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Formal Insertion of *o*-Carborynes into Ferrocenyl C−H Bonds: A Simple Access to *o*-Carboranylferrocenes

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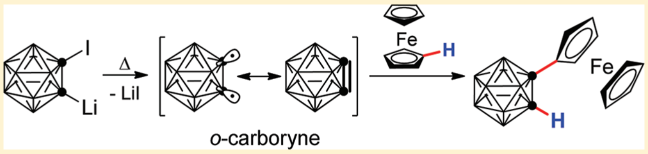
Ⓢ *Supporting Information*

ABSTRACT: Insertion of *o*-carborynes (1,2-dehydro-*o*-carboranes) into ferrocenyl C−H bonds has been described, providing a convenient methodology for the preparation of functionalized ferrocenyl *o*-carboranes. Reaction of the carboryne precursors 1-I-2-Li-9,12-Me_2-1,2-$C_2B_{10}H_8$ or 1-I-2-Li-3-R-1,2-$C_2B_{10}H_9$ (R = H, Ph, Me, Cl, Br, and I) with 2.5 equiv of ferrocene at 80 °C in cyclohexane afforded [1-(η^5-C_5H_4)(9,12-Me_2-1,2-$C_2B_{10}H_9$)]Fe(η^5-C_5H_5) and [1-(η^5-C_5H_4)-(3-R-1,2-$C_2B_{10}H_{10}$)]Fe(η^5-C_5H_5) (R = H, Ph, Me, Cl, Br, and I) in 19−44% isolated yields. On the other hand, in addition to the desired C−H bond insertion products [1-(η^5-C_5H_4)(3-X-1,2-$C_2B_{10}H_{10}$)]Fe(η^5-C_5H_5), bis(ferrocenyl)-*o*-carboranes 1,2-[(η^5-C_5H_5)Fe(η^5-C_5H_4)]$_2$-3-X-1,2-$C_2B_{10}H_9$ were isolated from the reactions of 1-I-2-Li-3-X-1,2-$C_2B_{10}H_9$ (X = Cl, Br, and I) in 12%, 15%, and 8% yields, respectively. Treatment of 1,2-dilithio-*o*-carborane or 1-lithio-2-methyl-*o*-carborane with ferrocenium hexafluorophosphate in cyclohexane also generated [1-(η^5-C_5H_4)(1,2-$C_2B_{10}H_{11}$)]Fe(η^5-C_5H_5) and [1-(η^5-C_5H_4)(2-Me-1,2-$C_2B_{10}H_{10}$)]Fe(η^5-C_5H_5) in 17% and 31% isolated yields, respectively. On the basis of these observations, it is suggested that the single-electron oxidation of ferrocene to the electrophilic ferrocenium cation by *o*-carborynes is crucial for the insertion reaction. Accordingly, a reaction mechanism is proposed.

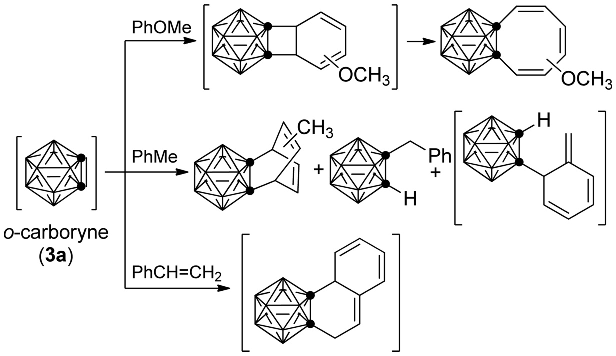


■ INTRODUCTION

o-Carboryne (1,2-dehydro-*o*-carborane) (**3a**), a very reactive intermediate reported first in 1990,[1] reacts readily with alkenes, dienes, alkynes, and polycyclic or heteroaromatics in [2 + 2] and [4 + 2] cycloaddition and ene reaction patterns,[2] similar to that of benzyne.[3] It can be generated in situ from either 1-Br-2-Li-1,2-$C_2B_{10}H_{10}$[1] or 1-Me_3Si-2-[IPh(OAc)]-1,2-$C_2B_{10}H_{10}$.[4]

Recently, we reported a more efficient precursor, 1-I-2-Li-1,2-$C_2B_{10}H_{10}$ (**2a**), readily prepared from *o*-carborane (**1a**), for the production of **3a**.[5a] Our preliminary results show that **3a** can exist in two resonance forms, a bonding form vs a biradical form, which exhibit significantly different reactivity patterns.[6,7] The biradical form can insert regioselectively into *α*-C−H bond of aliphatic ethers, affording *α*-carboranylated ethers.[6] On the other hand, the bonding form undergoes both [4 + 2] and [2 + 2] cycloaddition reactions with anisole and its derivatives. The resulting [2 + 2] cycloaddition intermediates simultaneously rearrange to cyclooctatetraenocarboranes via thermal [3,3] sigmatropic rearrangement.[7] Further studies show that **3a** can undergo [4 + 2] cycloaddition reaction, benzyl C−H bond insertion, and ene reaction with toluene[8] and exocyclic [4 + 2] cycloaddition reaction with styrenes,[9] in which the reactions exhibit a remarkable substituent effect (Scheme 1). As an ongoing project, we extended our research to include ferrocene, an intriguing aromatic organometallic complex.[10] Ferrocene consists of two cyclopentadienyls that can be viewed as carbanion species stabilized by aromaticity.[11,12] It is speculated that dearomatization of ferrocene with **3a** would generate energetically unstable species, from which new reaction patterns retaining the aromatic system would be anticipated. Indeed, *o*-carborynes **3** insert readily into the aromatic C−H bond of ferrocene, providing a simple access to ferrocenyl-substituted *o*-carboranes.[13] It is noted that no C−H bond insertion occurs between benzyne and ferrocene. These findings suggest that *o*-carboryne has unique properties of its own due to its higher electron deficiency, which is detailed in this article.

Scheme 1. Reaction of *o*-Carboryne (3a) with Organic Aromatics



■ RESULTS

A suspension of **2a** in cyclohexane, prepared in situ according to the reported procedures,[8,9] was heated at 110 °C for 24 h in the

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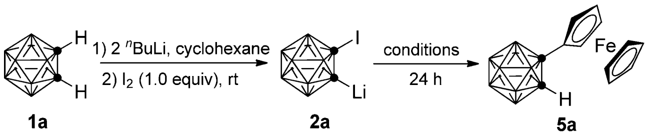
presence of 1.25 equiv of ferrocene (**4**). A new species (**5a**) was formed together with the regenerated *o*-carborane (**1a**) in a molar ratio of 45/55, as indicated by the ^{1}H NMR spectrum of the crude product mixture. They were inseparable by flash column chromatography on silica gel. However, **1a** was readily removed from the crude product mixture by sublimation. Accordingly, an unexpected C−H bond insertion product, 1-ferrocenylcarborane (**5a**), was obtained in 27% isolated yield (Table 1, entry 1). The characterization of **5a** was done by full comparison with the reported NMR data.[13] Lowering the reaction temperature to 80 °C or addition of a large excess of ferrocene (**4**) resulted in improved product yields (Table 1, entries 2 and 3). This reaction also proceeded smoothly in the dark under the same conditions (Table 1, entry 4). Alternatively, mixing ferrocene (**4**) and **1a** before adding ^{n}BuLi and I_2 gave an analogous result (Table 1, entry 5). Since the cage C−H proton of *o*-carborane (with a pK_a value of ∼23[14]) is more acidic than the ferrocenyl C−H proton (with a pK_a value of ∼39),[15] the competitive deprotonation of ferrocene by ^{n}BuLi is not anticipated. It has also been documented that ferrocene was readily oxidized to the deep blue species once elemental I_2 was added.[16] The above results may shed some light on the reaction mechanism (vide infra).

Table 1. Screening of Reaction Conditions

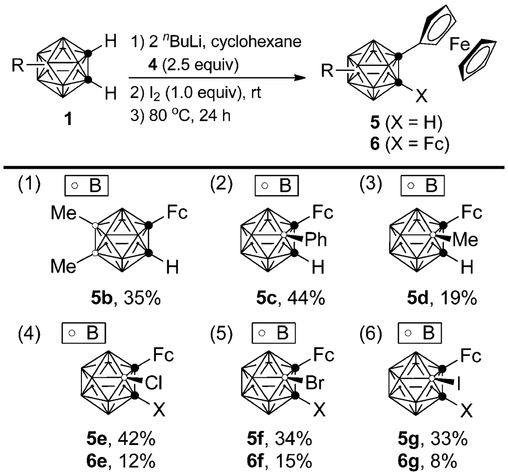


entry	conditions	isolated yield (**5a**, %)
1	**4** (1.25 equiv), 110 °C	27
2	**4** (1.25 equiv), 80 °C	31
3	**4** (2.5 equiv), 80 °C	36
4	**4** (2.5 equiv), in the dark, 80 °C	35
5	**4** (2.5 equiv), one-pot reaction, 80 °C	38

No corresponding C−H bond insertion product was obtained when benzyne was generated by treatment of 2-(trimethylsilyl)-phenyl trifluoromethanesulfonate with CsF in CH_3CN in the presence of 2.5 equiv of ferrocene (**4**), showing that *o*-carboryne has unique properties of its own.

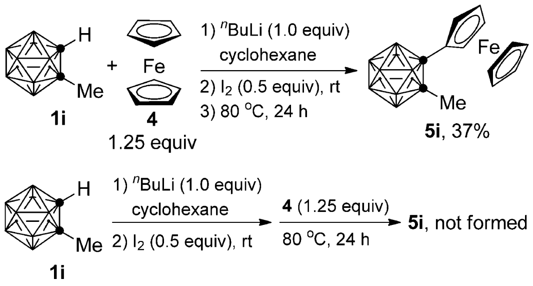
Under the reaction conditions shown in entry 5, Table 1, *o*-carborynes bearing B-substituents such as phenyl, halo, and methyl groups were subject to the above reaction. The results are summarized in Table 2. 9,12-Dimethyl-*o*-carboryne showed a similar reactivity to that of its parent *o*-carboryne (Table 2, entry 1). 3-Substituted *o*-carborynes exhibited various reactivities dependent on the substituents. 3-Phenyl-*o*-carboryne underwent a C−H insertion with **4** to give **5c** in an isolated yield of 44%, while 3-methyl-*o*-carboryne afforded the desired product **5d** in only 19% isolated yield (Table 2, entries 2 and 3). Interestingly, in addition to the C−H bond insertion products **5** in yields comparable to that of *o*-carboryne, reaction of ferrocene (**4**) with 3-halocarborynes generated bis(ferrocenyl)-*o*-carboranes **6** in 8−15% yields (Table 2, entries 4−6). These results suggested that electron-withdrawing substituents at the 3-position favor the insertion reactions. It is noteworthy that disubstituted *o*-carboranes were also produced from the C−H bond insertion reaction of *o*-carboryne with aliphatic ethers,[6] which may indicate that both reactions share some common features in the reaction mechanism.

Table 2. Effects of Cage B-Substituents on C−H Bond Insertion



Interestingly, treatment of a cyclohexane solution of 1-methyl-*o*-carborane (**1i**) and **4** with 1 equiv of ^{n}BuLi followed by addition of 0.5 equiv of I_2 and heating at 80 °C for 24 h afforded 1-ferrocenyl-2-methyl-*o*-carborane (**5i**) in 37% isolated yield based on I_2. In contrast, **5i** was not formed if ferrocene (**4**) was added after the consumption of elemental I_2, as shown in Scheme 2. This result may indicate that the oxidation of ferrocene to the ferrocenium cation by I_2 is crucial for the formation of **5i** (vide infra).[16]

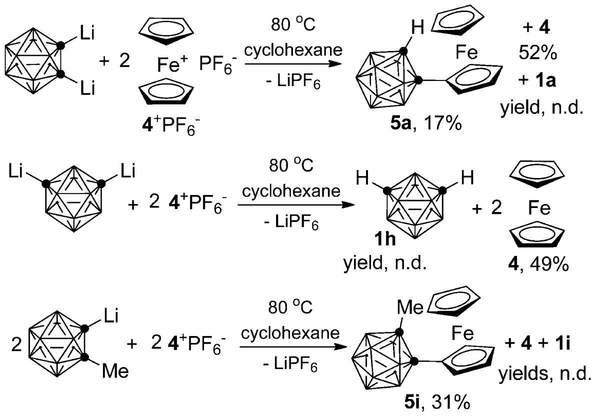
Scheme 2. Reaction of 1-Methyl-*o*-Carborane (1i) with Ferrocene



Accordingly, reactions of 1,2-dilithio-*o*-carborane, 1,7-dilithio-*m*-carborane, or 1-lithio-2-methyl-*o*-carborane with a commercially available ferrocenium salt, ferrocenium hexafluorophosphate ($4^+[PF_6]^-$), were carried out (Scheme 3). In addition to the reduction product ferrocene and *o*-carboranes, the anticipated ferrocenylcarboranes **5a** and **5i** were isolated in 17% and 31% yields, respectively. However, no coupling product was generated in the reaction of 1,7-dilithio-*m*-carborane with $4^+[PF_6]^-$.

All new compounds were purified by flash column chromatography on silica gel and characterized by various spectroscopic data. The ^{1}H NMR spectra of **5b** showed two doublets of doublets at 4.35 and 4.19 ppm corresponding to the η^5-C_5H_4 group, one singlet at 4.22 ppm of η^5-C_5H_5, one broad singlet at 3.52 ppm attributable to the cage C−H proton, and two singlets at 0.24 and 0.18 ppm assignable to two B−CH_3 units. For 1-ferrocenyl-3-phenyl-*o*-carborane (**5c**), three multiplets, at 4.06, 3.99, and 3.94 ppm, corresponding to the η^5-C_5H_4 unit were observed. These protons were slightly shielded by the 3-phenyl group. The other B(3)-substituted ferrocenyl *o*-carboranes, **5d** to **5g**, displayed four multiplets of the η^5-C_5H_4 group at 4.36, 4.24,

Scheme 3. Reaction of Lithiocarboranes with $4^+[PF_6]^-$



4.21, and 4.02 ppm (**5d**), 4.48, 4.30, 4.28, and 4.18 ppm (**5e**), 4.48, 4.30, 4.28, and 4.14 ppm (**5f**), and 4.47, 4.30, 4.28, and 4.09 ppm (**5g**), respectively. Such a splitting pattern was also found in the spectra of their corresponding 1,2-bis(ferrocenyl)-*o*-carboranes **6e**,**f**,**g**. For **5i**, two multiplets at 4.41 and 4.28 ppm of the η^5-C_5H_4 group were observed, similar to that of $[1\text{-}(\eta^5\text{-}C_5H_4)\text{-}(2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10})]_2Fe$.[13]

Molecular structures of **5b**,**c**,**e**,**f**,**i** and **6e** were further confirmed by single-crystal X-ray analyses (Figure 1). The measured cage C−C bond distances from 1.637(4) to 1.775(4) Å fall in the range normally observed in *o*-carboranes.[17] The cage C−C(Cp) distances vary from 1.480(4) to 1.495(4) Å, which are very close to the corresponding values found in the documented carboranyl metallocene complexes, for example, 1.487(7) Å in $[1\text{-}(\eta^5\text{-}C_5H_4)(1,2\text{-}C_2B_{10}H_{11})]Fe(\eta^5\text{-}C_5H_5)$,[13] 1.492(2) Å in $[1\text{-}(\eta^5\text{-}C_5D_4)(2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10})]RuD(PPh_3)_2$,[18a] and 1.495(6) Å in $[1,2\text{-}(\eta^5\text{-}MeHC\text{-}C_5H_3)(1,2\text{-}C_2B_{10}H_{10})]RuH(PPh_3)_2$.[19b]

■ DISCUSSION

A formal nucleophilic attack of $1\text{-}Li\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10}$ on the Cp ring bound to a ruthenium(II) center was reported.[18a] Further studies suggested the coupling between carboranyl and cyclopentadienyl groups resulted from the reductive elimination of a $CpRu(C_2B_{10}H_{10}R)$ complex promoted by sterically demanding coordinating ligands.[18b,19] Ferrocene, an electron-rich species, is susceptible to the *exo*-attack of electrophiles rather than nucleophiles.[20] Indeed, nucleophilic 1,2-dilithio-*o*-carborane did not react with ferrocene. On the other hand, electron-deficient cationic half-sandwich iron(II) complexes have been documented to undergo nucleophilic substitution on the cyclopentadienyl ring, inducing the hapticity change from η^5-Cp bonding mode to η^4-cyclopentadiene complexation.[21,22]

In the reaction of 1,2-dilithio-*o*-carborane with $4^+[PF_6]^-$ (Scheme 3), 1 equiv of ferrocenium hexafluorophosphate functions as the electrophile and the other one may act as the oxidant to oxidize the nucleophilic adducts **8a**; meanwhile, 1,2-dilithio-*o*-carborane also serves as a base to accept the leaving proton from the cyclopentadiene of **9a** (Scheme 4). After initial oxidation of ferrocene by I_2,[16] one-pot reaction with 1-methyl-*o*-carborane in Scheme 2 would enter the same reaction pathway, which can be regarded as oxidative activation of ferrocene for nucleophilic reaction.[23]

In view of a much higher yield of ferrocene (**4**) over the coupling product **5a** (52% vs 17%) in the reaction of 1,2-dilithio-*o*-carborane with $4^+[PF_6]^-$ (Scheme 3), a competitive direct redox reaction between the two substrates is likely to occur (Scheme 4),[24] which can be viewed as the reverse process of one-electron oxidation of **4** by *o*-carboryne (Scheme 5). The resulting carboranyl radicals then undergo hydrogen abstraction with solvents to regenerate *o*-carborane (**1a**).[2,9] Such a redox reaction predominates in the reaction of the *m*-carborane system, and thus only ferrocene (**4**) was regenerated in high yield together with **1h** (Scheme 3). This result suggests that *m*-lithiocarborane is a stronger reducing agent than its *ortho* counterpart, which is consistent with the observations for the *nido* species of carboranes.[25]

Theoretical calculations show that the LUMO (lowest unoccupied molecular orbital) energy of *o*-carboryne is much lower than that of benzyne;[26] that is, *o*-carboryne can more easily accommodate another external electron than benzyne. This may account for the different reactivities in their reactions with ferrocene. On the basis of the above results, a plausible mechanism is thus proposed in Scheme 5. Elimination of LiI from **2a** gives the reactive intermediate *o*-carboryne (**3a**), which is best described as a resonance hybrid of both bonding and biradical forms.[6] **3a** undergoes one-electron oxidation with ferrocene (**4**) to afford the ferrocenium cation $\mathbf{4}^+$ and the carboranyl radical anion **7a**, which may be a reversible process. Nucleophilic *exo*-attack of **7a** on one of the cyclopentadienyl rings in $\mathbf{4}^+$ results in the formation of adduct **8a**′,[21,22] which can be viewed as the reduced form of the protonated ferrocene.[27] There are two possible pathways from **8a**′ to the C−H bond insertion product **5a**: direct radical-induced hydrogen shift of **8a**′ generating **5a** (path I) or an intramolecular single-electron transfer of **8a**′ giving the protonated ferrocene **9a**,[27] which is rapidly deprotonated by the neighboring carboranyl anion to afford **5a** (path II). It should be pointed out that the carboranyl anion of **1** or **7** can deprotonate the insertion product **5** as well to give the 1-ferrocenyl-*o*-carboranyl anion, which can react with the electrophilic species $\mathbf{4}^+$ in a similar manner to that of the reaction of 1-lithio-2-methyl-*o*-carborane with $4^+[PF_6]^-$ (Scheme 4), yielding 1,2-bis(ferrocenyl)-*o*-carboranes **6**. For example, the reactions of 3-halo-*o*-carborynes **3e**,**f**,**g** with **4** gave **6** (Table 2, entries 4−6).

■ CONCLUSION

Insertion of *o*-carborynes into the ferrocenyl C−H bond has been described. It is suggested that the oxidation of ferrocene to the electrophilic ferrocenium cation via a single electron transfer by *o*-carborynes is crucial for the insertion reaction, which is confirmed by the reactions of lithiocarboranes with ferrocenium hexafluorophosphate. Such an aromatic C−H bond insertion reaction serves as a convenient methodology for the preparation of a series of functionalized ferrocenyl *o*-carboranes. This work demonstrates that carborynes not only have very rich reaction chemistry but also have unique properties of their own, which is different from that of benzyne.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were carried out in flame-dried glassware under an atmosphere of dry N_2 or Ar with the rigid exclusion of air and moisture using standard Schlenk techniques unless otherwise specified.[8] All organic solvents were freshly distilled from Na−K alloy immediately prior to use. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified. ^1H NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz. $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Bruker DPX 400

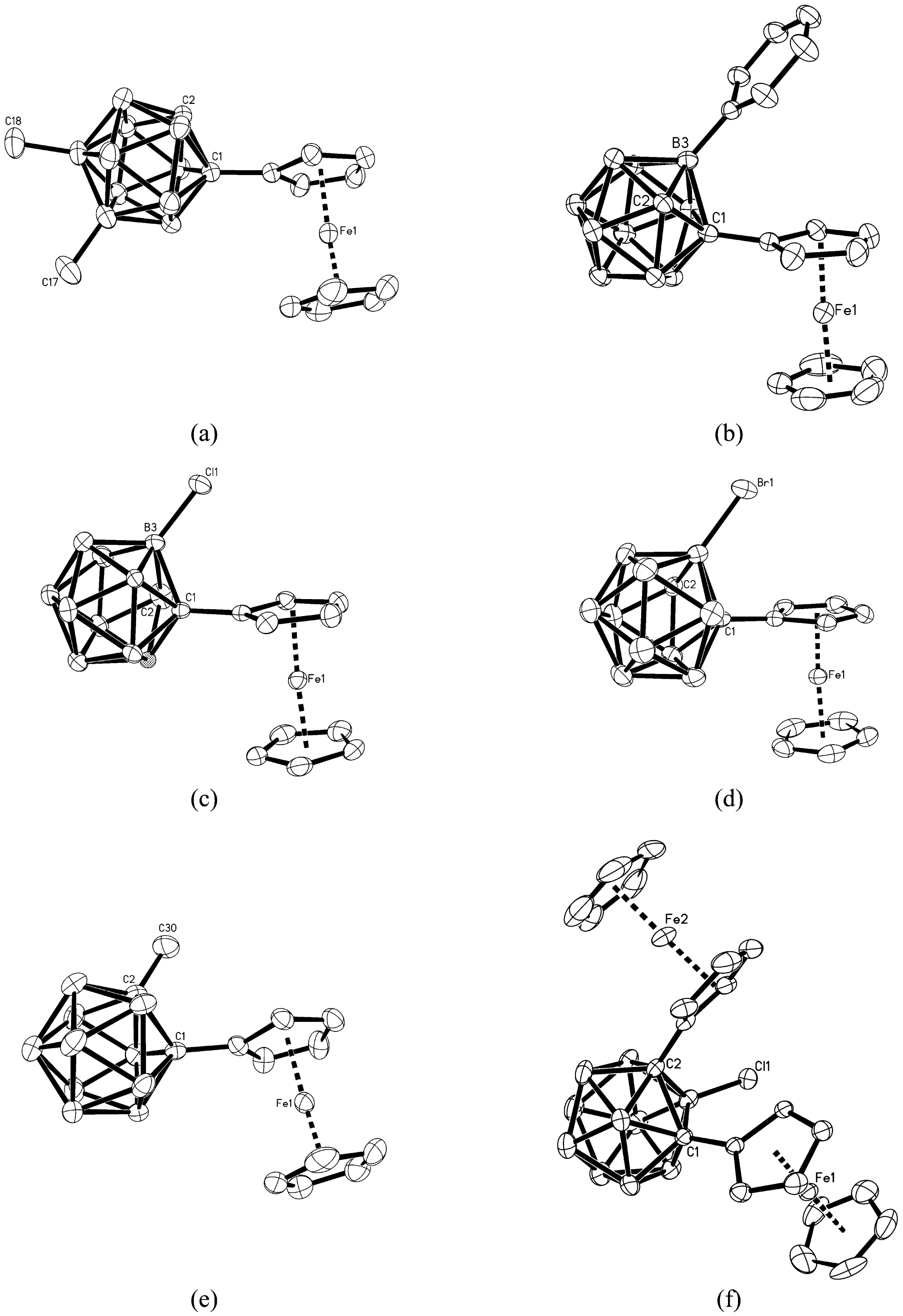
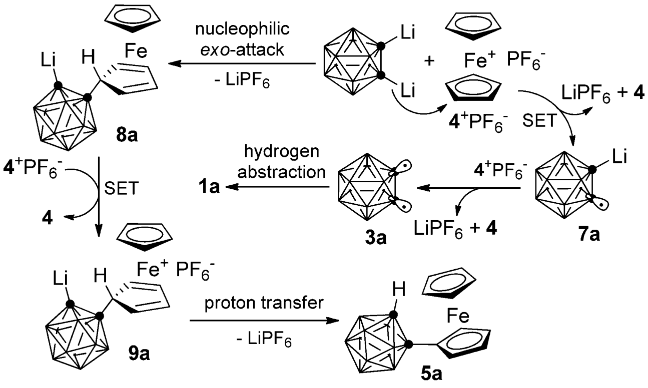


Figure 1. Molecular structures of (a) **5b**, (b) **5c**, (c) **5e**, (d) **5f**, (e) **5i**, and (f) **6e**. All hydrogen atoms are omitted for clarity.

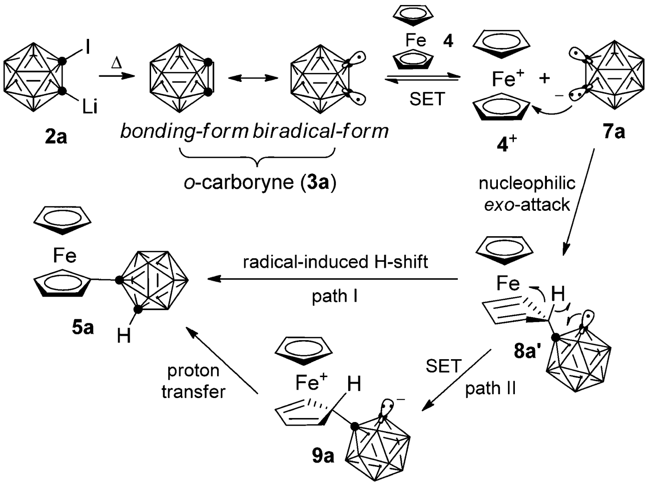
spectrometer at 100 MHz. ^{11}B NMR spectra were recorded on a Bruker DPX 300 spectrometer at 96 MHz or a Varian Inova 400 spectrometer at 128 MHz. Chemical shifts were reported in ppm with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.0 ppm) for boron chemical shifts. The data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br = broad), coupling constant(s) in Hz, integration, and assignment. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer.

Reaction of 2a with Ferrocene (4). To an in situ prepared cyclohexane solution (5 mL) of **2a** (0.4 mmol) at room temperature was added ferrocene (186.1 mg, 1.0 mmol). The reaction mixture was heated at 80 °C for 24 h and then quenched with wet *n*-hexane. The resulting suspension was quickly passed through a short column of silica gel to remove the inorganic salts and washed with ether (5 mL × 3). The organic portions were combined. After removal of solvents in vacuo, the residue was analyzed by ^{1}H NMR spectroscopy (**5a**/**1a** = 45/55). The regenerated *o*-carborane (**1a**) was removed by sublimation in vacuo, and the resulting residue was then subjected to flash column

Scheme 4. Possible Pathways for Reaction of 1,2-Dilithio-*o*-carborane with $4^+[PF_6]^-$



Scheme 5. Possible Pathways for Insertion of 3a into a Ferrocenyl C−H Bond



chromatography on silica gel (230−400 mesh) using *n*-hexane as eluent to give **5a** as yellow crystals (47.3 mg, 36%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.37 (m, 2H), 4.24 (s, 5H), 4.21 (m, 2H) (ferrocenyl C*H*), 3.72 (br, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 86.0, 75.8 (cage *C*), 70.03, 69.98, 68.7, 65.0 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ −2.2 (1B), −5.5 (1B), −10.0 (4B), −11.8 (2B), −13.1 (2B). These data are the same as the reported ones.[13]

Reaction of *o*-Carborane (1a) with Ferrocene (4) in the Presence of ^{n}BuLi and I_2. To a cyclohexane solution (5 mL) of *o*-carborane (57.6 mg, 0.4 mmol) and ferrocene (186.1 mg, 1.0 mmol) at room temperature was slowly added ^{n}BuLi (0.5 mL, 1.6 M in hexane, 0.8 mmol) with stirring. After stirring for 6 h, iodine (101.6 mg, 0.4 mmol) was added and a deep blue mixture was obtained after stirring at room temperature overnight. The reaction mixture was heated at 80 °C for 24 h and then quenched with wet *n*-hexane. The resulting suspension was quickly passed through a short column of silica gel to remove the inorganic salts and washed with ether (5 mL × 3). The organic portions were combined. After removal of solvents in vacuo, the residue was analyzed by ^1H NMR spectroscopy. The regenerated *o*-carborane (**1a**) was removed by sublimation in vacuo, and the resulting residue was then subjected to flash column chromatography on silica gel (230−400 mesh) using *n*-hexane as eluent to give **5a** as yellow crystals (49.6 mg, 38%).

Reaction of 4 with 1b−g,i in the Presence of ^{n}BuLi and I_2. These reactions were performed at a scale of 1.0 mmol of **4** and 0.4 mmol of **1** using the same procedures reported for **5a**.

1-Ferrocenyl-9,12-dimethyl-o-carborane, ***5b***. Yellow crystals. Yield: 49.9 mg (35%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.35 (dd, *J* = 2.0, 1.6 Hz, 2H), 4.22 (s, 5H), 4.19 (dd, *J* = 2.0, 1.6 Hz, 2H) (ferrocenyl C*H*), 3.52 (br, 1H) (cage C*H*), 0.24 (s, 3H), 0.18 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 85.7, 70.03, 69.87, 68.4, 58.3 (cage *C*), −0.1 (br), one cage carbon was not observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.6 (s, 1B), 4.5 (s, 1B), −7.8 (d, *J* = 145 Hz, 2B), −10.2 (d, *J* = 164 Hz, 2B), −13.2 (d, *J* = 161 Hz, 4B). HRMS (EI): calcd for $C_{14}H_{24}{}^{11}B_8{}^{10}B_2Fe^+$ 356.2232, found 356.2229.

1-Ferrocenyl-3-phenyl-o-carborane, ***5c***. Yellow crystals. Yield: 71.2 mg (44%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 3H), 7.19 (m, 2H) (aromatic C*H*), 4.21 (s, 5H), 4.06 (m, 1H), 3.99 (m, 1H), 3.94 (m, 2H) (ferrocenyl C*H*), 3.92 (br, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 133.5, 129.0, 127.6, 85.2, 70.3, 70.0, 68.1, 67.8, 67.7, 63.2 (cage *C*), one cage carbon was not observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ −2.4 (s, 1B), −4.6 (d, *J* = 147 Hz, 2B), −8.4 (d, *J* = 143 Hz, 2B), −11.4 (d, *J* = 152 Hz, 4B), −14.9 (d, *J* = 163 Hz, 1B). HRMS (EI): calcd for $C_{18}H_{24}{}^{11}B_8{}^{10}B_2Fe^+$ 404.2234, found 404.2240.

1-Ferrocenyl-3-methyl-o-carborane, ***5d***. Yellow crystals. Yield: 26.3 mg (19%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.36 (m, 1H), 4.27 (s, 5H), 4.24 (m, 1H), 4.21 (m, 1H), 4.02 (m, 1H) (ferrocenyl C*H*), 3.43 (br, 1H) (cage C*H*), 0.17 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 86.1, 75.3 (cage *C*), 70.2, 69.4, 68.5, 68.1, 66.8, 65.6 (cage *C*). ^{11}B NMR (128 MHz, $CDCl_3$): δ −2.1 (s, 1B), −4.9 (d, *J* = 137 Hz, 2B), −8.6 (d, *J* = 138 Hz, 1B), −9.5 (d, *J* = 142 Hz, 1B), −10.9 (d, *J* = 154 Hz, 2B), −11.9 (d, *J* = 140 Hz, 2B), −15.2 (d, *J* = 163 Hz, 1B). HRMS (EI): calcd for $C_{13}H_{22}{}^{11}B_8{}^{10}B_2Fe^+$ 342.2075, found 342.2079.

3-Chloro-1-ferrocenyl-o-carborane, ***5e***. Yellow crystals. Yield: 61.0 mg (42%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.48 (m, 1H), 4.30 (m, 1H), 4.28 (m, 6H), 4.18 (m, 1H) (ferrocenyl C*H*), 3.73 (br, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 84.4, 70.21, 70.16, 68.8, 68.6, 67.9, 67.1 (cage *C*), one cage carbon was not observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ −3.2 (s, 1B), −5.0 (d, *J* = 143 Hz, 1B), −5.4 (d, *J* = 148 Hz, 1B), −8.8 (d, *J* = 147 Hz, 1B), −9.7 (d, *J* = 134 Hz, 1B), −11.0 (m, 3B), −13.5 (d, *J* = 157 Hz, 1B), −15.3 (d, *J* = 172 Hz, 1B). HRMS (EI): calcd for $C_{12}H_{19}{}^{11}B_8{}^{10}B_2ClFe^+$ 363.1503, found 363.1503.

3-Chloro-1,2-bis(ferrocenyl)-o-carborane, ***6e***. Red-brown crystals. Yield: 26.4 mg (12%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.60 (m, 2H), 4.18 (s, 10H), 4.13 (m, 2H), 4.09 (m, 2H), 4.06 (m, 2H) (ferrocenyl C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 82.0, 72.3, 70.4, 70.3, 68.6, 68.2, cage carbons were not observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ −1.8 (s, 1B), −5.0 (d, *J* = 146 Hz, 2B), −8.5 (d, *J* = 159 Hz, 3B), −9.6 (d, *J* = 141 Hz, 3B), −14.9 (d, *J* = 149 Hz, 1B). HRMS (EI): calcd for $C_{22}H_{27}{}^{11}B_8{}^{10}B_2ClFe_2{}^+$ 547.1486, found 547.1486.

3-Bromo-1-ferrocenyl-o-carborane, ***5f***. Yellow crystals. Yield: 55.5 mg (34%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.48 (m, 1H), 4.30 (m, 1H), 4.28 (m, 6H), 4.14 (m, 1H) (ferrocenyl C*H*), 3.78 (br, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 85.3, 70.24, 70.18, 68.8, 68.5, 67.6, 67.1 (cage *C*), one cage carbon was not observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ −4.5 (d, *J* = 142 Hz, 1B), −5.1 (d, *J* = 150 Hz, 1B), −8.0 (br, 1B), −8.9 (br, 2B), −10.7 (br, 3B), −12.0 (br, 1B), −14.8 (d, *J* = 165 Hz, 1B). HRMS (EI): calcd for $C_{12}H_{19}{}^{11}B_8{}^{10}B_2BrFe^+$ 407.1010, found 407.1012.

3-Bromo-1,2-bis(ferrocenyl)-o-carborane, ***6f***. Red-brown crystals. Yield: 35.6 mg (15%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.71 (m, 2H), 4.18 (s, 10H), 4.16 (m, 2H), 4.11 (m, 2H), 4.03 (m, 2H) (ferrocenyl C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 86.1 (cage *C*), 82.6, 72.3, 70.8, 70.4, 68.5, 68.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ −4.5 (d, *J* = 145 Hz, 2B), −7.3 (s, 1B), −8.2 (br, 4B), −9.1 (d, *J* = 154 Hz, 2B), −13.5 (d, *J* = 147 Hz, 1B). HRMS (EI): calcd for $C_{22}H_{26}{}^{11}B_8{}^{10}B_2BrFe_2{}^+$($[M - H]^+$) 591.0895, found 591.0875.

1-Ferrocenyl-3-iodo-o-carborane, ***5g***. Yellow crystals. Yield: 60.3 mg (33%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.47 (m, 1H), 4.30 (m, 1H), 4.28 (m, 6H), 4.09 (m, 1H) (ferrocenyl C*H*), 3.81 (br, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 87.2, 70.3, 70.2, 68.8, 68.4, 67.4, 67.3 (cage *C*), one cage carbon was not observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ −3.5 (d, *J* = 143 Hz, 1B), −4.6 (d, *J* = 146 Hz, 1B), −6.7 (d, *J* = 160 Hz, 1B), −9.8 (br, 5B), −13.9 (d, *J* = 162 Hz, 1B), −23.1 (s, 1B). HRMS (EI): calcd for $C_{12}H_{19}{}^{11}B_8{}^{10}B_2IFe^+$ 454.0885, found 454.0893.

1,2-Bis(ferrocenyl)-3-iodo-o-carborane, ***6g***. Red-brown crystals. Yield: 20.5 mg (8%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.83 (m, 2H), 4.20 (m, 12H), 4.14 (m, 2H), 4.01 (m, 2H) (ferrocenyl C*H*). $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$): δ 85.7 (cage C), 83.4, 72.1, 71.5, 70.4, 68.4, 68.3. ^{11}B NMR (128 MHz, $CDCl_3$): δ −3.6 (d, J = 141 Hz, 2B), −6.7 (d, J = 131 Hz, 3B), −8.1 (br, 3B), −11.4 (d, J = 154 Hz, 1B), −21.3 (s, 1B). HRMS (EI): calcd for $C_{22}H_{27}{}^{11}B_8{}^{10}B_2IFe_2^+$ 638.0865, found 638.0871.

*1-Ferrocenyl-2-methyl-o-carborane, **5i**.* Yellow crystals. Yield: 50.6 mg (37%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.41 (m, 2H), 4.28 (m, 2H), 4.26 (s, 5H) (ferrocenyl C*H*), 1.49 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 83.4, 81.0 (cage C), 71.2, 70.6, 69.0, 22.7, one cage carbon was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ −4.7 (2B), −9.5 (6B), −11.6 (2B). HRMS (EI): calcd for $C_{13}H_{22}{}^{11}B_8{}^{10}B_2Fe^+$ 342.2075, found 342.2081.

Reaction of 1,2-Dilithio-*o*-carborane with Ferrocenium Hexafluorophosphate ($4^+[PF_6]^-$). To a cyclohexane solution (5 mL) of *o*-carborane (57.6 mg, 0.4 mmol) was slowly added ^{n}BuLi (0.5 mL, 1.6 M in hexane, 0.8 mmol) with stirring at room temperature. After the mixture was stirred for 6 h at room temperature, ferrocenium hexafluorophosphate (331.0 mg, 1.0 mmol) was added with stirring. The reaction mixture was heated at 80 °C for 24 h and then quenched with wet *n*-hexane. The resulting suspension was quickly passed through a short column of silica gel to remove the inorganic salts and washed with ether (5 mL × 3). The organic portions were combined. After removal of solvents in vacuo, the residue was analyzed by ^1H NMR spectroscopy and then subjected to flash column chromatography on silica gel (230−400 mesh) using *n*-hexane as eluent to give **5a** (22.6 mg, 17%) as yellow crystals and ferrocene (39.0 mg, 52%).

Reaction of 1,7-Dilithio-*m*-carborane or 1-Lithio-2-methyl-*o*-carborane with $4^+[PF_6]^-$. These reaction were performed at a scale of 1.0 mmol of $4^+[PF_6]^-$ using the same procedures reported for 1,2-dilithio-*o*-carborane.

4: This compound was isolated from the reaction of 1,7-dilithio-*m*-carborane as yellow crystals (72.2 mg, 49%).

5i: This compound was isolated from the reaction of 1-lithio-2-methyl-*o*-carborane as yellow crystals (42.5 mg, 31%).

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program.[28] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.[29] All hydrogen atoms were geometrically fixed using the riding model. Molecular structure of **5c** showed a half hexane of solvation. The chlorine atom in **6e** is disordered over two sets of positions (B(3) and B(6) positions) with 0.19:0.81 occupancies. For non-centrosymmetric structures of **5e** and **5i**, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[30] Crystal data and details of data collection and structure refinements are given in Table S1 in the Supporting Information. Further details are also included in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H, ^{13}C, and ^{11}B NMR spectra of all new compounds, Table S1, and crystallographic data in CIF format for **5b**,**c**,**e**,**f**,**i** and **6e**. 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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