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New Palladium-Catalyzed Cross-Coupling Routes to Carbon Functionalized Metallatricarbadecaboranes

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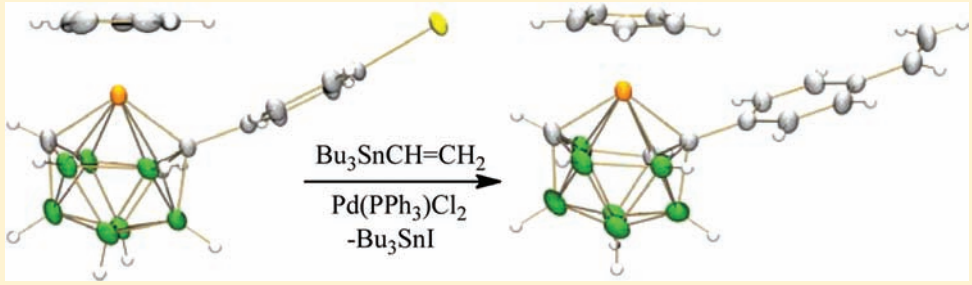
Supporting Information



ABSTRACT: A general method for the synthesis of cage-carbon-functionalized cyclopentadienyl iron and cyclopentadienyl ruthenium tricarbadecaboranyl complexes has been developed that employs palladium-catalyzed Sonogashira, Heck, and Stille cross-coupling reactions directed at a cage-carbon haloaryl substituent. The key $Li^+[6\text{-}(p\text{-}XC_6H_4)\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-]$ (X = I (**1**), Br (**2**), Cl (**3**)) haloaryl−tricarbadecaboranyl anionic ligands were synthesized in high yields via the reaction of the *arachno*-$4,6\text{-}C_2B_7H_{12}^-$ anion with the corresponding *p*-halobenzonitriles ($p\text{-}XC_6H_4\text{-}CN$). The reactions of the salts **1**−**3** with $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3PF_6$ were then used to produce the haloaryl complexes $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}(p\text{-}XC_6H_4)\text{-}closo\text{-}1,2,3,4\text{-}MC_3B_7H_9$ (M = Fe, X = I (**4**), Br (**5**), Cl (**6**) and M = Ru, X = I (**7**), Br (**8**), Cl (**9**)). The sonication-promoted Sonogashira coupling reactions of **4** with terminal alkynes catalyzed by $Pd(dppf)_2Cl_2$/CuI yielded the alkynyl-linked derivatives $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}p\text{-}RC_6H_4\text{-}closo\text{-}1,2,3,4\text{-}FeC_3B_7H_9$ (R = (PhC≡C)- (**10**), $(CH_3CH_2C(O)OCH_2C{\equiv}C)$- (**11**), $((\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4C{\equiv}C))$- (**12**)). Heck reactions of **4** with terminal alkenes catalyzed by $Pd(OAc)_2$ yielded the alkene-functionalized products $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}p\text{-}RC_6H_4\text{-}closo\text{-}1,2,3,4\text{-}FeC_3B_7H_9$ (R = $(PhCH_2CH{=}CH)$- (**13**), $(CH_3(CH_2)_2CH{=}CH)$- (**14**)), while the Stille cross-coupling reactions of **4** with organotin compounds catalyzed by $Pd(PPh_3)_2Cl_2$ afforded the complexes $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}p\text{-}RC_6H_4\text{-}closo\text{-}1,2,3,4\text{-}FeC_3B_7H_9$ (R = Ph- (**15**), $(CH_2{=}CH)$- (**16**), $(CH_2{=}CHCH_2)$- (**17**)). These reactions thus provide facile and systematic access to a wide variety of new types of functionalized metallatricarbadecaboranyl complexes with substituents needed for potential metallocene-like biomedical and/or optoelectronic applications.

INTRODUCTION

Our previous studies have demonstrated that the 6-R-5,6,9-*nido*-$C_3B_7H_9^-$ (R = Me, Ph) tricarbadecaboranide anions[1] have transition-metal coordination properties that are similar to those of the cyclopentadienide $C_5H_5^-$ anion with the ability to function as either η^6 six-electron or η^4 four-electron donors. These anions have now been used as ligands to generate a wide range of metallocene-like sandwich complexes (Figure 1). Furthermore, these complexes have been shown to have unique properties, including enhanced oxidative and hydrolytic stabilities and remarkably different electrochemical activities and bioactivities that complement their metallocene analogues.[2] We have also recently reported[3] that the palladium-catalyzed Sonogashira coupling reactions of B-halometallatricarbadecaboranes provide a route to more complex B-functionalized derivatives with substituent groups that could enable metallocene-like biomedical and/or optoelectronic applications. While this method provides a general route to many important derivatives, the low to moderate yields observed for the B-halo Sonogashira couplings and the poor reactivity of the B-halo complexes toward other types of palladium-catalyzed cross-coupling reactions have limited the utility of this approach. This stimulated our interest in the development of alternative higher yield and more versatile metal-catalyzed substitution strategies directed at a cage carbon.[4]

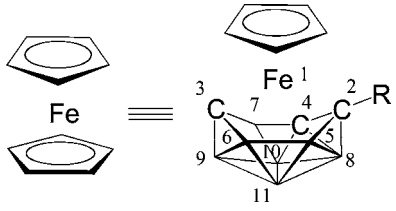


Figure 1. Comparison of the sandwich structures of ferrocene and $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}R\text{-}closo\text{-}1,2,3,4\text{-}FeC_3B_7H_9$.

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Traditional cage-carbon functionalization of carboranes and metallacarboranes has most commonly been achieved through metalation of the cage carbons followed by metathesis reactions.[5] In this paper, we describe an alternate pathway where palladium-catalyzed Sonogashira, Heck, and Stille cross-coupling reactions directed at a cage-carbon haloaryl substituent are employed to give good to excellent yields of a wide variety of functionalized metallatricarbadecaboranyl complexes.

EXPERIMENTAL SECTION

General Synthetic Procedures and Materials. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere using the high-vacuum or inert-atmosphere techniques described by Shriver.[6] *arachno*-4,6-$C_2B_7H_{13}$ was prepared by reported methods.[7] 4-Iodobenzonitrile, 4-bromobenzonitrile, 4-chlorobenzonitrile, phenylacetylene, ethynylferrocene, dicarbonylcyclopentadienyliodoiron, copper iodide, 1-pentene, allylbenzene, tetraallyltin, tributylphenyltin, tributylvinyltin, bis(diphenylphosphino)palladium(II) chloride, and diethyl amine (Aldrich), propargyl proprionate and trimethylsilylacetylene (Lancaster), bis(diphenylphosphino)ferrocene palladium(II) chloride (Pd(dppf)Cl_2), palladium(II) acetate, triphenylphosphine, and tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (Strem), and spectrochemical grade dichloromethane and hexanes (Fisher) were used as received. Glyme was freshly distilled from sodium–benzophenone ketyl. Dimethyl formamide was dried over magnesium sulfate. All other solvents were used as received unless noted otherwise.

Physical Methods. The ^{11}B NMR spectra (128.4 MHz, CD_2Cl_2, ppm, *J* in Hz) and the ^{1}H NMR spectra (400.1 MHz, CD_2Cl_2, ppm, *J* in Hz) were obtained on a Bruker DMX-400 spectrometer equipped with appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift. All ^{1}H chemical shifts were measured relative to internal residual protons in the lock solvents and are referenced to Me_4Si (0.0 ppm). High- and low-resolution mass spectra employing chemical ionization with negative ion detection were obtained on a Micromass AutoSpec high-resolution mass spectrometer. High- and low-resolution mass spectra employing electrospray ionization with negative ion detection were obtained on a Micromass LCT Premier XE high-resolution mass spectrometer. IR spectra were obtained on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were carried out at Robertson Microlit Laboratories in Madison, NJ or at the Microanalytical Facility at UC Berkeley, Berkeley, CA. Melting points were determined using a standard melting point apparatus and are uncorrected.

Ligand Syntheses: $Li^+[6\text{-}(p\text{-}XC_6H_4)\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-]$ (X = I, Br, Cl). *$Li^+[6\text{-}(p\text{-}IC_6H_4)\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-]$ (**1**).* LiH (26.9 mg, 3.4 mmol) was added to a stirring glyme (20 mL) solution of *arachno*-4,6-$C_2B_7H_{13}$ (430 mg, 3.5 mmol) under N_2. The solution was monitored by NMR until approximately 97% completion was achieved. At this point, a glyme solution of 4-iodobenzonitrile (2.6 g, 10.51 mmol) was added by syringe. The reaction mixture was stirred at reflux for 12 h and then cooled and filtered in a glovebag under N_2. The product was stored as a stock solution in the refrigerator. The exact concentration of the stock solution and the yield (92%, 0.16 M) were determined by integrating the resonances in the ^{11}B NMR spectrum of a $B_{10}H_{14}$ sample of known concentration and comparing that value with the integrated value of the resonances of the stock solution. ESI HRMS: *m*/*z* for $C_9H_{13}B_7I^-$ calcd 325.0713, found 325.0723. ^{11}B NMR: 7.7 (d, 122, 1B), 5.6 (d, 139, 1B), −4.4 (d, 139, 1B), −9.9 (d, 104, 1B), −13.4 (d, 104, 1B), −22.9 (d, 156, 1B), −28.2 (d, 156, 1B).

*$Li^+[6\text{-}(p\text{-}BrC_6H_4)\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-]$ (**2**).* Reactants: LiH (68.3 mg, 8.6 mmol), *arachno*-4,6-$C_2B_7H_{13}$ (1 g, 8.8 mmol), and 4-bromobenzonitrile (8 g, 44.4 mmol in 20 mL of glyme). Time: 12 h. Yield: 94% (0.10 M). ESI HRMS: *m*/*z* for $C_9H_{13}B_7Br^-$ calcd 279.1008, found 279.0847. ^{11}B NMR: 7.3 (d, ∼92, 1B), 5.4 (d, 139, 1B), −4.7 (d, 121, 1B), −9.9 (d, 121, 1B), −13.9 (d, 121, 1B), −22.6 (d, 173, 1B), −27.5 (d, 139, 1B).

*$Li^+[6\text{-}(p\text{-}ClC_6H_4)\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-]$ (**3**).* Reactants: LiH (13 mg, 1.7 mmol), *arachno*-4,6-$C_2B_7H_{13}$ (200 mg, 1.8 mmol), and 4-chlorobenzonitrile (730 mg, 5.31 mmol). Time: 12 h. Yield: 90% (0.12 M). ESI HRMS: *m*/*z* for $C_9H_{13}B_7Cl^-$ calcd 233.1357, found 233.1354. ^{11}B NMR: 7.5 (d, 122, 1B), 5.4 (d, 121, 1B), −4.6 (d, 121, 1B), −10.1 (d, 139, 1B), −13.5 (d, 139, 1B), −22.9 (d, 173, 1B), −28.5 (d, 139, 1B).

Metallatricarbadecaborane Syntheses: 1-(η^5-C_5H_5)-2-(*p*-XC_6H_4)-*closo*-1,2,3,4-$MC_3B_7H_9$ (X = I, Br, Cl; M = Fe, Ru). *1-(η^5-C_5H_5)-2-(p-IC_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ (**4**).* A glyme solution of **1** (8.2 mL of a 0.2 M solution, 1.6 mmol) was added dropwise to a stirred glyme (20 mL) solution of (η^5-C_5H_5)Fe(CO)$_2$I (500 mg, 1.6 mmol) under N_2. After it was refluxed for 3 h, the reaction mixture was exposed to air and filtered through a short silica gel plug, washing once with CH_2Cl_2 and then three times with ether. The solvent was vacuum-evaporated, and the oily blue residue was redissolved in CH_2Cl_2 and purified on a silica gel column using 2/1 hexanes/CH_2Cl_2 as the eluent to give **4** in 56% yield (399 mg, 0.89 mmol): dark blue; mp 192 °C. Anal. Calcd: C, 37.81; H, 4.08. Found: C, 38.19; H, 3.67. NCI HRMS: *m*/*z* for $C_{14}H_{18}B_7FeI^-$ calcd 446.0454, found 446.0472. ^{11}B NMR: 3.5 (d, 156, 1B), 0.4 (d, 156, 1B), −10.5 (d, 138, 1B), −11.2 (d, 104, 1B), −25.5 (d, 139, 1B), −28.3 (d, 156, 1B), −33.3 (d, 156, 1B). ^{1}H NMR: 8.32–7.23 (m, 4H, C_6H_4), 6.96 (s, 1H, C3*H*), 4.48 (s, 5H, Cp), 1.77 (s, 1H, C4*H*).

*1-(η^5-C_5H_5)-2-(p-BrC_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ (**5**).* Reactants: **2** (15 mL of a 0.1 M solution, 1.6 mmol) and (η^5-C_5H_5)Fe(CO)$_2$I (500 mg, 1.6 mmol). Time: 3.5 h. Yield: 35% (221 mg, 0.55 mmol) Dark blue. Mp: 194 °C. Anal. Calcd: C, 42.28; H, 4.56. Found: C 42.26; H, 4.71. NCI HRMS: *m*/*z* for $C_{14}H_{18}B_7BrFe^-$ calcd 398.0592, found 398.0640. ^{11}B NMR: 2.6 (d, 156, 1B), −0.5 (d, 173, 1B), −11.5 (d, 121, 1B), −12.3 (d, 104, 1B), −26.4 (d, 139, 1B), −29.3 (d, 156, 1B), −34.4 (d, 156, 1B). ^{1}H NMR: 8.46–7.35 (m, 4H, C_6H_4), 6.95 (s, 1H, C3*H*), 4.48 (s, 5H, Cp), 1.78 (s, 1H, C4*H*).

*1-(η^5-C_5H_5)-4-(p-ClC_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ (**6**).* Reactants: **3** (13 mL of a 0.12 M solution, 1.6 mmol) and (η^5-C_5H_5)Fe(CO)$_2$I (500 mg, 1.6 mmol). Time: 2 h. Yield: 76% (349 mg, 1.2 mmol). Dark blue. Mp: 147–149 °C. Anal. Calcd: C, 47.60; H, 5.14. Found: C, 47.64; H, 4.90. NCI HRMS: *m*/*z* for $C_{14}H_{18}B_7ClFe^-$ calcd 354.1098, found 354.1103. ^{11}B NMR: 3.8 (d, 155, 1B), 0.7 (d, 155, 1B), −10.2 (d, 121, 1B), −11.1 (d, 121, 1B), −25.2 (d, 138, 1B), −28.2 (d, 155, 1B), −33.1 (d, 155, 1B). ^{1}H NMR: 8.53–7.43 (m, 4H, C_6H_4), 6.96 (s, 1H, C3*H*), 4.48 (s, 5H, Cp), 1.79 (s, 1H, C4*H*).

*1-(η^5-C_5H_5)-2-(p-IC_6H_4)-closo-1,2,3,4-$RuC_3B_7H_9$ (**7**).* Reactants: **1** (6.8 mL of a 0.17 M solution, 1.15 mmol) and (η^5-C_5H_5)Ru(CH_3CN)$_3PF_6$ (500 mg, 1.15 mmol). Time: 5 h. Yield: 32% (180 mg, 0.37 mmol). Orange. Mp: 196 °C. Anal. Calcd: C, 34.32; H, 3.70. Found: 33.95; H, 3.59%. NCI HRMS: *m*/*z* for $C_{14}H_{18}B_7IRu^-$ calcd 492.0148, found 492.0180. ^{11}B NMR: 5.2 (d, 138, 1B), 2.7 (d, 172, 1B), −10.1 (d, 138, 1B), −10.9 (d, 138, 1B), −28.8 (d, 138, 1B), −29.8 (d, ∼140, 1B), −30.4 (d, ∼140, 1B). ^{1}H NMR: 7.78–7.46 (m, 4H, C_6H_4), 5.92 (s, 1H, C3*H*), 4.79 (s, 5H, Cp), 2.48 (s, 1H, C4*H*).

*1-(η^5-C_5H_5)-2-(p-BrC_6H_4)-closo-1,2,3,4-$RuC_3B_7H_9$ (**8**).* Reactants: **2** (2.2 mL of a 0.2 M solution, 0.44 mmol) and (η^5-C_5H_5)Ru(CH_3CN)$_3PF_6$ (190 mg, 0.44 mmol). Time: 24 h. Yield: 29% (147 mg, 0.33 mmol). Orange. Mp: 89 °C. NCI HRMS: *m*/*z* for $C_{14}H_{18}B_7BrRu^-$ calcd 444.0286; found 444.0322. ^{11}B NMR: 5.7 (d, 151, 1B), 3.0 (d, 188, 1B), −9.6 (d, 139, 1B), −10.7 (d, 139, 1B), −28.4 (d, 139, 1B), −29.2 (d, ∼140, 1B), −30.0 (d, ∼140, 1B). ^{1}H NMR: 7.57–7.55 (m, 4H, C_6H_4), 5.92 (s, 1H, C3*H*), 4.77 (s, 5H, Cp), 2.48 (s, 1H, C4*H*).

*1-(η^5-C_5H_5)-2-(p-ClC_6H_4)-closo-1,2,3,4-$RuC_3B_7H_9$ (**9**).* Reactants: **3** (1 mL of a 0.2 M solution, 0.23 mmol) and (η^5-C_5H_5)Ru(CH_3CN)$_3PF_6$ (100 mg, 0.23 mmol). Time: 24 h. Yield: 37% (34 mg, 0.08 mmol). Orange. Mp: 143–144 °C. Anal. Calcd: C, 42.20; H, 4.55. Found: C, 42.14; H, 4.42. NCI HRMS: *m*/*z* for $C_{14}H_{18}B_7ClRu^-$ calcd 400.0792, found 400.0768. ^{11}B NMR: 5.2 (d, 156, 1B), 2.7 (d, 173, 1B), −9.9 (d, 139, 1B), −11.1 (d, 156, 1B), −28.9 (d, 139, 1B), −29.6 (d, ∼140, 1B), −30.4 (d, ∼140, 1B). ^{1}H NMR: 7.63–7.30 (m, 4H, C_6H_4), 5.91 (s, 1H, C3*H*), 4.77 (s, 5H, Cp), 2.49 (s, 1H, C4*H*).

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Palladium Coupling Reactions: 1-(η^5-C_5H_5)-2-(*p*-RC_6H_4)-*closo*-1,2,3,4-$FeC_3B_7H_9$ Syntheses. *1-(η^5-C_5H_5)-2-(p-(PhC≡C)-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$* ***(10)***. Phenylacetylene (0.12 mL, 1.13 mmol) was added by syringe to a solution of **4** (50 mg, 0.11 mmol), $Pd(dppf)Cl_2$ (16.3 mg, 0.02 mmol), and CuI (3.4 mg, 0.02 mmol) in Et_2NH (10 mL). The solution was placed in a sonication bath for 1 h, after which it was filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 2/1 hexanes/CH_2Cl_2 as eluent to give blue crystals of **10** in 67% yield (31 mg, 0.08 mmol): dark blue; mp 192 °C. Anal. Calcd: C, 63.07; H, 5.54. Found: C 62.86; H, 5.40. NCI HRMS: *m/z* for $C_{22}H_{23}B_7Fe^-$ calcd 420.1800, found 420.1798. ^{11}B NMR: 3.8 (d, 110, 1B), 0.7 (d, ∼110, 1B), −10.2 (d, 129, 1B), −10.9 (d, 99, 1B), −25.2 (d, 139, 1B), −28.1 (d, 159, 1B), −33.2 (d, 139, 1B). ^{1}H NMR: 8.56−7.40 (m, 9H, Ph and C_6H_4), 6.97 (s, 1H, C3*H*), 4.48 (s, 5H, Cp), 1.83 (s, 1H, C4*H*).

1-(η^5-C_5H_5)-2-(p-($CH_3CH_2C(O)OCH_2C$≡C)-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ ***(11)***. Propargyl propionate (1.2 mL, 1.13 mmol) was added by syringe to a solution of **4** (50 mg, 0.11 mmol), $Pd(dppf)Cl_2$ (16.3 mg, 0.02 mmol), and CuI (3.4 mg, 0.02 mmol) in Et_2NH (10 mL). The solution was placed in a sonication bath for 1 h, after which it was filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 2/1 hexanes/CH_2Cl_2 as eluent to give blue crystals of **11** in 43% yield (21 mg, 0.05 mmol): R_f = 0.44; dark blue; mp 83 °C. Anal. Calcd: C, 56.00; H, 5.87. Found: C, 56.54; H, 6.21. NCI HRMS: *m/z* for $C_{20}H_{25}B_7O_2Fe^-$ calcd 430.1855, found 430.1909. ^{11}B NMR: 3.8 (d, 156, 1B), 0.4 (d, 156, 1B), −10.3 (d, 121, 1B), −25.4 (d, 139, 1B), −28.2 (d, 156, 1B), −33.2 (d, 156, 1B). ^{1}H NMR: 8.53−7.45 (m, 4H, C_6H_4), 6.97 (s, 1H, C3*H*), 4.95 (s, 2H -CH_2-C≡C−) 4.46 (s, 5H, Cp), 2.43 (q, 7.6, 2H, $CH_3CH_2C(O)O$−), 1.80 (s, 1H, C4*H*), 1.15 (t, 7.5, 3H, $CH_3CH_2C(O)O$).

1-(η^5-C_5H_5)-2-(p-((η^5-C_5H_5)Fe(η^5-C_5H_4C≡C))-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ ***(12)***. A solution of **4** (50 mg, 0.11 mmol), $Pd(dppf)Cl_2$ (16.3 mg, 0.02 mmol), CuI (3.4 mg, 0.02 mmol), and ethynylferrocene (47 mg, 0.226 mmol) in Et_2NH (10 mL) was placed in a sonication bath for 1 h, after which it was filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 2/1 hexanes/CH_2Cl_2 as eluent to give blue crystals of **12** in 92% yield (61 mg, 0.10 mmol): R_f = 0.43; dark blue; mp 184−187 °C. Anal. Calcd: C, 59.27; H, 5.17. Found: C, 60.47; H, 5.93. NCI HRMS: *m/z* for $C_{26}H_{28}B_7Fe_2^-$ calcd 529.1541, found 529.1588. ^{11}B NMR: 3.8 (br, 1B), 0.4 (d, ∼128, 1B), −10.3 (d, 143, 1B), −11.0 (d, 111, 1B), −25.2 (d, 155, 1B), −28.2 (d, 155, 1B), −33.1 (d, ∼141, 1B). ^{1}H NMR: 8.54−7.44 (m, 4H, C_6H_4), 6.95 (s, 1H, C3*H*), 4.57 (s, 3H, Cp), 4.47 (s, 5H, Cp), 4.29 (s, 7H, Cp), 1.82 (s, C4*H*).

1-(η^5-C_5H_5)-2-(p-$PhCH_2CH$=CH)-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ ***(13)***. Allylbenzene (0.15 mL, 1.1 mmol) was added by syringe to a solution under N_2 of **4** (50 mg, 0.11 mmol), $Pd(OAc)_2$ (3 mg, 0.01 mmol), and PPh_3 (6 mg, 0.01 mmol) in a 10/1 CH_3CN/NEt_3 (11 mL) mixture. The reaction mixture was stirred at 90 °C for 20 h and then opened to air and filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 2/1 hexanes/CH_2Cl_2 as eluent to give **13** in 37% yield (18.1 mg, 0.04 mmol): dark blue. NCI HRMS: *m/z* for $C_{23}H_{27}B_7Fe^-$ calcd 436.2113, found 436.2123. ^{11}B NMR: 3.4 (d, 148, 1B), 1.1 (d, 174, 1B), −10.5 (d, 139, 1B), −11.0 (d, 105, 1B), −25.4 (d, 131, 1B), −28.2 (d, 174, 1B), −33.1 (d, 157, 1B). ^{1}H NMR: 8.52−7.25 (m, 9H, Ph and C_6H_4), 6.91 (s, 1H, C3*H*), 6.56−6.44 (m, 1H, CH=CH), 4.46 (s, 5H, Cp), 3.66 (d, 6.7, 1H, CH_a), 3.61 (d, 6.3, 1H, CH_b), 1.82 (s, 1H, C4*H*).

1-(η^5-C_5H_5)-2-(p-($CH_3(CH_2)_2CH$=CH)-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ ***(14)***. An aliquot of 1-pentene (0.15 mL, 1.1 mmol) was added by syringe to a solution under N_2 of **4** (50 mg, 0.11 mmol), $Pd(OAc)_2$ (3 mg, 0.01 mmol), and PPh_3 (6 mg, 0.01 mmol) in a 10/1 CH_3CN/NEt_3 (11 mL) mixture. The reaction mixture was stirred at 55 °C for 24 h and then opened to air and filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 2/1 hexanes/CH_2Cl_2 as eluent to give **14** in 61% yield (26.8 mg, 0.07 mmol): R_f = 0.76; dark blue; mp 74 °C. Anal. Calcd: C, 58.98; H, 7.03. Found: C, 58.55; H, 7.05. NCI HRMS: *m/z* for $C_{19}H_{27}B_7Fe^-$ calcd 388.2113, found 388.2120. ^{11}B NMR: 3.2 (d, 139, 1B), 0.7 (d, 173, 1B), −10.5 (d, 139, 1B), −11.3 (d, 104, 1B), −25.6 (d, 139, 1B), −28.5 (d, 156, 1B), −33.2 (d, 139, 1B). ^{1}H NMR: 8.51−7.42 (m, 4H, C_6H_4), 6.91 (s, 1H, C3*H*), 6.35−6.53 (m, 1H, C*H*=CH), 4.46 (s, 5H, Cp), 2.25 (q, 6.4, 2H, CH_3CH_2-), 1.83 (s, 1H, C4*H*), 1.56 (q, 2H, 7.2, −CH_2-CH=CH), 1.02 (t, 7.4, 3H, CH_3-).

1-(η^5-C_5H_5)-2-(p-Ph-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ ***(15)***. A solution of **4** (100 mg, 0.22 mmol) and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol) in DMF (5 mL) was heated to 75 °C. Neat Bu_3SnPh (0.09 mL, 0.11 mmol) was added dropwise by syringe. The reaction mixture was stirred for 5 h and then opened to air and filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 3/1 hexanes/CH_2Cl_2 and then recrystallized from pentane and CH_2Cl_2 to give **15** in 69% yield (58.9 mg, 0.15 mmol): dark blue; mp 180−181 °C. Anal. Calcd: C, 60.83; H, 5.87. Found: C, 60.58; H, 5.88. NCI HRMS: *m/z* for $C_{20}H_{23}B_7Fe^-$ calcd 396.1800, found 396.1818. ^{11}B NMR: 3.5 (d, 156, 1B), 0.9 (d, 166, 1B), −10.3 (d, 192, 1B), −11.1 (107, d, 1B), −25.3 (d, 142, 1B), −28.2 (d, 156, 1B), −33.0 (d, 156, 1B). ^{1}H NMR: 8.66−7.40 (m, 9H, Ph and C_6H_4), 6.95 (s, 1H, C3*H*), 4.51(s, 5H, Cp), 1.89 (s, 1H, C4*H*).

1-(η^5-C_5H_5)-2-(p-(CH_2=CH)-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ ***(16)***. A solution of **4** (50 mg, 0.11 mmol) and $Pd(PPh_3)_2Cl_2$ in DMF (5 mL) was heated to 75 °C. Neat tributylvinyltin was added dropwise by syringe (0.03 mL, 0.11 mmol). The reaction mixture was stirred for 3.5 h and then opened to air and filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 3/1 hexanes/CH_2Cl_2 and then recrystallized from CH_2Cl_2 to give **16** in 91% yield (31.3 mg, 0.09 mmol): dark blue; mp 143−145 °C. Anal. Calcd: C, 55.72; H, 6.14. Found: C, 55.56; H, 6.26. NCI HRMS: *m/z* for $C_{16}H_{21}B_7Fe^-$ calcd 346.1644, found 346.1646. ^{11}B NMR: 3.5 (d, 163, 1B), 0.7 (d, 151, 1B), −10.4 (d, 133, 1B), −11.2 (d, 121, 1B), −25.4 (d, 139, 1B), −28.3 (d, 145, 1B), −33.1 (d, 157, 1B). ^{1}H NMR: 8.49−7.41 (m, 4H, C_6H_4), 6.89 (s, 1H, C3*H*), 6.80 (m, 2H, CH_2), 5.87 (d, 17.5, 1H, C*H*=CH_2), 4.43 (s, 5H, Cp), 1.80 (m, 1H, C4*H*).

1-(η^5-C_5H_5)-2-(p-(CH_2=$CHCH_2$)-C_6H_4)-closo-1,2,3,4-$FeC_3B_7H_9$ ***(17)***. A solution of **4** (50 mg, 0.11 mmol) and $Pd(PPh_3)_2Cl_2$ in DMF (5 mL) was heated to 75 °C. Neat tetraallyltin was added dropwise by syringe (0.03 mL, 0.11 mmol). The reaction mixture was stirred for 4 h and then opened to air and filtered through a short silica gel plug. The solvent was removed in vacuo, and the oily residue was chromatographed on silica gel plates using 8/1 hexanes/CH_2Cl_2 and then recrystallized from CH_2Cl_2 to give **17** in 79% yield (31 mg, 0.08 mmol): dark blue; 90−91 °C. Anal. Calcd: C, 56.89; H, 6.46. Found: C, 54.3; H, 6.37. NCI HRMS: *m/z* for $C_{17}H_{23}B_7Fe^-$ calcd 360.1801, found 360.1808. ^{11}B NMR: 3.8 (d, 144, 1B), 0.7 (d, 155, 1B), −10.3 (144, 1B), −11.1 (d, 99, 1B), −25.3 (d, 144, 1B), −28.2 (d, 155, 1B), −33.1 (d, 155, 1B). ^{1}H NMR: 7.42−7.34 (m, 4H, C_6H_4), 6.90 (s, 1H, C3*H*), 6.07 (m, 1H, C*H*=C), 5.20−5.14 (m, 2H, H_2C=C), 4.47 (s, 5H, Cp), 3.50 (d, 6.8, 2H, CH_2), 1.83 (s, 1H, C4*H*).

Crystallographic Data. Single crystals of **4**, **5**, **7**−**10**, **12**, **16**, and **17** were grown through slow solvent evaporation from dichloromethane solutions in air or through vapor−liquid diffusion of pentane into a dichloromethane solution.

Collection and Reduction of the Data. X-ray intensity data for **8** were collected on a Rigaku Mercury area detector diffractometer, while the data for **4**, **5**, **7**, **9**, **10**, **12**, **15**, and **16** were collected on a Bruker APEXII CCD diffractometer. Both instruments employed graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Rotation frames were integrated using SAINT,[8] producing a list of unaveraged F^2 and $\sigma(F^2)$ values that were then passed to the SHELXTL[9] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[10]

Solution and Refinement of the Structures. The structures were solved by direct methods (SIR97[11]). Refinement was by full-

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Table 1. Crystallographic Data Collection and Structure Refinement Information

	4	10	12	15	16
empirical formula	$C_{14}B_7H_{18}IFe$	$C_{22}B_7H_{23}Fe$	$C_{26}B_7H_{27}Fe_2$	$C_{20}B_7H_{23}Fe$	$C_{16}B_7H_{21}Fe$
formula wt	444.70	418.92	526.85	394.90	344.85
cryst class	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)	$C2/c$ (15)
Z	8	4	4	4	8
a, Å	16.8824(7)	13.4895(4)	10.8282(8)	13.9279(7)	21.9380(9)
b, Å	16.2754(6)	18.6032(5)	10.2318(8)	10.2317(5)	7.0010(3)
c, Å	12.3339(5)	8.4772(2)	22.0683(18)	14.2707(7)	21.9473(10)
β, deg	93.617(2)	102.2670(10)	93.233(4)	108.243(2)	96.456(2)
V, Å^3	3382.2(2)	2078.76(10)	2441.1(3)	1931.44(17)	3349.5(3)
D_{calcd}, g/cm^3	1.747	1.339	1.434	1.358	1.368
μ, mm^{-1}	2.706	0.732	1.203	0.783	0.892
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst size, mm	0.30 × 0.25 × 0.18	0.35 × 0.20 × 0.08	0.35 × 0.28 × 0.09	0.40 × 0.15 × 0.06	0.40 × 0.28 × 0.04
F(000)	1728	864	1080	816	1424
2θ angle, deg	6.22−55.20	3.08−55.24	3.70−55.06	3.08−55.18	3.74−55.06
temperature, K	100(1)	143(1)	143(1)	143(1)	143(1)
hkl collected	$-21 \le h \le 21$	$-17 \le h \le 17$	$-14 \le h \le 14$	$-18 \le h \le 18$	$-28 \le h \le 28$
	$-21 \le k \le 21$	$-24 \le k \le 23$	$-13 \le k \le 13$	$-13 \le k \le 13$	$-9 \le k \le 9$
	$-16 \le l \le 16$	$-11 \le l \le 11$	$-28 \le l \le 28$	$-18 \le l \le 18$	$-28 \le l \le 28$
no. of rflns measd	62 563	36 529	71 797	64 504	66 182
no. of unique rflns (R_{int})	7765 (0.0247)	4807 (0.0551)	5614 (0.0204)	4467 (0.0255)	3848 (0.0242)
no. of obsd rflns ($F > 4\sigma$)	7048	4443	5309	4136	3563
no. of rflns used in refinement	62 563	36 529	71 797	4467	66 182
no. of params	416	308	317	346	302
R^a indices ($F > 4\sigma$)					
R_1	0.0381	0.0574	0.0520	0.0229	0.0243
wR_2	0.0981	0.1291	0.1397	0.0599	0.0613
R^a indices (all data)					
R_1	0.0428	0.0617	0.0545	0.0256	0.0272
wR_2	0.1021	0.1305	0.1415	0.0621	0.0642
GOF^b	1.094	1.292	1.183	0.977	1.007
final diff peaks, e/Å^3	2.288	0.567	2.804	0.338	0.371

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. ^{b}GOF = $\{\sum w(F_o^2 - F_c^2)^2/(n-p)\}^{1/2}$, where n = no. of reflections and p = no. of parameters refined.

matrix least squares based on F^2 using SHELXL-97.[12] All reflections were used during refinement (values of F^2 that were experimentally negative were replaced with $F^2 = 0$). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically.

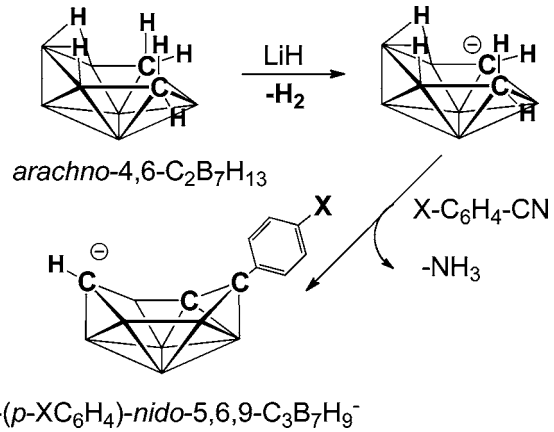
Crystal and refinement data for **4**, **10**, **12**, **15**, and **16** are given in Table 1, and those for **5** and **7**−**9** are given in Table S1 in the Supporting Information. Selected bond distances and angles are given in the corresponding figure captions in the main text and the Supporting Information.

RESULTS AND DISCUSSION

As shown in Scheme 1, the Kang method[1] was utilized for the high-yield syntheses of the series of lithium *p*-haloaryl-*nido*-tricarbadecaboranyl salts Li$^+$[6-(*p*-XC$_6$H$_4$)-*nido*-5,6,9-C$_3$B$_7$H$_9^-$], where X = I (**1**; 92%), Br (**2**; 94%) and Cl (**3**; 90%), via the reactions of *arachno*-4,6-C$_2$B$_7$H$_{12}^-$ with the corresponding 4-halobenzonitriles. In each case, ^{11}B NMR analyses of the reaction mixtures after 12 h of reflux showed the characteristic spectral pattern of the 6-R-*nido*-5,6,9-C$_3$B$_7$H$_9^-$ anions.[1] The salts were not isolated but stored as stock solutions under N$_2$ until use.

The reactions of (η^5-C$_5$H$_5$)Fe(CO)$_2$I and (η^5-C$_5$H$_5$)Ru(CH$_3$CN)$_3$PF$_6$ with the salts **1**−**3** then afforded the cage C2-substituted *p*-haloaryl metallatricarbadecaboranyl derivatives 1-(η^5-C$_5$H$_5$)-2-(*p*-XC$_6$H$_4$)-*closo*-1,2,3,4-MC$_3$B$_7$H$_9$ (M = Fe, X = I (**4**), Br (**5**), Cl (**6**) and M = Ru, X = I (**7**), Br (**8**), Cl (**9**), respectively) in moderate to good yields (Scheme 2). All compounds were easily purified by column chromatography and isolated as air- and moisture-stable solids that were soluble in a wide variety of polar and nonpolar solvents.

Scheme 1. Carbon-Insertion Syntheses of Li$^+$[6-(*p*-XC$_6$H$_4$)-*nido*-5,6,9-C$_3$B$_7$H$_9^-$] (X = I (1), Br (2), Cl (3))



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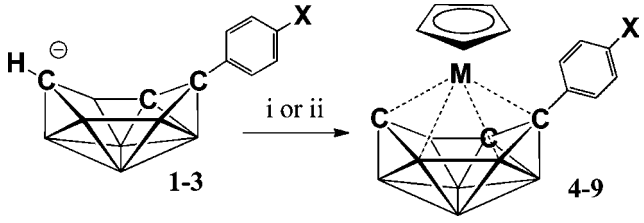
Scheme 2. Reactions of 1−3 with (i) (η^5-C_5H_5)Fe(CO)$_2$I and (ii) (η^5-C_5H_5)Ru(CH$_3$CN)$_3$PF$_6$ To Yield the Haloaryl Complexes 1-(η^5-C_5H_5)-6-(*p*-XC_6H_4)-*closo*-1,2,3,4-M$C_3B_7H_9$ (M = Fe, X = I (4), Br (5), Cl (6) and M = Ru, X = I (7), Br (8), Cl (9))



The chemical shifts and seven doublet patterns exhibited in the ^{11}B NMR spectra of **4**−**9** are consistent with those of other *closo*-1,2,3,4-M$C_3B_7H_9$ cluster systems.[2] Likewise, their ^{1}H NMR spectra each showed, in addition to the resonances of the η^5-C_5H_5 and *p*-XC_6H_4 groups, two characteristic cage C−H resonances, with the one at higher field (2.49−1.77 ppm) arising from the hydrogen attached to the higher coordinate C4 carbon adjacent to the metal and the other at lower field (6.96−5.91 ppm) from the hydrogen on the metal-adjacent lower coordinate C3 carbon.[2]

The structures of **4**, **5**, and **7**−**9** were crystallographically confirmed, with that of **4** shown in Figure 2 , and those of **5** and

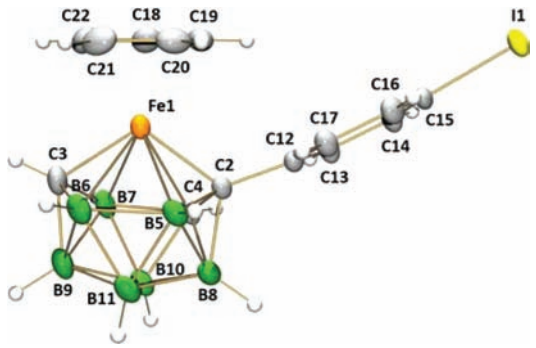


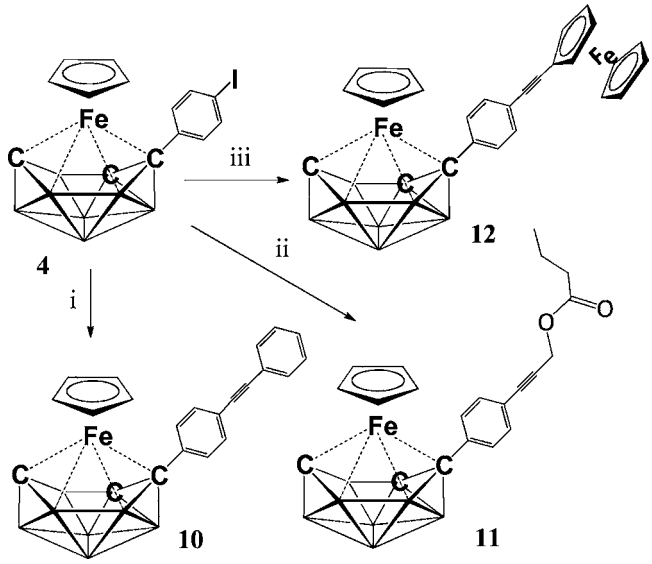
Figure 2. Crystallographically determined structure of **4**. Selected distances (Å) and angles (deg): Fe1−C2, 1.970(3); Fe1−C3, 1.963(4); Fe1−C4, 2.259(3); Fe1−B5, 2.235(4); Fe1−B6, 2.252(5); Fe1−B7, 2.273(4); Fe1−$Cp_{Centroid}$, 1.686; C2−B5, 1.592(5); B5−B6, 1.841(6); C3−B6, 1.579(6); C3−B7, 1.572(6); C4−B7, 1.741(5); C2−C4, 1.503(4); C2−C12, 1.490(5); C15−I1, 2.093(4); C3−Fe1−C2, 110.82(15); C12−C2−Fe1, 124.2(2).

7−**9** in Figures S1−S4 of the Supporting Information. In each complex, the metallatricarbadecaboranyl cage adopts an octadecahedral geometry with the metal η^6-coordinated to, and approximately centered over, the puckered face of the tricarbadecaboranyl fragment. The most significant metal to cage-atom interactions are with the two low-coordinate C2 and C3 carbons that are puckered toward the metals, with the distances from the metals to the substituted C2 carbons being ∼0.01 Å longer than their distances to the hydrogen-substituted C3 carbons. The metal distances to the C4 and B5−B7 atoms are ∼0.02−0.03 Å longer than those to C2 and C3. The Fe−C2 distances in **4** (1.970(3) Å) and **5** (1.9796(15) Å) and the Ru−C2 distances in **7**−**9** (2.078(2), 2.078(3), and 2.0787(15) Å) are only slightly shorter than those found in the phenyl-substituted complexes 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Fe$C_3B_7H_9$ (Fe−C2 = 1.982(3) Å) and 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Ru$C_3B_7H_9$ (Ru−C2 = 2.093(2) Å),[2h] indicating that the *p*-halo substituents have little if any effect on the metal−C2 cage bonding. Likewise, the *p*-I−C15 bond lengths in **4** (2.093(4) Å) and **7** (2.102(3) Å) are similar to those of iodobenzene (2.098(1) Å),[13] indicating little electronic influence of the metallatricarbadecaboranyl cages.

Palladium-catalyzed cross-coupling reactions have proven to be an extremely versatile synthetic tool, with the highest reactivity generally found for iodinated substrates.[14] Accordingly, the palladium-catalyzed Sonogashira, Heck, and Stille coupling reactions of 1-(η^5-C_5H_5)-2-(*p*-IC_6H_4)-*closo*-1,2,3,4-Fe$C_3B_7H_9$ (**4**) were investigated to establish the utility of these types of reactions for metallatricarbadecaborane functionalization at a *p*-haloaryl cage-carbon substituent.

The sonicated Sonogashira reactions in Scheme 3 of **4** with phenylacetylene, propargyl propionate, and ethynylferrocene

Scheme 3. Sonogashira Coupling Reactions of 4 with (i) Phenylacetylene, (ii) Propargyl Propionate, and (iii) Ethynylferrocene To Yield 1-(η^5-C_5H_5)-2-*p*-RC_6H_4-*closo*-1,2,3,4-Fe$C_3B_7H_9$ (R = (PhC≡C)- (10), ($CH_3CH_2C(O)OCH_2C$≡C)- (11)) and (η^5-C_5H_5)Fe(η^5-C_5H_4C≡C)- (12)[a]



[a]Reaction conditions: Pd^{II}/CuI, Et_2NH, sonication bath at ∼43 °C.

for only 1 h at room temperature in the presence of 20 mol % Pd[dppf]Cl_2/CuI using diethylamine as both a base and solvent readily afforded the alkynyl-linked products **10**−**12** in yields of 67%, 43%, and 97%, respectively.

We had previously been able to attach these same three substituents at a cage boron (B6) to form the complexes 1-(η^5-C_5H_5)-2-Ph-6-R-*closo*-1,2,3,4-Fe$C_3B_7H_9$ (R = PhC≡C-, $CH_3CH_2C(O)OCH_2C$≡C-, (η^5-C_5H_5)Fe(η^5-C_5H_4-C≡C)-) via analogous palladium-catalyzed Sonogashira reactions with the B-halo 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-Fe$C_3B_7H_9$ complex, but these reactions required much longer times (20−40 h) and provided yields of only 37%, 32%, and 21%, respectively.[3] Thus, the new Sonogashira reactions directed at the C-iodoaryl substituents are a considerable synthetic advance in enabling the attachment of these types of alkynyl-linked functional groups.

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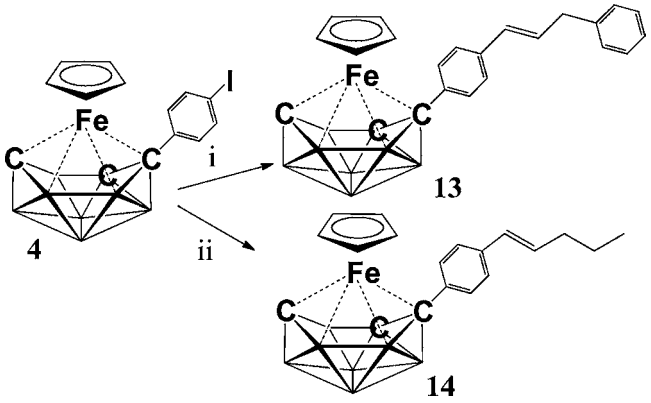
In our earlier work,[3] we were unsuccessful in achieving palladium-catalyzed Heck and Stille coupling reactions with the B-iodo complex 1-(η^5-C_5H_5)-2-Ph-6-I-*closo*-1,2,3,4-$FeC_3B_7H_9$. In contrast, the Heck reactions in Scheme 4 of **4** with

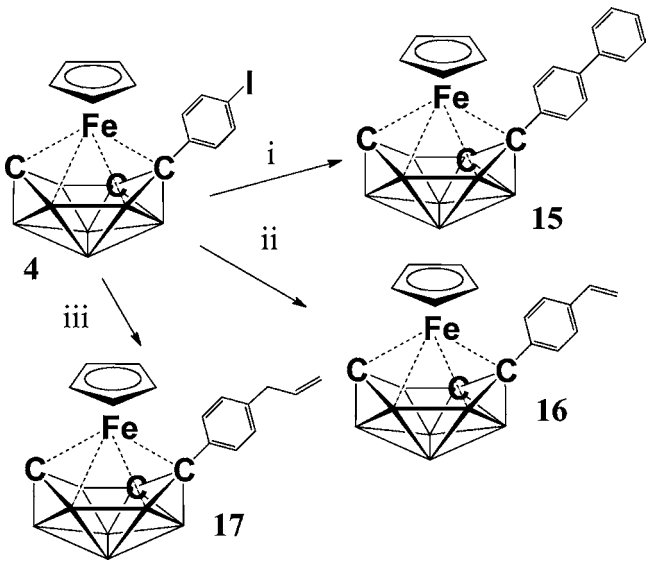
Scheme 4. Heck Coupling Reactions of 4 with (i) Allylbenzene and (ii) 1-Pentene To Yield 1-(η^5-C_5H_5)-2-*p*-RC_6H_4-*closo*-1,2,3,4-$FeC_3B_7H_9$ (R = ($PhCH_2CH$═CH)- (13), ($CH_3(CH_2)_2CH$═CH)- (14))[a]



[a]Reaction conditions: Pd^{II}, PPh_3, CH_3CN/NEt_3, 90 °C.

allylbenzene and pentene at 90 °C in the presence of 10 mol % $Pd(OAc)_2$ and 10 mol % PPh_3 using triethylamine as the base and acetonitrile as the solvent afforded the alkene-functionalized products **13** and **14** in 37% and 60% yields. Likewise, the Stille reactions shown in Scheme 5 of **4** with tributylphenyltin, tributylvinyltin, and tetraallyltin at 75 °C in the presence of 10 mol % $Pd(PPh_3)_2Cl_2$ and dry dimethylformamide as the solvent afforded **15**–**17** in 69%, 91%, and 79% yields.

Scheme 5. Stille Cross-Coupling Reactions of 4 with (i) Bu_3SnPh, (ii) $Bu_3Sn(CH$═$CH_2)$, and (iii) $Sn(CH_2CH$═$CH_2)_4$ To Yield 1-(η^5-C_5H_5)-2-*p*-RC_6H_4-*closo*-1,2,3,4-$FeC_3B_7H_9$ (R = Ph- (15), (CH_2═CH)- (16), (CH_2═$CHCH_2$)- (17))[a]



[a]Reaction conditions: Pd^{II}, DMF.

For all of the reactions, only one product was observed and **10**–**17** were again isolated as air- and moisture-stable solids that were soluble in a variety of polar and nonpolar solvents. The ^{11}B NMR spectra of **10**–**17** were nearly identical with that of the parent compound **4** and their ^1H NMR spectra again showed the two expected cage C–H resonances at low (6.97–6.89 ppm)- and high-field shifts (1.89–1.80 ppm), along with the resonances expected for their newly attached organic and organometallic substituents.

Crystallographic determinations of **10**, **12**, **15**, and **16** are shown in Figures 3 and 4. All complexes again exhibited the

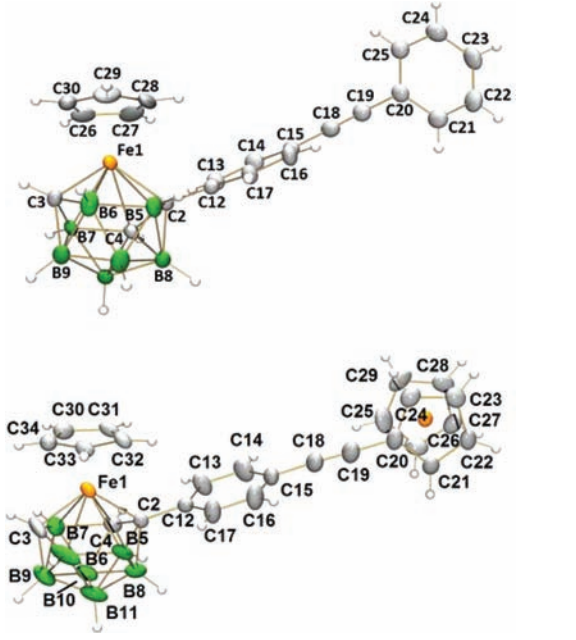


Figure 3. Crystallographically determined structures of (top) **10** and (bottom) **12**. Selected distances (Å) and angles (deg) are as follows. **10**: Fe1–C2, 1.975(3); Fe1–C3, 1.948(3); Fe1–C4, 2.262(3); Fe1–B5, 2.233(4); Fe1–B6, 2.245(4); Fe1–B7, 2.263(3); Fe1–$Cp_{Centroid}$, 1.683; C2–B5, 1.560(5); B5–B6, 1.830(5); C3–B6, 1.569(5); C3–B7, 1.571(5); C4–B7, 1.761(4); C2–C4, 1.522(4); C2–C12, 1.493(4); C15–C18, 1.446(4); C18–C19, 1.190(5); C19–C20, 1.447(4); C3–Fe1–C2, 111.11(12); C12–C2–Fe, 122.8(2); C19–C18–C15, 179.4(4); C18–C19–C20, 178.5(4). **12**: Fe1–C2, 1.960(3); Fe1–C3, 1.953(4); Fe1–C4, 2.227(4); Fe1–B5, 2.267(4); Fe1–B6, 2.278(5); Fe1–B7, 2.245(4); Fe1–$Cp_{Centroid}$, 1.685; Fe2–$Cp1_{Centroid}$, 1.637: Fe1–$Cp2_{Centroid}$, 1.644; C2–B5, 1.524(4); B5–B6, 1.766(8); C3–B6, 1.550(9); C3–B7, 1.573(7); C4–B7, 1.810(6); C2–C4, 1.575(5); C2–C12, 1.479(4); C15–C18, 1.434(5); C18–C19, 1.176(6); C19–C20, 1.433(5); C3–Fe1–C2, 110.83(16); C12–C2–Fe, 127.5(2); C19–C18–C15, 177.5(5); C18–C19–C20, 175.7(5).

octadecahedral cage geometry of the parent **4**. While the metals in **10**, **12**, and **15** sit reasonably centered in the tricarbadecaboranyl face, the Fe in **16** is slightly shifted toward the B5–B6 edge that is on the side away from the direction of the vinyl group. The C18–C19 distances in **10** (1.190(5) Å) and **12** (1.176(6) Å) and the C18–C19 distance in **16** (1.284(3) Å) confirm the presence of their acetylenic and olefinic structural units.

In conclusion, the new functionalization strategy reported herein employing palladium-catalyzed Sonogashira, Heck, and Stille cross-coupling reactions directed at the cage-carbon iodoaryl substituent of the 1-(η^5-C_5H_5)-2-(*p*-IC_6H_4)-*closo*-

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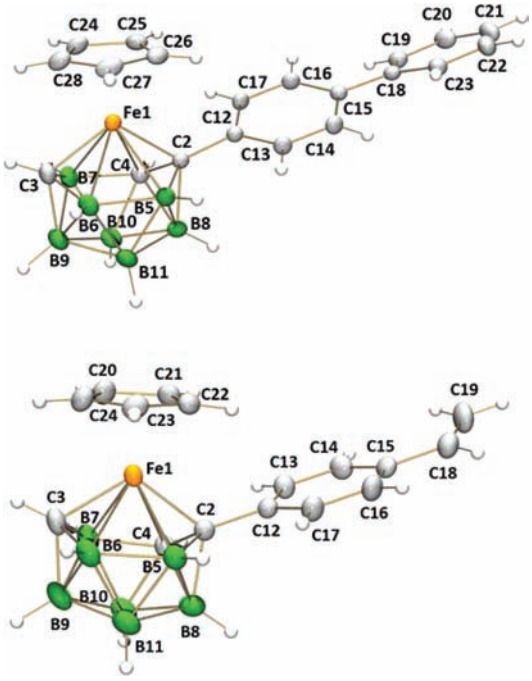

Figure 4. Crystallographically determined structures of (top) **15** and (bottom) **16**. Selected distances (Å) and angles (deg) are as follows. **15**: Fe1−C2, 1.9712(11); Fe1−C3, 1.9613(12); Fe1−C4, 2.2488(12); Fe1−B5, 2.2317(14); Fe1−B6, 2.2488(15); Fe1−B7, 2.2726(14); Fe1−$Cp_{Centroid}$, 1.683; C2−B5, 1.5923(17); B5−B6, 1.842(2); C3−B6, 1.580(2); C3−B7, 1.573(2); C4−B7, 1.7462(19); C2−C4, 1.5007(15); C2−C12, 1.4936(15); C15−C18, 1.4893(15); C3−Fe1−C2, 111.09(5); C12−C2−Fe1, 126.48(8). **16**: Fe1−C2, 1.9822(13); Fe1−C3, 1.9523(13); Fe1−C4, 2.2921(13); Fe1−B5, 2.2214(16); Fe1−B6, 2.2194(16); Fe1−B7, 2.2927(16); Fe1−$Cp_{Centroid}$, 1.683; C2−B5, 1.597(2); B5−B6, 1.844(2); C3−B6, 1.582(2); C3−B7, 1.572(2); C4−B7, 1.746(2); C2−C4, 1.4981(17); C2−C12, 1.4937(17); C15−C18, 1.485(2); C18−C19, 1.284(3); C3−Fe1−C2, 110.77(6); C12−C2−Fe1, 124.01(9); C15−C18−C19, 126.76(16).

1,2,3,4-$FeC_3B_7H_9$ complex has been shown to provide facile and systematic access to a wide variety of new types of functionalized metallatricarbadecaboranes. This strategy was made possible by the efficient high-yield synthesis of the key 6-(*p*-XC_6H_4)-*nido*-5,6,9-$C_3B_7H_9^-$ haloaryl-tricarbadecaboranyl anionic ligands. In contrast to the poor reactivity previously observed for B-halo metallatricarbadecaboranyl complexes toward many types of palladium-catalyzed cross-coupling reactions, the higher reactivity of the iodoaryl substituent results in both higher yields and an increase in the range of useful palladium-catalyzed reactions. This has increased the diversity of important substituents that can be readily attached to the complexes, including for example π-conjugated fragments containing alkynyl or alkenyl linkages (e.g., **10**, **12**, **15**, and **16**) and groups containing chemically active units that will facilitate further chemical modification (e.g., **11**, **13**, **16**, and **17**) and polymerization (**16** and **17**) reactions. This approach should now significantly enhance the ability to investigate potential metallocene-like biomedical and/or materials applications that exploit the unique properties of the metallatricarbadecaboranes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving IR data for all compounds, ORTEP diagrams of the X-ray structures of **5**, **7**−**9**, and crystallographic data for the structural determinations of **4**, **5**, **7**−**10**, **12**, **16**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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