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Synthesis, Molecular Structure, and Electrochemistry of 1-Ferrocenyl-1,2-dicarba-*closo*-dodecaboranes

Aleš Korotvička,[a] Ivan Šnajdr,[a] Petr Štěpnička,*[b]
Ivana Císařová,[b] Zbyněk Janoušek,[c] and Martin Kotora*[a]

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Bis(dimethylsulfido)decaborane, 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$, reacts smoothly with ferrocenyl alkynes FcC≡CR [**1a**–**h**; Fc = ferrocenyl, R = H (**1a**), CH_3 (**1b**), Ph (**1c**), 4-$MeO_2CC_6H_4$ (**1d**), Fc (**1e**), C≡CFc (**1f**), C(O)CH_3 (**1g**), and $CO_2CH_2CH_3$ (**1h**)] to afford the corresponding 1-ferrocenyl-1,2-dicarba-*closo*-dodecaboranes **2a**–**h** in good yields. Ester **2h** was further reduced to the respective hydroxymethyl derivative, 1-Fc-2-CH_2OH-1,2-*closo*-$C_2B_{10}H_{10}$ (**3**). The reaction of 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ with FcC≡CSiMe$_3$ proceeded in a different manner to produce (among other products) an SMe_2 adduct of an opened decaborane substituted with a 2-ferrocenyl-2-(trimethylsilyl)ethen-1-yl group (**4**). This compound probably results through hydroboration of the starting alkyne and migration of the $SiMe_3$ group. All prepared compounds were characterized by spectroscopic methods (^1H, ^{13}C, and ^{11}B NMR spectroscopy, IR spectroscopy, and mass spectrometry), and their molecular structures were determined by single-crystal X-ray diffraction analysis. In addition, the compounds were studied by cyclic and differential pulse voltammetry on a platinum disc electrode to reveal simple ferrocenyl-centered oxidations for the singly ferrocenylated carboranes and two consecutive oxidation waves for compounds **2e** and **2f**, which possess two ferrocenyl substituents.

Introduction

The reaction between decaborane adducts of type L_2-*arachno*-$B_{10}H_{12}$ (**L** = MeCN, Et_2S, Me_2S, and so on) and alkynes is one of the key procedures for the synthesis of mono- and disubstituted 1,2-*closo*-carboranes. This process is general with respect to the substituents attached to carbon atoms of the triple bond and usually proceeds well to afford the respective substituted carboranes in good yields.[1,2]

Ferrocenylalkynes constitute an attractive subclass among alkynes, mostly because their utilization in various addition and cycloaddition reactions provides direct access to compounds functionalized with the redox-active, metal-containing ferrocene moiety.[3] In addition, the bulky ferrocenyl group in the vicinity of the triple bond exerts steric hindrance that could in turn affect the reactivity of the triple bond. So far, monoferrocenylalkynes have been employed in transition-metal-catalyzed[4] or -mediated[5] [2+2+2] cycloadditions to provide the corresponding ferrocenylbenzenes, in reactions with reduced metallocenes to form the corresponding ferrocene-substituted metallacyclopentadienes or η^2-alkyne complexes,[6] in [4+2] cycloadditions with tetraalkylcyclobutadiene complexes to give rise to Dewar benzenes,[7] and as reaction partners in the C–C cleavage reaction of phenylenes.[8] The bulky diferrocenylethyne has been studied much less in this regard, very likely owing to a relatively difficult means of access to this compound.[9]

Given our interest in the synthesis of ferrocene-substituted compounds[5,7,8] and variously substituted carboranes,[10] it was rather surprising to find that there has not yet been undertaken any systematic study into the addition reactions of decaborane or its adducts (L_2-*arachno*-$B_{10}H_{12}$) and ferrocenylalkynes. In fact, there appear to be just two reports that concern the synthesis of (mono)ferrocenylcarborane by the reaction of decaborane with ferrocenylethyne in the presence of MeCN.[11] Likewise, studies into other ferrocenyl-substituted boranes and metallaboranes remain still scarce.[12] This provided a strong impetus for us to assess the scope of the reaction of decaborane derivative 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$ with variously substituted ferrocenylalkynes and to characterize in detail thus-accessible ferrocenylated *closo*-1,2-dicarbadodecaboranes.

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[a] Department of Organic Chemistry, Faculty of Science, Charles University,
Hlavova 8, 12843 Praha 2, Czech Republic
Fax: +420-221-951-326
E-mail: kotora@natur.cuni.cz
Homepage: http://orgchem.cz/kotora
[b] Department of Inorganic Chemistry, Faculty of Science, Charles University,
Hlavova 8, 12843 Praha 2, Czech Republic
Fax: +420-221-951-253
E-mail: stepnic@natur.cuni.cz
Homepage: http://web.natur.cuni.cz/~stepnic/
[c] Institute of Organic Chemistry and Biochemistry, AS CR, v.v.i.,
Flemingovo nám. 2, 16610 Praha 6, Czech Republic

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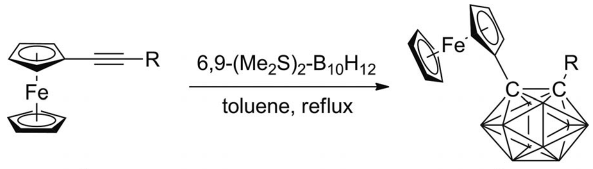
Results and Discussion

Synthesis and Spectra

The starting alkynes were all obtained from ferrocenylethyne **1a** by using the previously developed procedures. Thus, 1-ferrocenylpropyne **1b** was prepared by lithiation of **1a** with *n*BuLi followed by treatment with methyl iodide. A similar method (i.e., electrophilic quench of metalated **1a**) was used to prepare compounds **1g** and **1h**.[13] Phenyl- and (4-methoxycarbonyl)phenyl derivatives **1c** and **1d** were obtained by Sonogashira reaction of **1a** with the respective aryl halides, whereas diferrocenylethyne **1e** was synthesized by homo-alkyne metathesis of **1b**.[14] Diyne **1f** was obtained by the Glaser coupling.[15]

The reactions of ferrocenylalkynes **1** with 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$ were carried out under the usual conditions (i.e., the alkyne was heated with the decaborane adduct under reflux conditions in toluene for 16 h; Scheme 1).



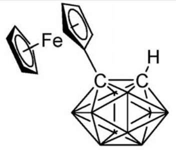
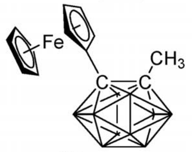
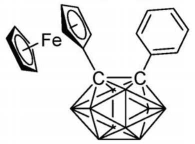
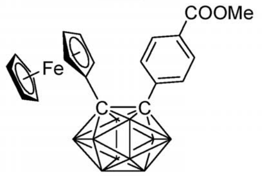
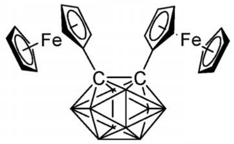
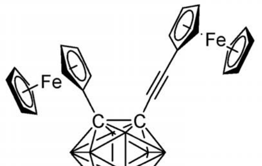
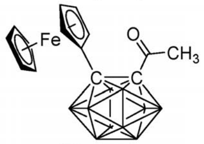
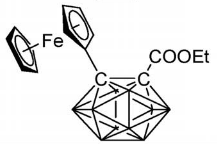
1 **2**

Scheme 1. Reaction of 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ with ferrocenylalkynes.

In all cases but one the reactions proceeded uneventfully to afford the expected 1-ferrocenyl-1,2-dicarba-*closo*-dodecaboranes (Table 1). The reactions with methyl-, phenyl-, and 4-$MeO_2CC_6H_4$-substituted ferrocenylalkynes **1b**–**1d** yielded the corresponding *closo*-carboranes **2b**–**2d** in good isolated yields of 21, 61, and 60 %, respectively. The reaction with the sterically hindered diferrocenylethyne **1e** also proceeded surprisingly well, which provided 1,2-diferrocenyl-1,2-dicarba-*closo*-dodecaborane **2e** in 58 % yield. Likewise, the reaction with 1,4-diferrocenylbutadiyne **1f** gave **2f** in 52 % isolated yield. The presence of two triple bonds in **1f** could in principle enable a twofold reaction, thereby giving rise to the corresponding bridged bis-carborane.[16] However, we did not isolate any such compound from the reaction mixture.

The general procedure also proved feasible for electron-deficient ferrocenyl alkynes **1g** and **1h**, which bear the reactive acetyl and carboxymethyl groups. The corresponding carboranes **2g**–**2h** were isolated in reasonable 29 and 55 % yields, respectively.

Table 1. Prepraration of ferrocenylcarboranes **2a**–**2h**.

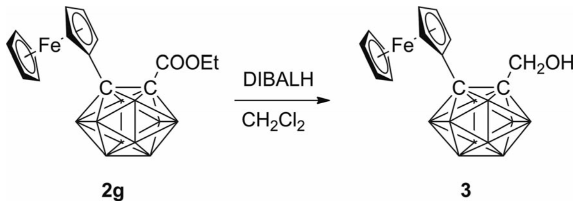
Entry	R in FcC≡CR (**1**)	Carborane (**2**)		Yield [%][a]
1	H (**1a**)		**2a**	26
2	CH_3 (**1b**)		**2b**	21
3	Ph (**1c**)		**2c**	60
4	C_6H_4COOMe (**1d**)		**2d**	61
5	Fc (**1e**)		**2e**	58
6	C≡CFc (**1f**)		**2f**	52
7	$COCH_3$ (**1g**)		**2g**	29
8	COOEt (**1h**)		**2h**	55

[a] Isolated yields.

For a comparison, the reaction with ferrocenylethyne **1a** was also performed as reported previously,[11] and compound **2a** was isolated in 26 % yield (isolated yields in the original reports were not given). Compound **2b** was recently obtained by a different route.[17] Furthermore, we attempted to carry out the direct reaction of decaborane $B_{10}H_{14}$ with representative alkynes **1a**, **1b**, and **1e** in ionic liquid (bmim)Cl (bmim = 1-butyl-3-methylimidazolium) as was described earlier for simple alkynes.[18] In the case of ethynylferrocene **1a**, a complex reaction mixture resulted, from which only acetylferrocene was isolated after the standard workup (33 % isolated yield; ^1H NMR spectroscopic data were in agreement with the published ones[19]). The presence of carborane **2a** in the reaction mixture was not confirmed. It is assumed that acetylferrocene was formed by hydroboration of the triple bond and subsequent hydrolysis. The reaction with 1-ferrocenylpropyne **1b** yielded the expected carborane **2b** in 28 % isolated yield, whereas the reaction with diferrocenylethyne **1e** did not proceed at all, and the starting alkyne was recovered unchanged. Although the direct reaction of decaborane with alkynes might represent a simpler and more straightforward approach to substituted carboranes, its scope seems to be limited compared to reactions with adducts **L**$_2$-*arachno*-$B_{10}H_{12}$. Safety issues with handling and manipulation of hazardous decaborane also disfavor the direct route.

The prepared 1,2-dicarbadodecaboranes **2a**–**2h** were characterized by a combination of multinuclear NMR spectroscopy (^{1}H, ^{13}C, and ^{11}B), IR spectroscopy, mass spectrometry, and elemental analysis. In addition to these conventional methods, all isolated compounds were characterized by single-crystal X-ray diffraction analysis, which unequivocally confirmed their formulation (see below). The ^{11}B NMR spectra of **2a**–**2h** display a pattern typical for symmetrically (**2e**) and unsymmetrically (**2a**–**2d**, **2f**–**2h**) substituted 1,2-dicarbadodecaboranes. The spectra of the symmetrically substituted 1,2-dicarba-*closo*-dodecaborane show the signals in the order δ_B: B(12,9) > B(8,10) > B(5,4,7,11) > B(3,6). The patterns seen for the unsymmetrically substituted 1,2-dicarba-*closo*-dodecaboranes depend on the electronic nature of the substituents.[20]

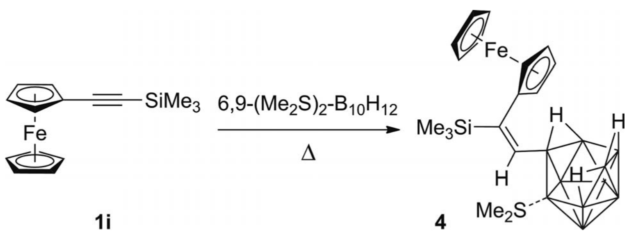
To extend the scope of accessible "*ortho*-carborane" derivatives, the ester derivative **2h** was converted into the corresponding alcohol **3** by reduction with diisobutylaluminium hydride (DIBAL-H) in dichloromethane (Scheme 2). The reduction proceeded cleanly and furnished the alcohol in a 96% isolated yield. The compound was characterized by spectroscopic methods and its structure was determined by X-ray diffraction analysis.



Scheme 2. Reduction of ester **2h** to alcohol **3**.

Finally, we attempted to treat 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$ with 1-trimethylsilyl-2-ferrocenylethyne (**1i**)[6] (Scheme 3). According to TLC analysis, which was used to monitor the course of the reaction, the starting alkyne disappeared completely under the standard reaction conditions to afford a complex reaction mixture. A tedious column chromatography provided several fractions, but none of them contained the expected product (as could be judged from the ^{1}H and ^{11}B NMR spectra). However, crystallization of one of the fractions provided crystalline *nido*-borane derivative (**4**; ca. 5% yield), which was fully characterized by NMR spectroscopy and elemental analysis. In addition, the compound afforded crystals suitable for a single-crystal X-ray analysis, which revealed a rather unusual structure (Figure 1).

First, the C–C triple bond was transformed into the double bond, and its trimethylsilyl substituent migrated from the terminal carbon atom of the original triple bond to the internal carbon atom of the newly formed double bond. Second, the product contains a dimethyl sulfide molecule, which comes from the starting decaborane adduct, and is bonded to one of the boron atoms at the opened ten-vertex borane cage. From a mechanistic viewpoint, the *nido*-borane **4** appears to be the product of hydroboration of the triple bond followed by 1,2-migration of the trimethylsilyl group. A similar rearrangement was previously observed only in the case of reactions of bis(trimethylsilyl)ethyne and (trimethylsilyl)propyne with 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$.[17]



Scheme 3. Reaction of 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ with **1h** to furnish compound **4**.

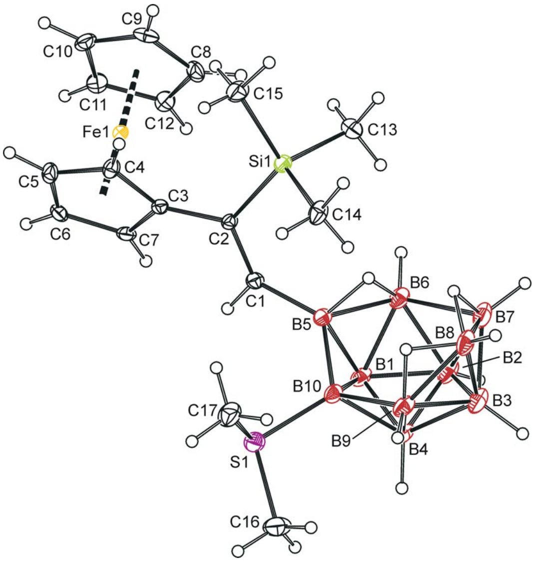


Figure 1. PLATON plot of the structure of **4** showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level. Selected distances and angles (in Å and °): S1–B5 1.890(4), S1–C16 1.796(4), S1–C17 1.795(4), B5–B6 1.670(5), B6–C1 1.561(5), C1–C2 1.350(4), C2–C3 1.487(4), C2–Si1 1.903(3); C1–C2–C3 117.4(2), C16–S1–C17 100.9(2), C1–C2–Si1 118.9(2), B6–C1–C2–Si1 –0.1(5), B–B (range) 1.670(5)–2.032(6); ferrocenyl moiety: Fe–C 2.028(3)–2.061(3) Å, tilt 1.7(2)°.

Description of Molecular Structures of 2a–h and 3

The molecular structures of **2a**–**h** and **3** were determined by single-crystal X-ray diffraction analysis. Compounds **2a**[11] and **2b**[21] have been structurally characterized already before, but for the sake of consistency, we have redetermined their crystal structures under the same conditions. The structures of **2c**, **2f**–**h**, and **3** are depicted in Figures 2, 3, 4, 5, 6, and 7, whereas those of **2a**, **2b**, and **2d** are presented in the Supporting Information (Figures S1–S3). Selected geometric data for all compounds are summarized in Table 2.

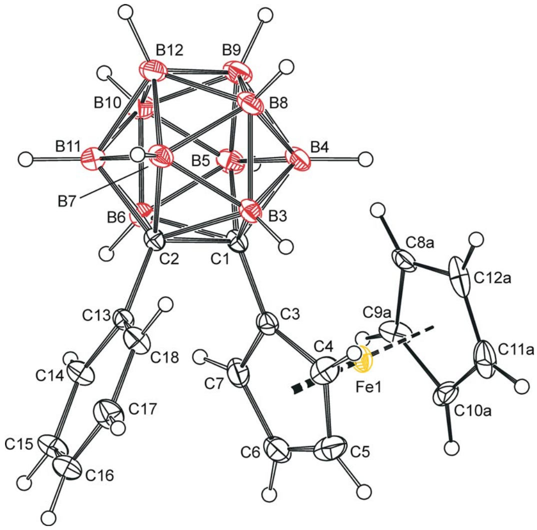


Figure 2. PLATON plot of **2c** showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level. Only one orientation of the disordered cyclopentadienyl ring C(9–12) is shown for clarity.

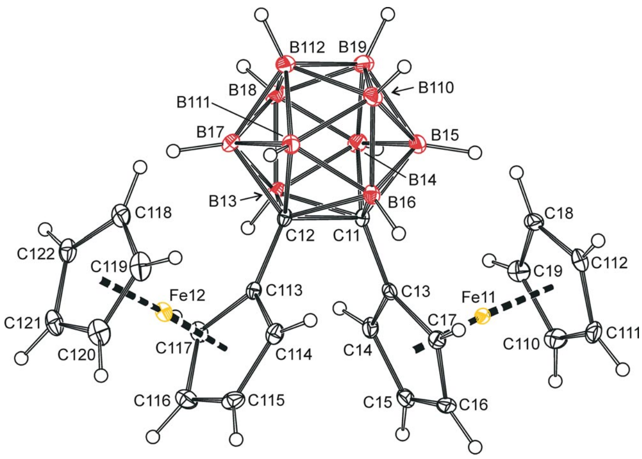


Figure 3. PLATON plot of **2e** (molecule 1) showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level. Note: Atomic labels in the second independent molecule are obtained by changing the first digit of the respective atomic labels to 2.

The structures of **2a**–**h** are essentially molecular[22] with the exception of alcohol **3**, which forms cyclic centrosymmetric arrays through O–H···O hydrogen bonds (Figure 8). Often, the compounds crystallize with two molecules per asymmetric unit (**2a**, **2e**, **2g**, and **3**). However, the independent molecules typically show only marginal differences.

Generally, the structural data for **2a**–**h** and **3** compare well with those reported earlier for fc(2-Me-1,2-$C_2B_{10}H_{10}$)$_2$ (fc = ferrocene-1,1′-diyl)[11b] and ferrocenylated carboranes reported recently by Xie and co-workers.[21] The geometry of the C_2B_{10} cages in the structurally characterized compounds are rather uniform and do not depart from the usual ranges (B–B 1.757–1.799 Å, B–C 1.690–1.745 Å for all structurally characterized compounds). The planes that bisect the carborane cage, namely, {C1,C2,B9,B12} and {B3,B6,B8,B10}, are mutually perpendicular (dihedral angles 89.6–90.0°), which reflects the rigidity of the compact *closo*-carborane cage. Compound **2a**, which bears the smallest substituent (hydrogen atom) at C2, exhibits the shortest C1–C2 distance, and its ferrocenyl substituent is oriented above the C1–C2 bond and tilted with respect to the {C1,C2,B9,B12} plane, which bisects the carborane cage (see parameter δ in Table 2). All other structurally characterized ferrocenylated *closo*-carboranes assume a different conformation. The ferrocenyl substituents in their

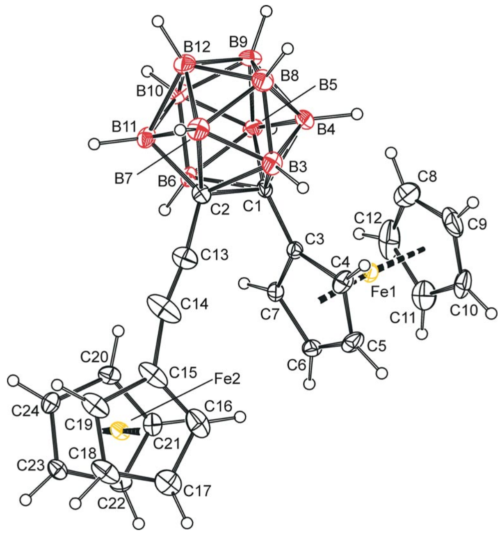


Figure 4. PLATON plot of **2f** (molecule 1) showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level (see note in the caption to Figure 3).

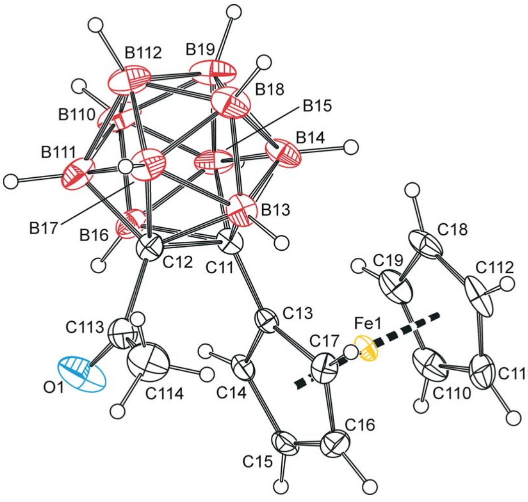


Figure 5. PLATON plot of **2g** showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level.

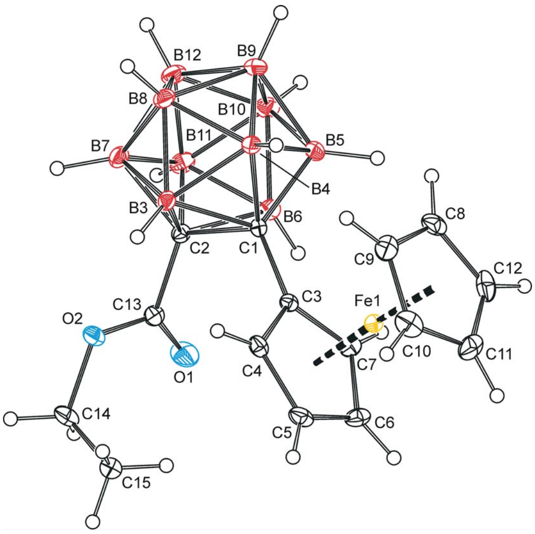


Figure 6. PLATON plot of **2h** showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level.

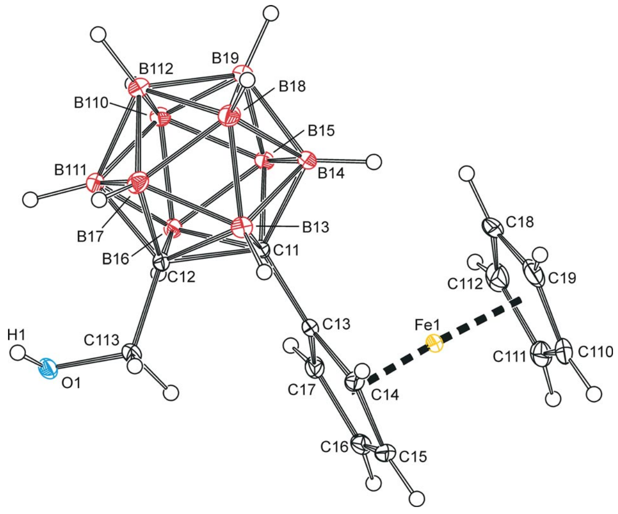


Figure 7. PLATON plot of **3** (molecule 1) showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level (see note in the caption to Figure 3).

Table 2. Selected geometric data for compounds **2a**–**h** and **3** (in Å and °).[a,b]

	2a[c]	**2b**	**2c**[b]	**2d**[d]	**2e**[e]	**2f**[f]	**2g**[g]	**2h**[h]	**3**[i]
C1–C2	1.653(2) [1.653(3)]	1.701(2)	1.733(2)	1.718(4)	1.764(2) [1.757(2)]	1.714(4)	1.691(3) [1.701(3)]	1.697(2)	1.712(2) [1.713(2)]
C1–C3	1.490(2) [1.490(2)]	1.491(2)	1.484(2)	1.481(4)	1.483(2) [1.485(2)]	1.486(3)	1.485(3) [1.484(3)]	1.487(2)	1.489(2) [1.488(2)]
C2–C1–C3	120.6(1) [120.5(2)]	116.5(1)	115.5(1)	114.3(2)	116.7(1) [115.7(1)]	114.9(2)	115.7(2) [116.1(1)]	116.01(9)	117.3(1) [117.7(1)]
C2–C13	n.a.	1.515(2)	1.503(2)	1.498(4)	1.479(3) [1.488(2)]	1.448(4)	1.546(4) [1.538(3)]	1.528(2)	1.531(2) [1.525(2)]
C1–C2–C13	n.a.	117.6(1)	118.0(1)	118.4(2)	117.2(1) [116.5(1)]	114.1(2)	117.0(2) [117.2(2)]	115.28(9)	116.5(1) [117.6(1)]
C3–C1–C2–C13	n.a.	0.4(2)	2.6(2)	2.8(3)	0.4(2) [0.5(2)]	–2.2(3)	–1.0(3) [–5.5(2)]	–2.6(1)	2.8(2) [1.5(2)]
ϕ	44.22(6) [42.58(8)]	21.61(5)	20.72(6)^{c}	26.3(1)	23.00(7) (Fe11)/23.69(6) (Fe12) [20.64(7) (Fe21)/ 22.96(7) (Fe22)]	17.3(1)	19.47(8) [21.0(1)]	22.08(5)	22.42(5) [23.66(5)]
δ	71.1(1) [71.7(1)]	89.04(9)	89.3(1)	69.3(2)	82.7(1) (Fe11)/88.9(1) (Fe12) [88.3(1) (Fe21)/ 89.4(1) (Fe22)]	89.5(2)	84.3(2) [78.9(1)]	83.97(8)	81.73(8) [89.44(9)]
Fe–Cg1	1.6447(8) [1.6438(9)]	1.6449(7)	1.6405(9)	1.644(1)	1.6433(9) (Fe11)/1.6480(9) (Fe12) [1.6419(9) (Fe21)/ 1.6554(9) (Fe22)]	1.639(1)	1.636(1) [1.639(1)]	1.6460(6)	1.6492(7) [1.6473(7)]
Fe–Cg2	1.6537(9) [1.657(1)]	1.6522(7)	1.6696(6)/ 1.6323(6)^{d}	1.653(2)	1.653(1) (Fe11)/1.6559(9) (Fe12) [1.6489(9) (Fe21)/ 1.662(1) (Fe22)]	1.651(2)	1.644(1) [1.651(1)]	1.6536(7)	1.6548(7) [1.6542(7)]
τ	6.2(1) [4.8(1)]	3.05(9)	3.2(1)^{c}	2.3(2)	4.3(1) (Fe11)/4.6(1) (Fe12) [5.0(1) (Fe21)/3.7(1) (Fe22)]	4.0(2)	3.5(1) [4.1(2)]	3.66(8)	4.08(9) [4.26(9)]

[a] Definitions: Cp1 and Cp2 are planes of the cyclopentadienyl rings C3–C7 and C8–C12, respectively. Cg1 and Cg2 denote their respective centroids. ϕ = angle subtended by the vectors Cg···Cg2 and C1–C2; δ = the dihedral angle subtended by the plane {C1,C2,B9,B12} and the plane of the substituted cyclopentadienyl ring (Cp1). τ denotes the dihedral angle of the cyclopentadienyl planes Cp1 and Cp2 (i.e., the tilt angle). Values in square brackets correspond to the second structurally independent molecule in the crystal structure. The labeling schemes in molecules 1 and 2 are strictly analogous, with the respective atomic labels having 1 or 2 added as the first digit. [b] Further data for **2c**: The dihedral angle of the phenyl ring and the {C1,C2,B9,B12} plane is 71.3(1)°. [c] Value for the more populated orientation of the unsubstituted Cp ring. [d] Further data for **2d**: C19–O1 1.206(4)°, C19–O2 1.326(4)°, O1–C19–O2 124.1(3)°; dihedral angle of the phenyl ring and the {C1,C2,B9,B12} plane is 79.4(2)°; dihedral angle of the {C19, O1, O2} plane and the phenyl ring is 12.3(4)°. [e] For clarity, the labels of the iron atoms are specified for values relating to the two independent ferrocenyl substituents. [f] Further data for **2f**: C13–C14 1.158(5)°, C14–C15 1.426(5)°, C2–C13–C14 165.5(3)°, C13–C14–C15 166.6(4)°. Compound **2e**: Fe–Cg1/Cg2 distances for the FcC≡C group are 1.642(1)/1.648(1), the tilt angle is 2.0(2)°. [g] Further data for **2g**: C=O 1.203(3) [1.190(3)], C(O)–CH$_3$ 1.468(4) [1.456(4)], O=C–CH$_3$ 123.0(3) [122.5(3)]. [h] Further data for **2h**: C13–O1 1.193(2), C13–O2 1.323(2), O2–C14 1.467(2). [i] Further data for **3**: CH$_2$–O 1.408(2) [1.410(2)].

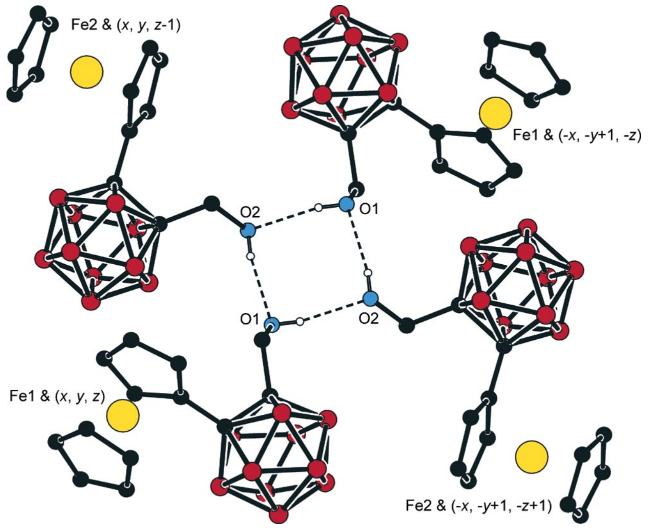


Figure 8. View of the cyclic hydrogen-bonded array in the crystal structure of alcohol **3**. The hydrogen-bond parameters are as follows: O1–H1···O2, O1···O2 2.747(2) Å, angle at H1 169(2)°; O2–H2···O1, O2···O1 2.836(2) Å; angle at H2 169(2)°.

molecules are rotated above the adjacent trigonal CB_2 face (C1, B4, B5), presumably to avoid spatial contacts with the substituent at C2. As a result, the ferrocenyl groups are near to perpendicular to the central {C1,C2,B9,B12} plane and show δ angles in the range of approximately 69–90°. It is also noteworthy that variation in the C1–C2 bond lengths (1.69–1.73 Å) in **2a**–**h** and **3** does not seem to follow any obvious trend (e.g., with electronic and/or properties of the substituents at C2).

Ferrocene moieties in **2a**–**h** and **3** are regular and show tilt angles below approximately 6° [maximum: 6.2(1)° for **2a**, molecule 1]. In all cases, the distance of the iron atom from the centroid of the substituted cyclopentadienyl ring (Fe–Cp1) is slightly shorter than that between the iron atom and the centroid of the unsubstituted cyclopentadienyl ring. Such a difference in the Fe–Cp distances very likely reflects the electron-withdrawing nature of the electron-deficient carborane cage, thereby resulting in a transfer of electron density from the ferrocenyl group to the C_2B_{10} skeleton and strengthening the Fe–C_5H_4 bonding relative to Fe–C_5H_5.[23]

Electrochemistry

The electrochemical behavior of carboranes **2** and **3** was studied by cyclic and square-wave voltammetry on a platinum disc electrode by using approximately 0.5 mM solutions in 1,2-dichloroethane that contained 0.1 M $Bu_4N[PF_6]$ as the supporting electrolyte. The pertinent data are presented in Table 3.

Compounds that contain one ferrocenyl substituent (**2a**–**d**, **2g**, **2h**, and **3**) expectedly displayed a single redox change within the accessible potential window, which can be attributed to the ferrocene/ferrocenium couple ($Fe^{II/III}$; Figure 9). These redox processes were controlled by diffusion [i_{pa} [vprop] ($\nu^{1/2}$); i_{pa} is anodic peak current and ν the scan rate], were electrochemically reversible, and corresponded to a one-electron redox transition. The associated redox potentials were found in a rather narrow range ($\Delta E^{\circ\prime} \approx 30$ mV; see Table 3), which indicates a limited electronic influence of the second substituent (2-R) attached to the 1-Fc-1,2-$C_2B_{10}H_{10}$ cage on the redox properties of the ferrocenyl group.

Table 3. Summary of the redox potentials for carboranes **2a**–**h** and **3**.[a]

	R	$E^{\circ\prime}$ [V versus FcH/FcH$^+$]
2a	H	0.265
2b	Me	0.275
2c	Ph	0.250
2d	4-$C_6H_4CO_2CH_3$	0.270
2e	Fc	0.200, 0.345
2f	C≡CFc	E_{pa} = 0.330, E_{pc} = 0.175
2g	Ac	0.270
2h	$CO_2CH_2CH_3$	0.280
3	CH_2OH	0.275

[a] $E^{\circ\prime} = 1/2(E_{pa} + E_{pc})$, in which E_{pa} (E_{pc}) are anodic (cathodic) peak potentials in cyclic voltammetry. Conditions: Pt disc electrode, 1,2-dichloroethane solutions containing 0.1 M $Bu_4N[PF_6]$ as the supporting electrolyte scan rate: 200 mV s^{-1}.

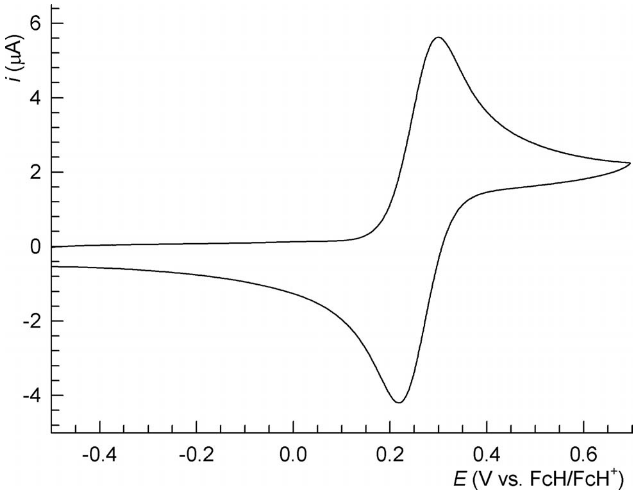


Figure 9. Cyclic voltammogram of **2a** as recorded on a Pt disc electrode in 1,2-dichloroethane (scan rate 0.2 V s^{-1}).

Introduction of a second ferrocenyl group such as in **2e** was reflected by an appearance of a second redox wave (Figure 10). Thus, compound **2e** was oxidized in two distinct one-electron redox steps, thus suggesting some electronic communication between the chemically equivalent ferrocenyl groups. The separation of the redox waves (ca. 145 mV) suggests this compound to be a weakly coupled redox system, at the borderline between class I and II systems according to the Robin–Day classification.[24] The ethynyl spacer present in **2f** makes the two ferrocenyl groups more distant and further lowers their interaction. Consequently, the individual waves become closer than in **2e** and appear convoluted (Figure 11).

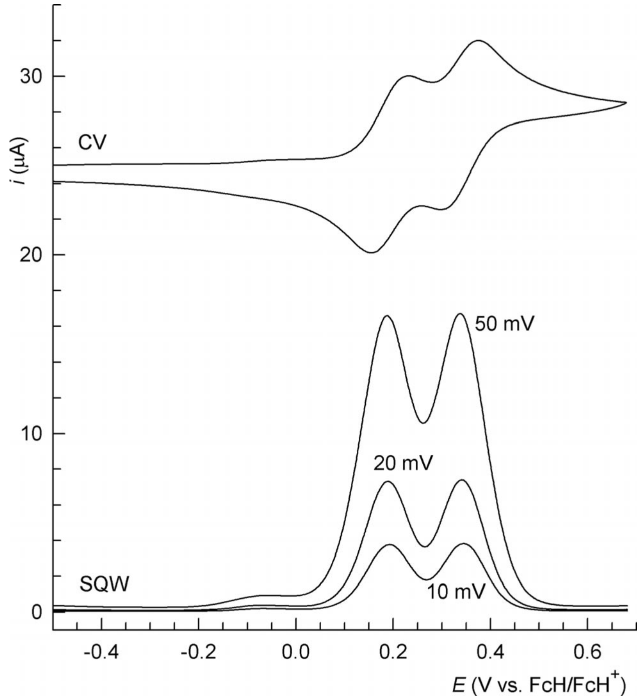


Figure 10. Cyclic (CV) and square-wave (SQW) voltammograms of **2e** (conditions: Pt disc electrode, 1,2-dichloroethane). Modulation amplitude is given for the SQW voltammograms. For clarity, the cyclic voltammogram (scan rate 0.2 V s^{-1}) is shifted by +25 μA.

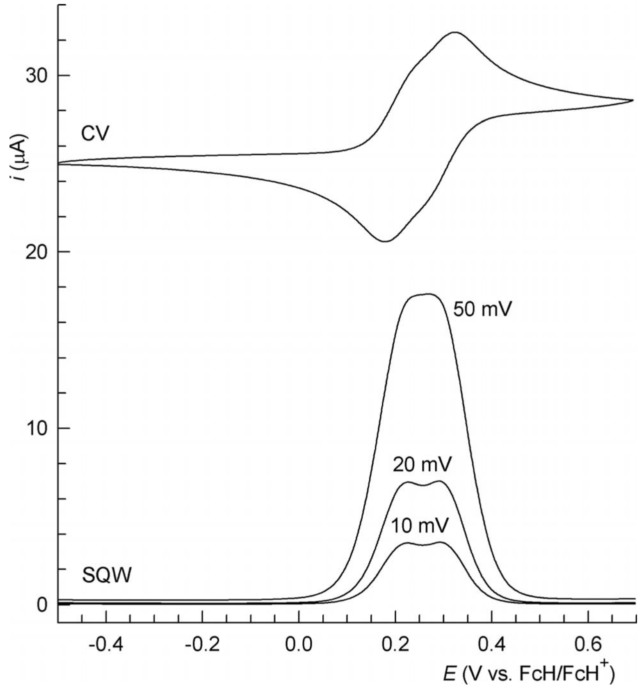


Figure 11. Cyclic (CV) and square-wave (SQW) voltammograms of **2f** (conditions: Pt disc electrode, 1,2-dichloroethane). Modulation amplitude is specified for the SQW voltammograms. The cyclic voltammogram (scan rate 0.2 V s^{-1}) is shifted by +25 μA to avoid overlaps.

Conclusion

Our systematic study demonstrates that reactions of 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$ with ferrocenyl alkynes FcC≡CR bearing simple and functional (organic) substituents provide a viable route to the corresponding 1-ferrocenyl-2-R-1,2-dicarba-*closo*-dodecaboranes. An analogous reaction with FcC≡CSiMe$_3$ surprisingly takes a different course, thereby producing a complicated product mixture from which an unusual opened borane–dimethyl sulfide adduct bearing the 2-ferrocenyl-2-(trimethylsilyl)-ethen-1-yl group was isolated in tiny amounts. The 1,2-dicarba-*closo*-dodecaboranes possess similar compact icosahedral structures decorated with the substituents (Fc and R) at the outer side. No clear trends were detected among the structural parameters, thereby reflecting a possible influence of the attached substituent (R). Similarly, the influence of the R moiety on the redox response of the monoferrocenylated carboranes, which all undergo reversible one-electron oxidation that is attributable to the ferrocene/ferrocenium couple, is also very limited. Introduction of a second ferrrocenyl moiety is reflected by another more or less separated wave, which indicates some electronic communication between the redox-active ferrocenyl pendants.

Experimental Section

Materials and Methods: Ethynylferrocene (**1a**) was obtained from Acros. Alkynylferrocenes **1b**–**1h**[6,13–15] and 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$[25] were synthesized according to the literature procedures. Toluene was distilled from Na/benzophenone ketyl prior to use. All reactions were carried out in flame-dried glassware under an atmosphere of dry N_2 or Ar.

NMR spectra were recorded on spectrometers with different operating frequencies (^{1}H: 600 or 400 MHz; ^{13}C: 150 or 101 MHz, ^{11}B: 128 MHz). Boron signals were assigned with the aid of ^{11}B,^{11}B COSY and ^{1}H[^{11}B(selective)] NMR spectroscopic experiments. The samples were dissolved in [D$_6$]benzene and the spectra were referenced to the residual solvent signal (C_6D_6: δ_H = 7.16 ppm, δ_C = 128.0 ppm), tetramethylsilane (internal standard, $\delta_H = \delta_C = 0$ ppm) or $BF_3{\cdot}OEt_2$ (internal standard for ^{11}B NMR spectroscopy). TLC analyses were performed on silica gel 60 F254 aluminum sheets, column chromatography was carried out on silica gel 60 or Brockmann II alumina.

Electrochemical measurements were carried out with a computer-controlled polarograph μAUTOLAB III (Eco Chemie, The Netherlands) at room temperature (ca. 22 °C) using a three-electrode cell equipped with a platinum disc working electrode (2 mm diameter), a platinum sheet auxiliary electrode, and a double-junction Ag/AgCl (3 M KCl) reference electrode. The compounds were dissolved in anhydrous 1,2-dichloroethane (Sigma–Aldrich) to give a solution that contained approximately 0.5 mM of the analyzed compound and 0.1 M $Bu_4N[PF_6]$ (Fluka, p.a. for electrochemistry). The solutions were deaerated by bubbling with argon and then kept under an argon blanket. The redox potentials were calculated as $E^{\circ\prime} = 1/2(E_{pa} + E_{pc})$, in which E_{pa} and E_{pc} are the anodic and cathodic peak potentials in cyclic voltammetry, and are given relative to internal ferrocene/ferrocenium reference. The values were reproducible within approximately 5 mV.

General Procedure for the Preparation of Carboranes 2: 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (147 mg, 0.6 mmol) and the corresponding alkyne (0.4 mmol) were placed into a round-bottomed flask equipped with a condenser and an argon inlet. Toluene (4 mL) was added, and the reaction mixture was heated in an oil bath at 120 °C under argon for 16 h. After cooling, methanol (2 mL) was added to the reaction mixture, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product by using chloroform or dichloromethane/hexane mixtures as the eluent. Particular synthetic details and characterization data are given below.

1-Ferrocenyl-1,2-dicarba-*closo*-dodecaborane (2a): Ethynylferrocene (105 mg, 0.50 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (183 mg, 0.75 mmol). Column chromatography (6:1 hexane/CH_2Cl_2) yielded 43 mg (26%) of **2a** as an orange solid. Spectral characteristics were in agreement with the published data,[11b] m.p. 121–123 °C ($CHCl_3$). ^1H NMR (600 MHz, C_6D_6): δ = 3.92 (apt, J = 2.0 Hz, 2 H, Fc), 3.87 (s, 5 H, Fc), 3.70 (apt, J = 2.0 Hz, 2 H, Fc), 2.86 (s, 1 H, CH) ppm. ^{13}C NMR (150 MHz, C_6D_6): δ = 65.3 (C–carborane), 69.0 (Fc), 70.5 (Fc), 70.6 (Fc), 76.5 (Fc), 86.4 (C–carborane) ppm.

1-Ferrocenyl-2-methyl-1,2-dicarba-*closo*-dodecaborane (2b): (Propyn-1-yl)ferrocene, (90 mg, 0.40 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (146 mg, 0.60 mmol). Column chromatography (10:1 hexane/CH_2Cl_2) yielded 29 mg (21%) of the title compound as an orange solid. Spectral characteristics were in agreement with the published data,[21] m.p. 127 °C ($CHCl_3$). $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 4.02 [apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc], 3.98 (s, 5 H, Fc), 3.76 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.11 (br. s, 1 H, B12–H), 3.00 (br. s, 1 H, B9–H), 2.93 [br. s, 2 H, B(8,10)–H], 2.73 [br. s, 2 H, B(3,6)–H], 2.50 [s, 2 H, B(5,4)-H], 2.36 [s, 2 H, B(7,11)–H], 1.04 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 84.3 (C–carborane), 82.1 (C–carborane), 78.0 (Fc), 72.0 (Fc), 71.6 (Fc), 69.7 (Fc), 23.0 (CH_3) ppm. ^{11}B NMR (128 MHz, C_6D_6, BF_3·OEt_2): δ = –4.80 [d, $J_{B,H}$ = 155 Hz, 2 B, B(9,12)], –9.97 [d, $J_{B,H}$ = 165 Hz, 6 B, B(4,5; 7,11; 8,10)], –11.85 [d, $J_{B,H}$ = 152 Hz, 2 B, B(3,6)] ppm. HRMS calcd. for $C_{13}H_{22}{}^{10}B_2{}^{11}B_8Fe$: 342.2069; found 342.2069. MS (ESI): m/z (%) = 342 (100) [M^+], 256 (7), 228 (27). $C_{13}H_{22}B_{10}Fe$ (344.20): calcd. C 45.62, H 6.48, Fe 16.32; found C 45.68, H 6.27, Fe 16.03. IR (KBr): $\tilde{\nu}$ = 2624, 2596, 2575, 2563, 1106, 1135, 829 cm^{-1}. R_f (10:1 hexane/CH_2Cl_2) = 0.3.

1-Ferrocenyl-2-phenyl-1,2-dicarba-*closo*-dodecaborane (2c): (2-Phenylethynyl)ferrocene (100 mg, 0.35 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (128 mg, 0.53 mmol). Column chromatography (2:1 hexane/$CHCl_3$) yielded 85 mg (60%) of the title compound as an orange solid, m.p. 171–174 °C ($CHCl_3$). $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 7.23 (d, $J_{H,H}$ = 7.7 Hz, 2 H, Ar–H), 6.77 (t, $J_{H,H}$ = 7.4 Hz, 1 H, Ar–H), 6.70 (t, $J_{H,H}$ = 7.8 Hz, 2 H, Ar–H), 3.93 (s, 5 H, Fc), 3.91 (t, $J_{H,H}$ = 1.9 Hz, 2 H, Fc), 3.51 (t, $J_{H,H}$ = 1.8 Hz, 2 H, Fc), 3.42 (br. s, 1 H, B12–H), 3.28 (br. s, 1 H, B9–H), 3.17 [br. s, 2 H, B(3,6)–H], 3.13 [br. s, 2 H, B(8,10)–H], 2.97 [br. s, 2 H, B(7,11)–H], 2.89 [br. s, 2 H, B(4,5)–H] ppm. ^{13}C NMR (151 MHz, C_6D_6): δ = 131.73 (C–Ar), 131.49 (C–Ar), 130.34 (C–Ar), 128.68 (C–Ar), 86.29 (C–carborane), 85.98 (C–carborane), 83.65 (Fc), 71.77 (Fc), 71.04 (Fc), 69.02 (Fc) ppm. ^{11}B NMR (128 MHz, C_6D_6, BF_3·OEt_2): δ = –0.97 (d, $J_{B,H}$ = 110 Hz, 1 B, B12), –1.78 (d, $J_{B,H}$ = 114 Hz, 1 B, B9), –7.86 [d, $J_{B,H}$ = 142 Hz, 4 B, B(8,10; 7,11)], –9.29 [d, $J_{B,H}$ = 110 Hz, B(3,6)], –10.02 [d, $J_{B,H}$ = 110 Hz, 2 B, B(4,5)] ppm. HRMS (EI) calcd. for $C_{18}H_{24}{}^{10}B_2{}^{11}B_8Fe$: 404.2231; found 404.2227. MS (EI): m/z (%) = 404.2 (100) [M^+], 278.2 (5), 200.1 (10), 121.2 (20). $C_{18}H_{24}B_{10}Fe$ (406.22): calcd. C 53.48, H 5.98, Fe 13.81; found C 53.63, H 5.81, Fe 13.56. IR (KBr): $\tilde{\nu}$ = 2642, 2600, 2582, 2561, 1416, 1281, 1045, 1003, 830 cm^{-1}. R_f (2:1 hexane/$CHCl_3$) = 0.4.

1-Ferrocenyl-2-[4-(methoxycarbonyl)phenyl]-1,2-dicarba-*closo*-dodecaborane (2d): {[4-(Methoxycarbonyl)phenyl]ethynyl}ferrocene (69 mg, 0.2 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (64 mg, 0.26 mmol). Column chromatography (2:1 hexane/$CHCl_3$) yielded 56 mg (61%) of the title compound as an orange solid, m.p. 162–164 °C ($CHCl_3$). $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 7.66 (d, J = 8.5 Hz, 2 H, H–Ar), 7.22 (d, J = 8.6 Hz, 2 H, Ar–H), 3.91 (s, 5 H, Fc), 3.89–3.86 (m, 2 H, Fc), 3.52–3.47 (m, 2 H, Fc), 3.33 (s, 4 H, CH_3 and 12-H), 3.16 (br. s, 1 H, B9–H), 3.06 [br. s, 2 H, B(3,6)–H], 2.96 [br. s, 2 H, B(8,10)–H], 2.86 [br. s, 2 H, B (7,11)–H], 2.72 [br. s, 2 H, B(4,5)–H] ppm. ^{13}C NMR (151 MHz, C_6D_6): δ = 165.79 (C=O), 135.79 (C–Ar), 132.36 (C–Ar), 131.58 (C–Ar), 129.74 (C–Ar), 128.68 (C–Ar), 86.16 (C–carborane), 85.01 (C–carborane), 83.37 (Fc), 71.72 (Fc), 71.09 (Fc), 69.23 (Fc), 52.06 (CH_3) ppm. ^{11}B NMR (128 MHz, C_6D_6, BF_3·OEt_2): δ = –0.54 (d, $J_{B,H}$ = 152 Hz, 1 B, B12), –1.83 (d, $J_{B,H}$ = 131 Hz, 1 B, B9), –7.91 [d, $J_{B,H}$ = 130 Hz, 4 B, B(8,10; 7,11)], –9.84 [d, $J_{B,H}$ = 115 Hz, 4 B, B(3,6; 4,5)] ppm. HRMS (EI) calcd. for $C_{20}H_{26}{}^{10}B_2{}^{11}B_8O_2Fe$: 462.2285; found 462.2286. MS (EI): m/z (%) = 462.2 (100) [M^+], 279.2 (10), 216.1 (20), 121.0 (20). $C_{20}H_{26}B_{10}FeO_2$ (464.22): calcd. C 51.95, H 5.67, Fe 12.08; found C 51.68, H 5.69, Fe 11.39. IR (KBr): $\tilde{\nu}$ = 2591, 2573, 2552, 1724, 1434, 1287, 1123, 836 cm^{-1}. R_f (2:1 hexane/$CHCl_3$) = 0.5.

1,2-Diferrocenyl-1,2-*closo*-dicarbadodecaborane (2e): Diferrocenylethyne (39 mg, 0.1 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (37 mg, 0.15 mmol). Column chromatography (4:1 hexane/$CHCl_3$) yielded 30 mg (58%) of the title compound as a red solid, m.p. 259–261 °C ($CHCl_3$). $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 3.97–3.90 (m, 14 H, Fc), 3.64–3.58 (m, 4 H, Fc), 3.36 [br. s, 2 H, B(9,12)–H], 3.13 [br. s, 4 H, B(3,6; 4,5)–H], 2.89 [br. s, 4 H, B(7,11; 8,10)–H] ppm. ^{13}C NMR (151 MHz, C_6D_6): δ = 86.04 (C–carborane), 83.64 (Fc), 72.08 (Fc), 71.02 (Fc), 68.88 (Fc) ppm. ^{11}B NMR (128 MHz, C_6D_6, BF_3·OEt_2): δ = –1.81 [d, J = 114 Hz, 2 B, B(9,12)], –7.95 [d, J = 106 Hz, 6 B, B(3,6; 4,5; 7,11)], –11.11 [d, J = 125 Hz, 2 B, B(8,10)] ppm. HRMS (EI) calcd. for $C_{22}H_{28}{}^{10}B_2{}^{11}B_8Fe_2$: 512.1893; found 512.1887. MS (EI): m/z (%) = 512.2 (100) [M^+], 447.2 (10), 256.1 (20), 121.2 (80). $C_{22}H_{28}B_{10}Fe_2$ (514.18): calcd. C 51.58, H 5.51; found C 51.45, H 5.29. IR (KBr): $\tilde{\nu}$ = 2663, 2603, 2576, 1443, 1269, 1108, 821 cm^{-1}. R_f (4:1 hexane/$CHCl_3$) = 0.6.

1-Ferrocenyl-2-(ferrocenylethyn-1-yl)-1,2-dicarba-*closo*-dodecaborane (2f): 1,4-Diferrocenyl-1,3-butadiyne (84 mg, 0.2 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (59 mg, 0.24 mmol). Column chromatography (5:1 hexane/CH_2Cl_2) yielded 56 mg (52%) of the title compound as an orange solid, m.p. 211 °C (benzene/chloroform). ^1H $\{^{11}B\}$ NMR (400 MHz; C_6D_6): δ = 4.44 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 4.08 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 4.00 (s, 5 H, Fc), 3.92 (s, 5 H, Fc), 3.88 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.76 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.20 (br. s, 1 H, B12–H), 3.03 (br. s, 1 H, B9–H), 3.01 [br. s, 6 H, B(4,5; 7,11; 8,10)–H], 2.83 [br. s, 2 H, B(3,6)–H] ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 86.8 (C–carborane), 84.8 (C–carborane), 84.1 (Fc), 80.1 (Fc), 72.8 (Fc), 72.7 (Fc), 72.5 (C–alkyne), 71.5 (Fc), 71.0 (Fc), 70.3 (Fc), 69.8 (Fc), 62.4 (C–alkyne) ppm. ^{11}B NMR (128 MHz, C_6D_6, BF_3·OEt_2): δ = –1.71 (d, $J_{B,H}$ = 151 Hz, 1 B, B12), –4.11 (d, $J_{B,H}$ = 151 Hz, 1 B, B9), –9.13 [d, $J_{B,H}$ = 143 Hz, 6 B, B(4,5; 8, 0; 7,11)], –10.28 [d, $J_{B,H}$ = 150 Hz, 2 B, B(3,6)] ppm. HRMS calcd. for $C_{24}H_{28}{}^{10}B_2{}^{11}B_8Fe_2$: 536.1893; found 536.1894. MS (EI): m/z (%) = 536 (47) [M^+], 268 (8), 186 (21), 121 (44), 84 (100). $C_{24}H_{28}B_{10}Fe_2$ (538.18): calcd. C 53.75, H 5.26, Fe 20.83; found C 53.83, H 5.07, Fe 20.14. IR (KBr): $\tilde{\nu}$ = 2636, 2600, 2583, 2572, 2234, 1106, 1046, 1022, 829, 821, 506, 486 cm^{-1}. R_f (5:1 hexane/CH_2Cl_2) = 0.3.

1-Ferrocenyl-2-acetyl-1,2-dicarba-*closo*-dodecaborane (2g): 4-Ferrocenylbut-3-yn-2-one (108 mg, 0.4 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$

(147 mg, 0.6 mmol). Column chromatography (3:1 hexane/CH_2Cl_2) yielded 43 mg (29%) of the title compound as an orange solid, m.p. 107 °C (hexane). ^1H {^{11}B} NMR (400 MHz; C_6D_6): δ = 4.09 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.91 (s, 5 H, Fc), 3.70 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.25 (br. s, 1 H, B12–H), 3.10 [br. s, 2 H, B(3,6)–H] 2.94 (br. s, 1 H, B9–H), 2.92 [br. s, 2 H, B(8,10)–H], 2.87 [s, 4 H, B(4,5; 7,11)–H], 1.51 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 85.1 (C–carborane), 83.9 (C–carborane), 83.6 (Fc), 72.3 (Fc), 71.5 (Fc), 69.9 (Fc), 28.8 (CH_3) ppm. ^{11}B NMR (128 MHz, C_6D_6, $BF_3{\cdot}OEt_2$): δ = 0.53 [d, $J_{B,H}$ = 148 Hz, 1 B, B(12)], –2.90 (d, $J_{B,H}$ = 150 Hz, 1 B, B9), –7.62 [d, $J_{B,H}$ = 165 Hz, 2 B, B(8,10)], –9.52 [d, $J_{B,H}$ = 163 Hz, 6 B, B(3,6; 4,5; 7,11)] ppm. HRMS calcd. for $C_{14}H_{22}{}^{10}B_2{}^{11}B_8OFe$: 370.2023; found 370.2018. MS (EI): m/z (%) = 370 (100) [M^+], 326 (8), 121 (17), 75 (21). $C_{14}H_{22}B_{10}FeO$ (372.20): calcd. C 45.41, H 5.99, Fe 15.08; found C 45.27, H 5.74, Fe 14.87. IR (KBr): $\tilde{\nu}$ = 2585, 2559, 1728, 1356, 1264, 1107, 1036, 825, 501 cm^{-1}. R_f (3:1 hexane/CH_2Cl_2) = 0.3.

1-Ferrocenyl-2-(ethoxycarbonyl)-1,2-dicarba-*closo*-dodecaborane (2h): Ethyl 3-ferrocenylpropynoate (113 mg, 0.4 mmol), 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ (147 mg, 0.6 mmol). Column chromatography (3:1 hexane/CH_2Cl_2) yielded 88 mg (55%) of the title compound as an orange solid, m.p. 129 °C (hexane). ^1H{^{11}B} NMR (400 MHz, C_6D_6): δ = 4.19 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.94 (s, 5 H, Fc), 3.74 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.46 (q, $J_{H,H}$ = 6.9 Hz, 2 H, CH_2), 3.28 (br. s, 1 H, B12–H), 3.10 [br. s, 2 H, B(3,6)–H], 3.00 (br. s, 2 H, B9–H), 2.96 [br. s, 2 H, B(8,10)–H], 2.87 [br. s, 2 H, B(3,4)–H], 2.82 [br. s, 2 H, B(7,11)–H], 0.54 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 159.0 (CO), 84.5 (C–carborane), 83.9 (C–carborane), 78.6 (Fc), 72.5 (Fc), 71.5 (Fc), 69.7 (Fc), 64.6 (CH_2), 14.0 (CH_3) ppm. ^{11}B NMR (128 MHz, C_6D_6, $BF_3{\cdot}OEt_2$): δ = –0.16 (d, $J_{B,H}$ = 151 Hz, 1 B, B12), –3.62 (d, $J_{B,H}$ = 150 Hz, 1 B, B9), –8.91 [d, $J_{B,H}$ = 189 Hz, 2 B, B(8,10)], –10.25 [d, $J_{B,H}$ = 154 Hz, 6 B, B(3,6; 4,5; 7,11)] ppm. HRMS calcd. for $C_{15}H_{24}{}^{10}B_2{}^{11}B_8O_2Fe$: 400.2129; found 400.2132. MS (EI^+): m/z (%) = 400 (100) [M^+], 372 (37) [M^+ – Et], 327 (14) [M^+ – COOEt], 121 (49). $C_{15}H_{24}B_{10}FeO_2$ (402.21): calcd. C 45.01, H 6.04, Fe 13.95; found C 44.92, H 5.76, Fe 13.70. IR (KBr): $\tilde{\nu}$ = 2600, 2581, 1744, 1257, 1108, 1025, 822, 493 cm^{-1}. R_f (3:1 hexane/CH_2Cl_2) = 0.35.

Preparation of 1-Ferrocenyl-2-(hydroxymethyl)-1,2-dicarba-*closo*-dodecaborane (3): Compound **2h** (72 mg, 0.18 mmol) was dissolved in anhydrous CH_2Cl_2 (1 mL) and the solution was cooled to 0 °C. Then a solution of diisobutylaluminium hydride (0.45 mL, 0.45 mmol, 1 M solution in CH_2Cl_2) was added dropwise. After stirring for 30 min, the reaction was quenched with addition of diatomite (0.5 g), ethanol (5 drops) and water (one drop). After 30 min anhydrous $MgSO_4$ was added, and the reaction mixture was filtered. The solid phase was washed by $CHCl_3$ (3 × 1.5 mL). Volatiles were removed under reduced pressure to obtain pure alcohol **3** (62 mg, 96% yield) as an orange solid, m.p. 111–112 °C (hexane). ^1H{^{11}B} NMR (400 MHz, C_6D_6): δ = 4.06 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.96 (s, 5 H, Fc), 3.77 (apt, $J_{H,H}$ = 2.0 Hz, 2 H, Fc), 3.21 (s, 1 H, B12–H), 3.11 (s, 2 H, CH_2), 2.99 (s, 1 H, B9–H), 2.90 [s, 2 H, B(8,10)–H], 2.74 [s, 2 H, B(3,6)–H], 2.46 [s, 4 H, B(5,10; 7,11)–H], 1.12 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 83.6 (C-carborane), 83.6 (C-carborane), 83.0 (Fc), 72.1 (Fc), 71.6 (Fc), 70.0 (Fc), 63.5 (CH_2) ppm. ^{11}B NMR (128 MHz, C_6D_6, $BF_3{\cdot}OEt_2$): δ = –2.20 (d, $J_{B,H}$ = 157 Hz, 1 B, B12), –3.60 (d, $J_{B,H}$ = 177 Hz, 1 B, B9), –9.05 [d, $J_{B,H}$ = 176 Hz, 2 B, B(8,10)], –10.80 [d, J = 149 Hz, 6 B, B(3,6; 4,5; 7,11)] ppm. HRMS calcd. for $C_{13}H_{22}{}^{10}B_2{}^{11}B_8OFe$: 358.2023; found 358.2022. MS (EI): m/z (%) = 358 (100) [M^+], 326 (12), 121 (72), 87 (47). IR (KBr): $\tilde{\nu}$ = 3324, 2410, 2592, 1262, 1070, 1024, 837, 823, 501 cm^{-1}. R_f (1:1 hexane/CH_2Cl_2) = 0.23.

Reaction of 6,9-$(Me_2S)_2$-$B_{10}H_{12}$ with [(Trimethylsilyl)ethynyl]ferrocene: Isolation of **4**: [(Trimethylsilyl)ethynyl]ferrocene (171 mg, 0.6 mmol), $B_{10}H_{12}{\cdot}(Me_2S)_2$ (222 mg, 0.9 mmol). Column chromatography (3:1 hexane/$CHCl_3$) yielded 62 mg (35%) of a crude compound as an orange solid. This solid was extracted with hexane/CH_2Cl_2 (3 mL), and the extract was filtered through a short pad of silica gel (1:1 hexane/CH_2Cl_2) to afford 12 mg (5%) of analytically pure **4** as an orange solid, m.p. (hexane) 152 °C. ^1H{^{11}B} NMR (400 MHz, C_6D_6): δ = 7.73 (s, 1 H, CH), 4.32 (dt, $J_{H,H}$ = 2.5, 1.3 Hz, 1 H, Fc), 4.24 (dt, $J_{H,H}$ = 2.5, 1.3 Hz, 1 H, Fc), 4.11 (s, 5 H, Fc), 4.15 (dt, $J_{H,H}$ = 2.4, 1.3 Hz, 1 H, Fc), 4.07 (dt, $J_{H,H}$ = 2.4, 1.3 Hz, 1 H, Fc), 3.96 [br. s, 1 H, B(1 or 3)–H], 3.55 [br. s, 2 H, B(8,10)–H], 3.37 [br. s, 1 H, B(1 or 3)–H], 3.32 (br. s, 1 H, B7–H), 2.32 (br. s, 1 H, B9–H), 1.68 (br. s, 1 H, B2–H), 1.54 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.36 (br. s, 1 H, B4–H), 0.01 (s, 9 H, $SiMe_3$), –2.22 (br. s, 1 H, μ-H), –2.48 (br. s, 1 H, μ-H), –2.68 (br. s, 1 H, μ-H) ppm. ^{13}C NMR (150 MHz, C_6D_6): δ = 147.9 (CH), 143.8 (C) 93.8 (C), 69.3 (Fc), 68.0 (Fc), 67.8 (Fc), 67.4 (Fc), 25.7 (CH_3), 22.1 (CH_3), 0.9 ($SiMe_3$) ppm. ^{11}B NMR (128 MHz, C_6D_6, $BF_3{\cdot}OEt_2$): δ = 29.22 (br. s, 1 B, B6), 2.40 [d, J = 133 Hz, 2 B, B(1,3)], –2.91 (s, 1 B, B5), –4.95 (d, J = 148 Hz, 1 B, B10), –7.43 [d, J = 212 Hz, 2 B, B(7,8)], –12.35 (d, J = 101 Hz, 1 B, B9), –24.5 (d, J = 146 Hz, 1 B, B2), –42.05 (d, J = 151 Hz, 1 B, B4) ppm. HRMS calcd. for $C_{17}H_{36}{}^{10}B_2{}^{11}B_8FeSSi$: 464.2660; found 464.2658. MS (ES^+): m/z (%) = 464 (25) [M^+], 309 (8), 301 (100), 279 (16). $C_{17}H_{36}B_{10}FeSSi$ (466.26): calcd. C 43.95, H 7.81, S 6.90, Fe 12.02; found C 44.18, H 7.77, S 6.89, Fe 12.42. IR (KBr): $\tilde{\nu}$ = 2588, 2567, 2552, 2528, 1425, 1248, 1105, 1036, 991, 860, 824. R_f (3:1 hexane/$CHCl_3$) = 0.4.

X-ray Crystallography: Full-set diffraction data ($\pm h \pm k \pm l$; θ_{max} = 26–27.5°, data completeness: 99.1–100.0%) were collected with an Apex2 diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and were corrected for absorption by using the methods incorporated in the diffractometer software. The measurements were usually carried out at 150(2) K. In the cases, when extensive cooling caused disintegration of the available crystals, the lowest applicable temperature was roughly estimated and then used for the measurement (see Table S1 in the Supporting Information).

The structures were solved by direct methods (SHELXS-87[26]) and refined by full-matrix least-squares cycles on the basis of F^2 (SHELXL-97[26]). The non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on the boron cage were always clearly detectable on the difference Fourier maps but were included in their idealized positions. Nonetheless, good-quality diffraction data obtained for **2b**, **2e**, **2h**, and **3** allowed us to refine these hydrogen atoms with unconstrained positional parameters while U_{iso}(H) was kept fixed to 1.2 U_{eq}(B). CH hydrogen atoms were included in their calculated positions and refined as riding atoms with U_{iso}(H) assigned to a multiple of U_{eq}(C) of their bonding carbon atom. Crystals of **2d** and **2h** are chiral. Whereas the former compound proved to be a racemic twin, the crystal of **2h** was found to be enantiomerically pure.

Relevant crystallographic data and structure refinement parameters are available as Supporting Information (Table S1). Geometric data and structural drawings were obtained with a recent version of the PLATON program.[27] All numerical values were rounded with respect to their estimated standard deviations (ESDs) given in one decimal. Parameters that relate to atoms in constrained positions (hydrogen atoms) are given without ESDs.

CCDC-893330 (for **2a**), -893331 (for **2b**), -893332 (for **2c**), -893333 (for **2d**), -893334 (for **2e**), -893335 (for **2f**), -893336 (for **2g**) -893337 (for **2h**), -893338 (for **3**), and -893339 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H, ^{13}C, and ^{11}B NMR spectra for all compounds; view of the molecular structure of compounds **2a**, **2b**, and **2d** (Figures S1–3); and summary of crystallographic data (Table S1).

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