_2Cl_2/hexanes solution to afford 65 mg of **25** (84% yield) as a brown, air-stable solid. ^{1}H NMR ($CDCl_3$): δ 5.55 (dist d, 2H, *J* = 3 Hz, *o*-C_6H_5), 5.42 (dist d, 3H, *m*,*p*-C_6H_5), 5.33 (s, 6H, C_6H_6), 2.66, 2.59, 2.38, 2.21 (sextet, 2H, *J* = 7 Hz, ethyl CH_2), 1.31, 1.16 (t, 6H, *J* = 7 Hz, ethyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 93.2, 91.4 (C_2B_4), 89.7 (*o*-C_6H_5), 84.6 (C_6H_6), 82.9 (*m*-C_6H_5), 82.1 (*p*-C_6H_5), 24.5, 24.3 (ethyl CH_2), 15.1, 14.9 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 14.8 (s, 1B, *B*−Ph), 5.5 (1B, unresolved), 4.2 (1B, unresolved), 3.5 (1B, unresolved), 0.7 (d, 4B, *J* = 137 Hz). IR (KBr pellet, cm^{-1}): 3071 (m), 2964 (s), 2929 (s), 2870 (s), 2836 (m), 2533 (s), 1442 (s), 1400 (m), 1375 (s), 1275 (s), 1245 (s), 1011 (s), 891 (m), 872 (s), 833 (s), 814 (s), 790 (m), 488 (s), 427 (s), 403 (m). UV−vis (CH_2Cl_2, nm (%)): 229 (81), 273 (100), 366 (9), 422 (4) ϵ_{max} = 19 500 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 526 ([M$^+$], 100). Anal. Calcd for $C_{24}H_{38}B_8Fe_2$: C, 54.93; H, 7.30. Found: C, 55.06; H, 7.14.

$(C_6H_6)Fe(Et_2C_2B_4H_3$-5-Ph$)Fe(Et_2C_2B_4H_3$-5-I) (26). In a 50 mL Schlenk flask under dinitrogen, 50 mg of **25** (0.095 mmol) was dissolved in 10 mL of dry dichloromethane and cooled to 0 °C. To this solution was added 22 mg of *N*-iodosuccinimide (0.098 mmol), with a subsequent color change to red. After 0.5 h the mixture was warmed to room temperature and stirred for an additional 1 h. The resulting solution was then passed through a 3 cm column of silica gel with dichloromethane to give 60 mg (97% yield) of air-stable dark-red crystalline **26**. ^{1}H NMR ($CDCl_3$): δ 5.52 (s, 5H, C_6H_5), 5.29 (s, 6H, C_6H_6), 2.66, 2.54, 2.39, 2.13 (sextet, 2H, *J* = 7 Hz, ethyl CH_2), 1.32, 1.10 (t, 6H, *J* = 7 Hz, ethyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 93.3, 92.7 (C_2B_4), 90.3 (*o*-C_6H_5), 85.6 (*p*-C_6H_5), 84.7 (C_6H_6), 84.6 (*m*-C_6H_5), 24.5, 23.8 (ethyl CH_2), 15.0, 14.9 (ethyl CH_3). ^{11}B NMR (160.4 MHz, $CDCl_3$): δ 13.8 (s, 1B, *B*−Ph), 5.3 (1B, BH unresolved), 0.9 (6B, BH unresolved). IR (KBr pellet, cm^{-1}): 3068 (w), 2965 (s), 2931 (m), 2869 (m), 2549 (vs), 1443 (m), 1374 (m), 1013 (m), 886 (w), 861 (m), 838 (m), 829 (m), 810 (m), 534 (w), 480 (m), 409 (m). UV−vis (CH_2Cl_2, nm (%)): 230 (84), 271 (100), 363 (sh, 15), 419 (6) ϵ_{max} = 24 300 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 651 ([M$^+$ − H], 48), 574 ([M$^+$ − C_6H_6], 87).

$(C_6H_6)Fe(Et_2C_2B_4H_3$-5-Ph$)Fe(Et_2C_2B_4H_3$-5-Ph) (27). Into a 50 mL Schlenk flask under dinitrogen, 10 mL of dry, degassed THF and 44 mg of anhydrous $ZnCl_2$ (0.32 mmol) were placed. To this solution was added 0.19 mL of a 1.63 M solution of phenyllithium in hexanes (0.31 mmol) dropwise, and the contents were stirred. After 0.5 h, 40 mg of **26** (0.061 mmol) and 6 mg of $Pd(PPh_3)_4$ (0.005 mmol) were added and the contents were stirred overnight. A 1 mL portion of distilled water was added to the brown solution, and the solvent was removed in vacuo. The remaining residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/1 CH_2Cl_2/hexanes solution, affording 25 mg of **27** (68% yield) as an air-stable, oily brown solid. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, 2H, *J* = 7 Hz, *o*-C_6H_5), 7.28 (t, 2H, *J* = 7 Hz, *m*-C_6H_5), 7.16 (t, 1H, *J* = 7 Hz, *p*-C_6H_5), 5.48 (d, 2H, *J* = 6 Hz, *o*-C_6H_5), 5.41 (t, 2H, *J* = 6 Hz, *m*-C_6H_5), 5.28 (t, 1H, *J* = 6 Hz, *p*-C_6H_5), 5.18 (s, 6H, C_6H_6), 2.66, 2.58, 2.40, 2.19 (sextet, 2H, *J* = 7 Hz, ethyl CH_2), 1.33, 1.15 (t, 6H, *J* = 7 Hz, ethyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 135.3, 90.0 (*o*-C_6H_5), 126.9, 83.3 (*m*-C_6H_5), 125.0, 83.6 (*p*-C_6H_5), 93.3, 92.8 (C_2B_4), 84.5 (C_6H_6), 24.5, 24.1 (ethyl CH_2), 15.1, 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 14.8 (s, 2B, *B*−Ph), 5.4 (1B, unresolved), 3.8 (1B, unresolved), 0.5 (4B, unresolved). IR (KBr pellet, cm^{-1}): 3059 (w), 2964 (s), 2929 (s), 2870 (m), 2529 (s), 1443 (s), 1375 (s), 1275 (m), 1245 (s), 1010 (m), 889 (m), 855 (s), 833 (m), 812 (s), 767 (m), 703 (s), 604 (m), 489 (s), 426 (s). UV−vis (CH_2Cl_2, nm (%)): 232 (95), 272 (100), 319 (sh, 37), 413 (7) ϵ_{max} = 19 700 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 602 ([M$^+$], 96), 524 ([M$^+$ − C_6H_6], 100).

$(C_6H_6)Fe(Et_2C_2B_4H_3$-5-Ph$)Fe(Et_2C_2B_4H_3$-5-Ph$)Fe(Et_2C_2B_4H_4)$ (28). Using a procedure analogous to that described above for $(C_6H_6)Fe(Et_2C_2B_4H_3$-5-Ph$)Fe(Et_2C_2B_4H_4)$, 40 mg of **27** (0.067 mmol) was reacted with 100 mg of (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) (0.343 mmol) for 20 min at 190 °C. The crude extract was then chromatographed on silica gel TLC plates with a 1/2 CH_2Cl_2/hexanes solution, affording 38 mg of **28** (73% yield) as an air-stable red solid. ^{1}H NMR ($CDCl_3$): δ 5.58 (q, 2H, *J* = 2 Hz, *o*-C_6H_5), 5.46 (t, 3H, *J* = 2 Hz, *m*,*p*-C_6H_5), 5.40 (d, 2H, *J* = 6 Hz, *o*-C_6H_5), 5.30 (t, 2H, *J* = 6 Hz, *m*-C_6H_5), 5.23 (t, 1H, *J* = 6 Hz, *p*-C_6H_5), 5.14 (s, 6H, C_6H_6), 2.66, 2.57, 2.56, 2.40, 2.20, 2.12 (sextet, 2H, *J* = 7 Hz, ethyl CH_2), 1.34, 1.18, 1.11 (t, 6H, *J* = 7 Hz, ethyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 93.5, 92.1, 91.5 (C_2B_4), 90.4 (*o*-C_6H_5), 83.6, 82.3 (*m*-C_6H_5), 83.3, 81.1 (*p*-C_6H_5), 84.5 (C_6H_6), 24.5, 24.1 (ethyl CH_2), 15.1, 15.0 (ethyl CH_3). ^{11}B NMR ($CDCl_3$): δ 14.8 (s, 1B, *B*−Ph), 13.4 (s, 1B, *B*−Ph), 5.5 (1B, BH unresolved), 3.3 (3B, BH unresolved), 0.4 (d, 6B, *J* = 95 Hz). IR (KBr pellet, cm^{-1}): 3065 (w), 2963 (s), 2929 (s), 2870 (m), 2527 (vs), 1443 (m), 1400 (w), 1375 (m), 1276 (w), 1245 (w), 1012 (w), 893 (w), 862 (w), 836 (m), 816 (w), 606 (w), 490 (m), 428 (m). UV−vis (CH_2Cl_2, nm (%)): 228 (72), 275 (100), 364 (16), 413 (6) ϵ_{max} = 36 000 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 788 ([M$^+$], 100). Anal. Calcd for $C_{36}H_{56}B_{12}Fe_3$: C, 55.01; H, 7.18. Found: C, 55.56; H, 7.20.

$[(C_6H_6)Fe(Et_2C_2B_4H_3$-5-C≡C$)]_2$ (29). In a 25 mL Schlenk flask under dinitrogen, 50 mg of **6** (0.17 mmol), 2 mg of CuI (0.01 mmol), and 6 mg of $PdCl_2(PPh_3)_2$ (0.009 mmol) were dissolved in 5 mL of dry, degassed Et_3N. Iodine (22 mg, 0.087 mmol) was added all at once with an immediate precipitate formation. The mixture was stirred for 2 h, and the solvent was removed in vacuo. The remaining residue was slurried in dichloromethane and filtered to yield 23 mg of **29** as a very insoluble orange solid. The solvent was removed from the filtrate to afford 8 mg of recovered **6** (50% yield, 55% yield based on **6** consumed). ^{1}H NMR ($CDCl_3$): δ 5.48 (s, 12H, C_6H_6), 2.61, 2.32 (sextet, 4H, *J* = 7 Hz, ethyl CH_2), 1.24 (t, 12H, *J* = 7 Hz, ethyl CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, d_7-DMF, 65 °C): δ 86.2 (C_6H_6), 24.6 (ethyl CH_2), 15.0 (ethyl CH_3). ^{11}B NMR (d_7-DMF, 75 °C): δ 3.5 (4B, BH unresolved), 1.1 (4B, BH unresolved). IR (KBr pellet, cm^{-1}): 3080 (w), 2965 (m), 2932 (m), 2871 (w), 2532 (vs), 2169 (vw), 1443 (m), 1383 (m), 1163 (w), 1123 (w), 1062 (w), 887 (m), 861 (m), 600 (m), 544 (m), 480 (m), 459 (m). UV−vis (CH_2Cl_2, nm (%)): 230 (100), 333 (48), 427 (8) ϵ_{max} = 33 000 cm^{-1} M^{-1}. CI$^+$-MS: *m/z* (%) 573 ([M$^+$ − H], 100). Anal. Calcd for $C_{28}H_{38}B_8Fe_2$: C, 58.71; H, 6.69. Found: C, 58.90; H, 6.42.

$[(C_6H_6)Fe(Et_2C_2B_4H_3$-5-C≡C$)]_3C_6H_3$ (30). In a 10 mm air-free NMR tube under dinitrogen, 19.5 mg of **6** (0.0678 mmol), 9 mg of 1,3,5-triiodobenzene (0.02 mmol), 2 mg of CuI (0.01 mmol), and 3 mg of $PdCl_2(PPh_3)_2$ (0.004 mmol) were dissolved in 0.6 mL of dry, degassed THF and 50 μL of Et_3N (0.36 mmol) was added. The mixture was stirred for 20 h, and the solvent was removed in vacuo. The remaining residue was slurried in dichloromethane and the slurry filtered to give 4 mg of **30** as an air-stable yellow solid (19% yield). ^{1}H NMR (d_7-DMF): δ 7.32 (s, 3H, C_6H_3), 5.74 (s, 18H, C_6H_6), 2.72, 2.34 (sextet, 6H, *J* = 7 Hz, ethyl CH_2), 1.22 (t, 18H, *J* = 7 Hz, ethyl CH_3). ^{13}C{^{1}H} NMR (d_7-DMF, 50 °C): δ 131.3 (*o*-C_6H_3), 127.6 (*i*-C_6H_3), 108.2 (C_6H_3C≡CB), 92.9 (C_2B_4), 86.3 (C_6H_6), 24.5 (ethyl CH_2), 15.1 (ethyl CH_3). ^{11}B NMR (d_7-DMF, 70 °C): δ 3.4 (s, 3B, $C_6H_3C{\equiv}C\mathit{B}$), 2.5 (d, 3B, $J = 163$ Hz), 0.9 (d, 6B, $J = 134$). IR (KBr pellet, cm^{-1}): 3079 (w), 2966 (s), 2931 (m), 2872 (w), 2545 (s), 2158 (w), 1571 (s), 1443 (m), 1406 (w), 1383 (w), 1234 (w), 1114 (w), 1063 (w), 874 (w), 809 (w), 516 (w), 487 (m), 431 (w). UV−vis (CH_2Cl_2, nm (%)): 255 (100), 265 (98), 297 (84), 421 (6). CI$^+$-MS: *m*/*z* (%) 935 ([M$^+$ − H], 100).

[(C_6H_6)Fe($Et_2C_2B_4H_3$-7-C≡C)]$_2$ (31). In a 10 mm air-free NMR tube under dinitrogen, 10 mg of (C_6H_6)Fe($Et_2C_2B_4H_3$-7-C≡CH) (**13**; 0.035 mmol), 6.5 μL of chloroacetone (0.082 mmol), 2 mg of CuI (0.01 mmol), and 4 mg of Pd(PPh_3)$_4$ (0.003 mmol) were dissolved in 0.3 mL of dry, degassed pyridine and 20 μL of Et_3N (0.14 mmol) was added. The mixture was stirred for 22 h, and the solvent was removed in vacuo. The remaining residue was slurried in dichloromethane and the slurry filtered to remove insoluble salts. The filtrate was then chromatographed on a silica gel TLC plate with a 1/2 CH_2Cl_2/hexanes solution, affording 5 mg of **31** (50% yield) as an air-stable brown solid. ^{1}H NMR ($CDCl_3$): δ 5.36 (s, 12H, $C_6\mathit{H}_6$), 2.48, 2.20 (sextet, 4H, $J = 7$ Hz, ethyl $C\mathit{H}_2$), 1.31 (t, 12H, $J = 7$ Hz, ethyl $C\mathit{H}_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 94.8 (C_2B_4), 86.3 (BC≡*CC*≡CB), 84.8 (C_6H_6), 24.5 (ethyl $\mathit{C}H_2$),14.7 (ethyl $\mathit{C}H_3$). ^{11}B NMR (CD_2Cl_2): δ 5.6 (2B, BH unresolved), 0.1 (4B, BH unresolved), −2.6 (s, 2B, *B*C≡CC≡C*B*). IR (KBr pellet, cm^{-1}): 3079 (w), 2968 (s), 2931 (s), 2874 (m), 2538 (vs), 2091 (m), 1443 (s), 1378 (w), 1132 (m), 1098 (m), 1070 (m), 981 (m), 799 (vs), 432 (s). UV−vis (CH_2Cl_2, nm (%)): 229 (37), 290 (100), 357 (6) $\epsilon_{\max} =$ 77 000 cm^{-1} M^{-1}. CI$^+$-MS: *m*/*z* (%) 574 ([M$^+$], 100).

[(C_6H_6)Fe($Et_2C_2B_4H_3$-7-C≡C)]$_3$$C_6H_3$ (32). In a 25 mL Schlenk flask under dinitrogen, 25 mg of **13** (0.087 mmol), 13 mg of 1,3,5-triiodobenzene (0.029 mmol), 2 mg of CuI (0.01 mmol), and 3 mg of $PdCl_2(PPh_3)_2$ (0.004 mmol) were dissolved in 5 mL of dry, degassed THF and 5 mL of dry, degassed Et_3N (40 mmol) was added. The mixture was stirred for 40 h, and the solvent was removed in vacuo. The remaining residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1/2 CH_2Cl_2/hexanes solution, yielding three bands. The last band afforded 10 mg of **32** as an air-stable, yellow solid (37% yield). ^{1}H NMR ($CDCl_3$): δ 6.85 (s, 3H, $C_6\mathit{H}_3$), 5.40 (s, 18H, $C_6\mathit{H}_6$), 2.55, 2.28 (sextet, 6H, $J = 7$ Hz, ethyl $C\mathit{H}_2$), 1.36 (t, 18H, $J = 7$ Hz, ethyl $C\mathit{H}_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 133.8 (*o*-C_6H_3), 123.4 (*i*-C_6H_3), 94.3 (C_2B_4), 85.5 ($C_6H_3\mathit{C}{\equiv}CB$), 84.4 ($\mathit{C}_6H_6$), 24.2 (ethyl $\mathit{C}H_2$), 14.2 (ethyl $\mathit{C}H_3$). ^{11}B NMR ($CDCl_3$, 55 °C): δ 5.3 (s, 3B, $C_6H_3C{\equiv}C\mathit{B}$), −0.5 (9B, BH unresolved). IR (KBr pellet, cm^{-1}): 3079 (w), 2967 (m), 2931 (m), 2873 (w), 2536 (s), 2173 (w), 1576 (m), 1442 (m), 1410 (m), 1383 (w), 1216 (m), 1093 (w), 980 (w), 880 (w), 784 (s), 683 (w), 647 (w), 483 (m), 419 (w). UV−vis (CH_2Cl_2, nm (%)): 229 (31), 284 (100) $\epsilon_{\max} = 110\,000$ cm^{-1} M^{-1}. CI$^+$-MS: *m*/*z* (%) 936 ([M$^+$], 100).

X-ray Structure Determination on 9. Diffraction data were collected at −80 °C on a Rigaku AFC6S diffractometer using Mo Kα radiation ($\lambda = 0.710\,69$ Å). Details of the data collection and structure determination are listed in Table 1. The unit cell dimensions were determined by least-squares refinement of the setting angles of 25 high-angle reflections. The intensities of 3 standard reflections, monitored throughout, showed no significant variation. Empirical absorption corrections were applied following ψ scanning of several high-angle reflections (transmission factors are reported in Table 1). Calculations were performed on a VAX Station 3520 computer employing the TEXSAN 5.0 crystallographic software package[33] and in later stages on a Silicon Graphics Personal Iris 4D35 computer using the teXsan 1.7 package.[34] The structure was solved by direct methods in SIR88.[35] Full-matrix least-squares refinement with anisotropic thermal displacement parameters was carried out for all non-hydrogen atoms. The hydrogen atoms were located from the difference Fourier maps and were included in the calculations without further refinement.

X-ray Structure Determinations on 18, 24, and 26. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer at −120 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). A hemisphere of frame data was collected using ω and ϕ scans, and empirical absorption corrections were applied. Structures were solved by direct methods using the SHELXTL-97 suite of programs,[36] and the refinement was by full-matrix least squares on F^2 with all measured reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters for **18** and **26**. All hydrogens were located in the final difference map and refined isotropically for **18** and **26**. Owing to disorder in the triphenylene linker of **24,** only the non-hydrogen atoms of the ferracarborane unit were refined anisotropically. Disorder in the linker was effectively modeled with two orientations of the three rings each given 50% occupancy. H(4B), H(6B), and H(7B) of the carborane were located and refined isotropically; the remaining were placed in idealized positions based on geometry. All ORTEP representations were created with ORTEP-III.[37] Crystallographic data for all structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 176282 (**9**), 176283 (**18**), 176284 (**24**), 176285 (**26**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, www: http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and calculated mean planes for all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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