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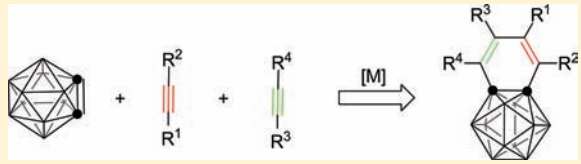
Transition-Metal-Promoted or -Catalyzed Exocyclic Alkyne Insertion via Zirconacyclopentene with Carborane Auxiliary: Formation of Symmetric or Unsymmetric Benzocarboranes

Shikuo Ren, Zaozao Qiu, and Zuowei Xie*

Department of Chemistry and State Key Laboratory on Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

Supporting Information

ABSTRACT: Reactions of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ with alkynes $R^1C{\equiv}CR^2$ gave as insertion products zirconacyclopentenes incorporating a carboranyl unit, 1,2-$[Cp_2ZrC(R^1){=}C(R^2)]$-1,2-$C_2B_{10}H_{10}$ (**1**). Treatment of **1** with another type of alkyne $R^3C{\equiv}CR^4$ in the presence of stoichiometric amounts of $NiCl_2$ and $FeCl_3$ or a catalytic amount of $NiCl_2$ afforded symmetric or unsymmetric benzocarboranes. The regioselectivity was dominated by the polarity of the corresponding alkynes. These reactions could also be carried out in one pot, leading to the equivalent of a three-component [2 + 2 + 2] cycloaddition of carboryne and two different alkynes promoted by transition metals. A reaction mechanism was proposed after the isolation and structural characterization of the key intermediate nickelacycle. These results show that nickel complexes are more reactive than the iron ones toward the insertion of alkynes but that the latter do not initiate the trimerization of alkynes, making the insertion of activated alkynes possible. This work also demonstrates that a catalytic amount of nickel works as well as a stoichiometric amount of nickel in the presence of excess $FeCl_3$ for the reactions. Such a catalytic reaction may shed some light on the development of zirconocene-based catalytic reactions.



INTRODUCTION

Transition-metal-mediated C−C coupling reactions, as a powerful strategy for constructing useful molecules, have found many applications in organic synthesis, mechanistic studies, and the synthesis of functional materials.[1,2] For example, the [2 + 2 + 2] cycloaddition reaction of alkynes serves as a very effective tool for the synthesis of substituted arenes. A variety of transition-metal complexes can catalyze this type of reaction.[3,4] The challenge in this area is how to control the chemoselectivity in the intermolecular [2 + 2 + 2] cycloaddition of three different alkynes. One approach is to use preinstalled functionalities, such as a boron tether, allowing partially intramolecular coupling of the in situ-generated diyne intermediate. The resulting metallacycle inserts regioselectively the third equivalent of alkyne to give the chemoselective three-component cycloaddition product.[5] Another method is to employ unsymmetrical zirconacyclopentadienes, prepared from oxidative coupling of two different alkynes with $Cp_2Zr(II)$,[6] as intermediates to react with the third alkyne in the presence of $NiBr_2(PPh_3)_2$[7] or with the third alkyne having at least one electron-withdrawing group in the presence of CuCl.[8]

We recently extended transition-metal-mediated [2 + 2 + 2] cycloaddition reactions to include *o*-carborynes (1,2-dehydro-*o*-carboranes) and 1,3-dehydro-*o*-carboranes.[9] Subsequently, a class of benzocarboranes[10,11] and dihydrobenzocarboranes[12] can be prepared. However, when two different alkynes are introduced to the reaction of Ni−carboryne, a mixture of benzocarboranes is obtained, as the transition metal cannot distinguish two similar alkynes. On the other hand, the zirconocene−carboryne can react with only 1 equiv of alkyne to give a zirconacyclopentene incorporating a carboranyl moiety even under forced reaction conditions in the presence of excess alkynes.[13] In sharp contrast, the corresponding nickelacyclopentene incorporating a carboranyl unit was identified as a very reactive intermediate in the above nickel-mediated [2 + 2 + 2] cycloaddition of carborynes with alkynes.[10] These results clearly indicate that the nature of the transition metal dominates the reactivity of the corresponding metallacycles. In this connection, transmetalation from the zirconacycle to nickel should allow the insertion of the second alkyne, making chemoselective [2 + 2 + 2] cycloaddition of *o*-carborynes with two different alkynes possible.

In this article, we report the reactions of zirconacyclopentenes incorporating a carboranyl moiety with alkynes in the presence of stoichiometric amounts of $NiCl_2$ and $FeCl_3$ or a catalytic amount of $NiCl_2$ and the corresponding reaction mechanism with the confirmation of the reaction intermediate. These reactions lead to the one-pot synthesis of highly substituted benzocarboranes via the equivalent of a three-component [2 + 2 + 2] cycloaddition of a carboryne with two different alkynes.[14]

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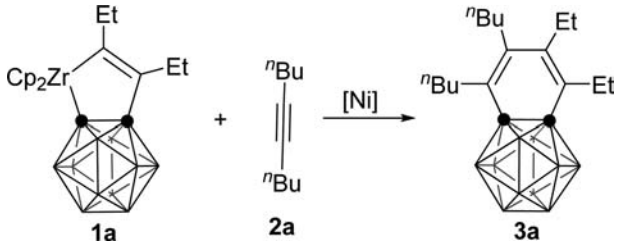
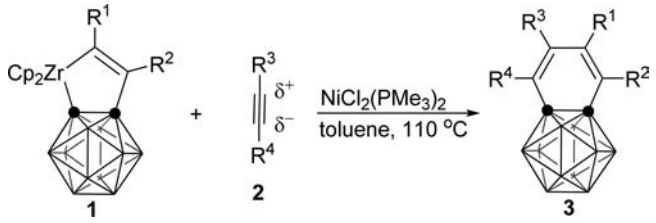
Table 1. Optimization of the Reaction Conditions[a]



entry	T (°C)	solvent	[Ni]	**1a**/**2a**	time (h)	yield (%)[b]
1	110	toluene	$NiCl_2$	1/3.5	72	0
2	110	THF	$NiCl_2$	1/3.5	72	6
3	110	THF	$NiCl_2/2PPh_3$	1/3.5	48	76
4	110	THF	$NiCl_2(PMe_3)_2$	1/3.5	72	42
5	110	DME	$NiCl_2(PMe_3)_2$	1/3.5	72	48
6	90	toluene	$NiCl_2(PMe_3)_2$	1/3.5	48	37
7	110	toluene	$NiCl_2(PMe_3)_2$	1/3.5	48	89
8	110	toluene	$NiCl_2$(dppe)	1/3.5	48	88
9	110	toluene	$NiCl_2$(dppp)	1/3.5	48	78
10	110	toluene	$NiCl_2(PPh_3)_2$	1/3.5	48	68
11	110	toluene	$NiCl_2(PMe_3)_2$	1/3.5	36	82
12	110	toluene	$NiCl_2(PMe_3)_2$	1/2.0	48	86

[a]Reaction conditions: **1a** (0.02 mmol), alkyne **2a**, and [Ni] (0.02 mmol) in the solvent (0.6 mL) in a closed vessel. After the reaction was complete, the mixture was treated with H_3O^+ and subjected to analysis by GC−MS. [b]GC yields.

Table 2. $NiCl_2(PMe_3)_2$-Promoted Cycloaddition Reactions[a]



entry	**1**, R^1/R^2	**2**, R^3/R^4	product **3**	isolated yield (%)
1	**1a**, Et/Et	**2a**, ^{n}Bu/^{n}Bu	**3a**	84
2	**1a**, Et/Et	**2b**, ^{n}Pr/^{n}Pr	**3b**	81
3	**1a**, Et/Et	**2c**, Et/Et	**3c**	78
4	**1a**, Et/Et	**2d**, Ph/Ph	**3d**	30 (70)[b]
5	**1a**, Et/Et	**2e**, Me/Ph	**3e**	76
6	**1a**, Et/Et	**2f**, Et/Ph	**3f**	81
7	**1a**, Et/Et	**2g**, ^{n}Bu/Ph	**3g**	83
8	**1a**, Et/Et	**2h**, ^{n}Bu/^{t}Bu	**3h**	71 (83/17)[c]
9	**1a**, Et/Et	**2i**, Me/^{i}Pr	**3i**	67 (81/19)[c]
10	**1a**, Et/Et	**2j**, Me/Et	**3j**	33 (57/43)[c]
11	**1a**, Et/Et	**2k**, $CH_3C{\equiv}C(CH_2)_4$/Me	**3k**	29 (66/34)[c]
12	**1a**, Et/Et	**2l**, $(Me)_2NCH_2$/Ph	**3l**	21
13	**1a**, Et/Et	**2m**, $MeOCH_2$/Ph	**3m**	31
14	**1a**, Et/Et	**2n**, $(CH_2{=}CH)CH_2$/Ph	**3n**	35 (74)[d]
15	**1b**, Ph/Ph	**2c**, Et/Et	**3d**	81
16	**1b**, Ph/Ph	**2a**, ^{n}Bu/^{n}Bu	**3r**	83
17	**1c**, Ph/Me	**2a**, ^{n}Bu/^{n}Bu	**3s**	85
18	**1d**, Ph/^{n}Bu	**2a**, ^{n}Bu/^{n}Bu	**3t**	81
19	**1d**, Ph/^{n}Bu	**2c**, Et/Et	**3u**	80
20	**1d**, Ph/^{n}Bu	**2e**, Me/Ph	**3v**	36 (73)[b]
21	**1e**, Ph/$(CH_2)_3Cl$	**2c**, Et/Et	**3w**	77

[a]Reaction conditions: **1** (0.20 mmol), alkyne **2** (0.70 mmol), and $NiCl_2(PMe_3)_2$ (0.21 mmol) in toluene (10 mL) at 110 °C for 48 h. The product was isolated by flash column chromatography on silica gel using hexane as the eluent. [b]The yield in parentheses was obtained by extending the reaction time to 5 days. [c]An inseparable mixture of two regioisomers was obtained. Their molar ratio was measured by GC−MS analysis. [d]The yield in parentheses was obtained using 2 equiv of $NiCl_2(PMe_3)_2$ and 1.5 equiv of alkyne.

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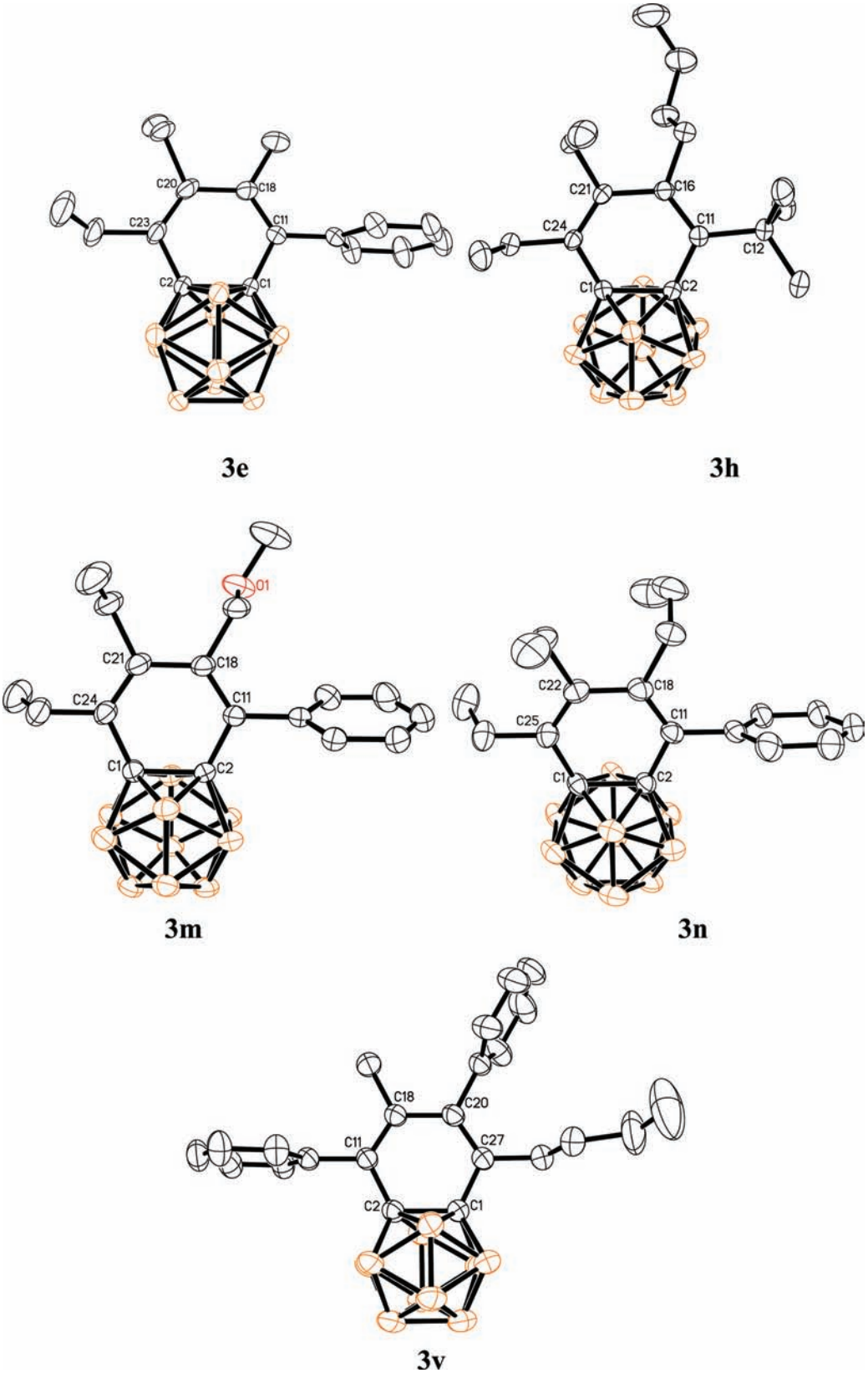

Figure 1. Molecular structures of **3e**, **3h**, **3m**, **3n**, and **3v**.

RESULTS AND DISCUSSION

Reaction of Zirconacyclopentenes Bearing a Carboranyl Unit with Alkynes in the Presence of a Stoichiometric Amount of $NiCl_2$. The reaction of 1,2-[$Cp_2ZrC(Et)$═$C(Et)$]-1,2-$C_2B_{10}H_{10}$ (**1a**) with ^{n}BuC≡CBu^n (**2a**) was initially examined in the presence of Ni(II) species in different solvents. The results are summarized in Table 1. Almost no reaction proceeded in the presence of $NiCl_2$ (Table 1, entries 1 and 2).

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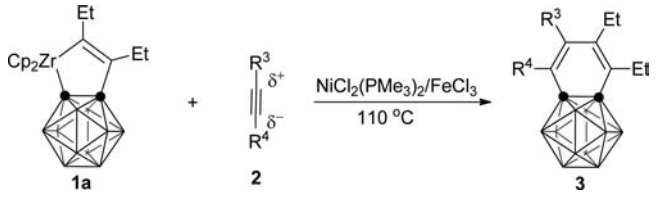
Table 3. Ni(II)-Catalyzed Cycloaddition Reactions[a]



entry	2, R^3/R^4	$FeCl_3$/Ni(II)/1a	time (h)	toluene/THF (v/v)	3	yield (%)[b]
1	**2a**, ^{n}Bu/^{n}Bu	0/1/1	48	1:0	**3a**	89
2	**2a**, ^{n}Bu/^{n}Bu	0/0.15/1	96	1:0	**3a**	12
3	**2a**, ^{n}Bu/^{n}Bu	1/0/0	96	1:0	**3a**	0
4	**2a**, ^{n}Bu/^{n}Bu	3/0.15/1	96	1:0	**3a**	39
5	**2a**, ^{n}Bu/^{n}Bu	3/0.15/1	48	0:1	**3a**	87
6	**2a**, ^{n}Bu/^{n}Bu	3/0.15/1	48	2:1	**3a**	87
7	**2a**, ^{n}Bu/^{n}Bu	3/0.10/1	48	2:1	**3a**	85
8	**2a**, ^{n}Bu/^{n}Bu	3/0.05/1	48	2:1	**3a**	74
9	**2a**, ^{n}Bu/^{n}Bu	2/0.10/1	48	2:1	**3a**	83
10	**2b**, ^{n}Pr/^{n}Pr	3/0.10/1	48	2:1	**3b**	90
11	**2d**, Ph/Ph	3/0.10/1	48	2:1	**3d**	87
12	**2e**, Me/Ph	3/0.10/1	48	2:1	**3e**	65[c]
13	**2e**, Et/Ph	3/0.10/1	48	2:1	**3f**	82[c]
14	**2o**, MeO_2C/CO_2Me	3/0.10/1	48	2:1	**3o**	41
15	**2q**, Ph/TMS	3/0.10/1	48	2:1	**3q**	42

[a]3.5 equiv of alkyne was used. [b]GC yield. [c]Two isomers were obtained in a ratio of 50/15 (entry 12) or 60/22 (entry 13).

However, addition of 2 equiv of PPh_3 resulted in the formation of the desired benzocarborane 1,2-[C(Et)=C(Et)−C(Bu^n)=C(Bu^n)]-1,2-$C_2B_{10}H_{10}$ (**3a**) in 76% yield (Table 1, entry 3). In general, all $NiCl_2$(phosphine)$_2$ complexes were able to mediate the C−C coupling reaction (Table 1, entries 4−12). Toluene was a better solvent than tetrahydrofuran (THF) and dimethoxyethane (DME) (Table 1, entry 7 vs entries 4 and 5). Temperature also played an important role (Table 1, entry 6 vs 7). The optimal reaction conditions were found to be those shown in entry 7, which offered the product **3a** in 89% yield.

Subsequently, a series of zirconacyclopentenes and alkynes were studied under the above optimal conditions. It was noted that an excess amount of alkyne was necessary in the reactions since some were cyclotrimerized in the presence of Ni(0) to form substituted benzenes.[10] These results are compiled in Table 2. Symmetrical alkynes generally offered very high yields of cycloaddition products **3** (Table 2, entries 1−3). Alkynes containing functional groups such as those in **2l,m** gave low yields, probably because of the possible coordination of the heteroatom to Ni, which would prevent the coordination of the C≡C unit (Table 2, entries 12−13). Unsymmetrical alkynes produced two regioisomers, and their ratios were largely affected by steric/electronic factors. In general, for polar alkynes, only the major isomers that were consistent with the polarity of Ph−C≡C−R were generated (Table 2, entries 5−7, 12−14, and 20).[15] Very sterically demanding alkynes such as Me_3Si−C≡C−$SiMe_3$ did not react with **1**. Terminal alkynes could protonate **1** to give 1-[CHR^1=CR^2]-1,2-$C_2B_{10}H_{11}$ under the reaction conditions as a result of the high acidity of the C(sp)−H proton. Very reactive alkynes such as MeO_2CC≡CCO_2Me were cyclotrimerized in the presence of Ni(0) prior to the insertion.

It was noted that these benzocarboranes could also be prepared in similar yields from the one-pot reaction of $Cp_2Zr(\mu\text{-Cl})(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$[16] with alkyne followed by treatment with another type of alkyne in the presence of $NiCl_2(PMe_3)_2$ under the same reaction conditions. This approach represents an equivalent of a three-component [2 + 2 + 2] cycloaddition of carboryne with two different alkynes.

The ^{11}B NMR spectra of the benzocarboranes showed a 2:5:3 pattern in the range from −6.7 to −13.4 ppm. The characteristic carbons of conjugated diene units and the cage carbons were observed at about 130 and 77 ppm, respectively, in their ^{13}C NMR spectra, which are very close to those in reported benzocarborane derivatives.[10] The ^{13}C NMR chemical shifts of the cage carbons in the benzocarboranes fell in the range between those of *o*-carboranes[17] and metal−carboryne complexes.[18]

The molecular structures of **3e**, **3h**, **3m**, **3n**, and **3v** were further confirmed by single-crystal X-ray analyses and are shown in Figure 1 (for selected bond lengths and angles, see Table 6). It is noted that the six-membered ring (labeled as C1−C6 in Table 6) is planar with alternating long and short C−C bond lengths of ca. 1.65, 1.49, 1.34, 1.47, 1.35, and 1.49 Å and internal bond angles of ca. 116, 121, 123, 123, 121, and 116°.

Reaction of Zirconacyclopentenes Bearing a Carboranyl Unit with Alkynes in the Presence of a Catalytic Amount of $NiCl_2$. In the transmetalation of zirconacycles to transition metals, stoichiometric amounts of transition-metal complexes are required.[6−8,19,20] The corresponding catalytic version has been very limited.[21] In the aforementioned Ni-mediated cycloaddition reactions, the end product is Ni metal. The Ni(0) center is believed to be oxidized by the action of $FeCl_3$ according to their redox potentials.[22] With this in mind, various reaction conditions were examined, and the results are summarized in Table 3. Pure toluene was found to be a poor solvent for the reaction because of the very low solubility of $FeCl_3$ in toluene (Table 3, entry 4). Addition of THF to the above solution significantly improved the yields in the presence of 15 mol % $NiCl_2(PMe_3)_2$ and 3 equiv of $FeCl_3$ (Table 3, entries 5 and 6). Almost the same yield was achieved when the

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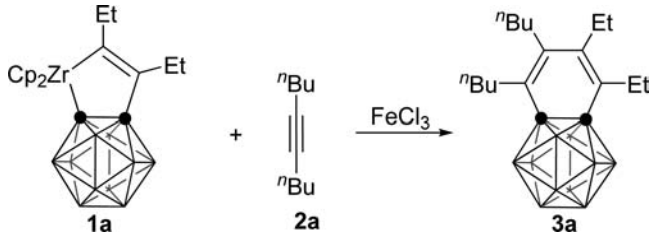
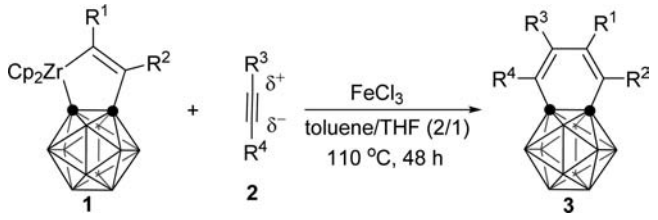
Table 4. Optimization of $FeCl_3$-Promoted Cycloaddition Reactions



entry	**1a**/**2a**/$FeCl_3$	time (h)	toluene/THF (v/v)	temperature (°C)	yield[a] (%)
1	1/2/2	72	1:0	110	0
2	1/2/2	48	0:1	110	24
3	1/2/2	48	2:1	110	78
4	1/2/2	48	1:1	110	73
5	1/2/2	48	10:1	110	37
6	1/1.5/2	48	2:1	110	77
7	1/3/2	48	2:1	110	76
8	1/2/1.5	48	2:1	110	39
9	1/2/1	48	2:1	110	31
10	1/2/3	48	2:1	110	18
11	1/2/3	48	2:1	110	76
12	1/2/2	72	2:1	110	80
13	1/2/2	24	2:1	110	38
14	1/2/2	48	2:1	90	12
15	1/2/2/4 (PPh_3)	48	2:1	110	73

[a]GC yield.

Table 5. $FeCl_3$-Promoted Cycloaddition Reactions[a]



entry	**1**, R^1/R^2	**2**, R^3/R^4	product **3**	isolated yield (%)[b]
1	**1a**, Et/Et	**2a**, ^{n}Bu/^{n}Bu	**3a**	47 (78)
2	**1a**, Et/Et	**2b**, ^{n}Pr/^{n}Pr	**3b**	39 (66)
3	**1a**, Et/Et	**2c**, Et/Et	**3c**	30 (60)
4	**1a**, Et/Et	**2d**, Ph/Ph	**3d**	43 (66)
5	**1a**, Et/Et	**2i**, Me/^{i}Pr	**3i**	34 (54)[c]
6	**1a**, Et/Et	**2j**, Me/Et	**3j**	45 (74)[c]
7	**1a**, Et/Et	**2m**, $MeOCH_2$/Ph	**3m**	– (15)
8	**1a**, Et/Et	**2o**, CO_2Me/CO_2Me	**3o**	20 (40)
9	**1a**, Et/Et	**2p**, ^{n}Bu/TMS	**3p**	53 (74)
10	**1a**, Et/Et	**2q**, Ph/TMS	**3q**	59 (82)
11	**1f**, ^{n}Pr/^{n}Pr	**2b**, ^{n}Pr/^{n}Pr	**3x**	44 (71)

[a]Reaction conditions: **1** (0.20 mmol), **2** (0.40 mmol), and $FeCl_3$ (0.40 mmol) in 10 mL of 2:1 (v/v) toluene/THF in a closed vessel at 110 °C for 48 h. [b]The yields in parentheses were obtained by GC–MS. [c]Two isomers were obtained in a ratio of 66/34 (entry 5) or 52/48 (entry 6).

amount of $NiCl_2(PMe_3)_2$ was reduced to 10 mol % (Table 3, entry 7). However, the yield decreased to 74% when the amount of $NiCl_2(PMe_3)_2$ was further reduced to 5 mol % (Table 3, entry 8). The best reaction conditions were identified as $FeCl_3/NiCl_2(PMe_3)_2$/**1a**/**2** = 3/0.1/1/3.5 in 2:1 (v/v) toluene/THF at 110 °C (Table 3, entry 7). Under such conditions, the catalytic reaction was as good as the stoichiometric one (entry 7 in Table 3 vs entry 1 in Table 2). It is noteworthy that both $MeO_2CC{\equiv}CCO_2Me$ (DMAD) and PhC≡CTMS gave the cycloaddition products **3o** and **3p** in 41 and 42% yield, respectively (Table 3, entries 14 and 15). In sharp contrast, no desired cycloaddition products were observed when DMAD and PhC≡CTMS were used as substrates in the presence of 1 equiv of $NiCl_2(PMe_3)_2$. On the other hand, the yield of **3d** was greatly increased to 87% (Table 3, entry 11) from 30% (Table 2, entry 4) under the catalytic conditions. This may be ascribed to the trimerization of the above alkynes prior to insertion in the presence of a large amount of Ni(0) species.

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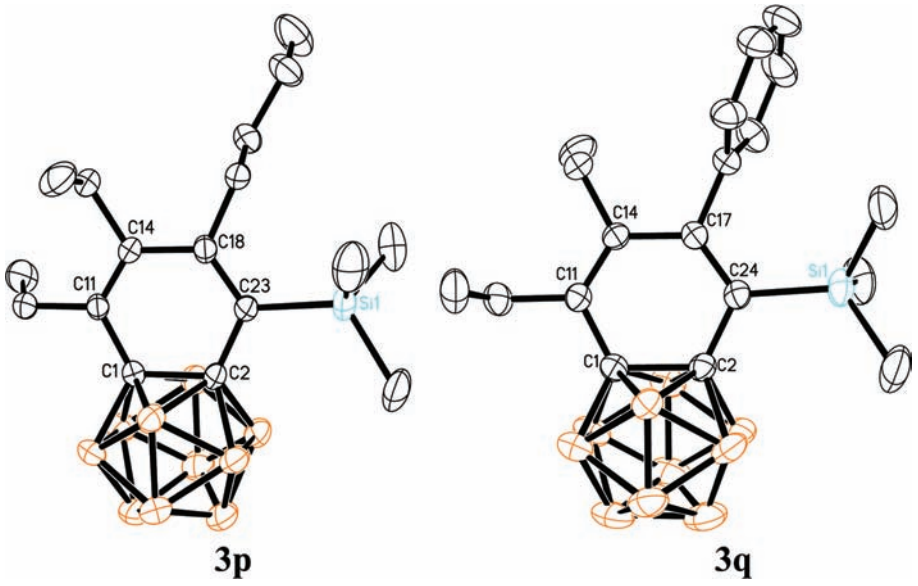
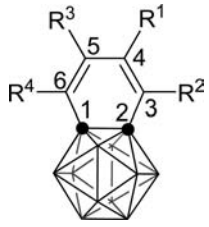


Figure 2. Molecular structures of **3p** and **3q**.

Table 6. Selected Bond Lengths (Å) and Angles (deg)



	3e	3h	3m	3n	3p	3q	3v
C1−C2	1.638(4)	1.673(3)	1.646(3)	1.636(2)	1.659(4)	1.671(3)	1.640(4)
C2−C3	1.489(4)	1.485(5)	1.498(3)	1.484(2)	1.473(4)	1.474(3)	1.488(3)
C3−C4	1.354(4)	1.341(4)	1.344(3)	1.345(2)	1.343(6)	1.342(3)	1.344(4)
C4−C5	1.475(4)	1.476(3)	1.470(3)	1.473(3)	1.482(4)	1.487(3)	1.476(4)
C5−C6	1.347(4)	1.366(5)	1.348(3)	1.347(3)	1.359(4)	1.358(3)	1.343(4)
C6−C1	1.484(4)	1.520(4)	1.489(2)	1.486(2)	1.489(6)	1.493(3)	1.494(3)
C1−C2−C3	116.2(2)	116.6(2)	115.6(2)	116.6(1)	116.4(3)	116.5(2)	116.3(2)
C2−C3−C4	120.7(3)	119.4(3)	120.8(2)	120.7(2)	120.3(3)	120.4(2)	120.4(2)
C3−C4−C5	122.8(3)	123.6(3)	123.2(2)	122.9(2)	123.5(3)	122.6(2)	123.8(2)
C4−C5−C6	123.1(3)	123.9(3)	123.4(2)	123.1(2)	123.8(3)	125.7(2)	122.8(2)
C5−C6−C1	121.1(3)	117.2(3)	120.7(2)	121.1(2)	118.9(3)	117.7(2)	120.8(2)
C6−C1−C2	115.9(2)	115.7(2)	116.0(2)	115.6(1)	116.7(3)	116.8(2)	115.9(2)

Reaction of Zirconacyclopentenes Bearing a Carboranyl Unit with Alkynes in the Presence of $FeCl_3$. Transmetalation of zirconacycles to iron has never been documented in the literature, although many iron-mediated/catalyzed organic transformations have been reported.[23] During the course of these studies, we discovered that $FeCl_3$ alone was also able to mediate the cycloaddition reactions in toluene/THF solvent. Various reaction conditions were examined, and the results are summarized in Table 4.

No reaction was observed in pure toluene, whereas the benzocarborane was produced in 24% yield in THF (Table 4, entries 1 and 2). Two equivalents of $FeCl_3$ was required for the reaction. Excess amounts of alkyne had little effect on the yields of the products, since no trimerization of alkynes was detected. A large excess amount of $FeCl_3$ (3 equiv) did not improve the yield (Table 4, entry 11). Prolonged heating slightly improved the yield (Table 4, entry 12). Shortening the reaction time or lowering the reaction temperature dramatically decreased the yield (Table 4, entries 13 and 14). No effect was observed upon the addition of PPh_3 to the reaction system (Table 4, entry 15).

Under the optimal reaction conditions (Table 4, entry 3), various alkynes were examined. The results are compiled in Table 5. The presence of excess $FeCl_3$ introduced difficulty in separating the products, resulting in low isolated yields. These results also showed that the iron complex was less reactive than the nickel one, leading to lower yields in general. On the other hand, DMAD was able to insert into the iron complex, affording the corresponding cycloaddition product **3o** in 20% isolated yield (Table 5, entry 9), whereas only the DMAD cyclotrimerization product was observed when an equimolar amount of $NiCl_2(PMe_3)_2$ was used. It is noteworthy that $FeCl_2$ also worked well in the transmetalation reaction and offered yields of cycloaddition products very similar to those of $FeCl_3$ under the same reaction conditions.

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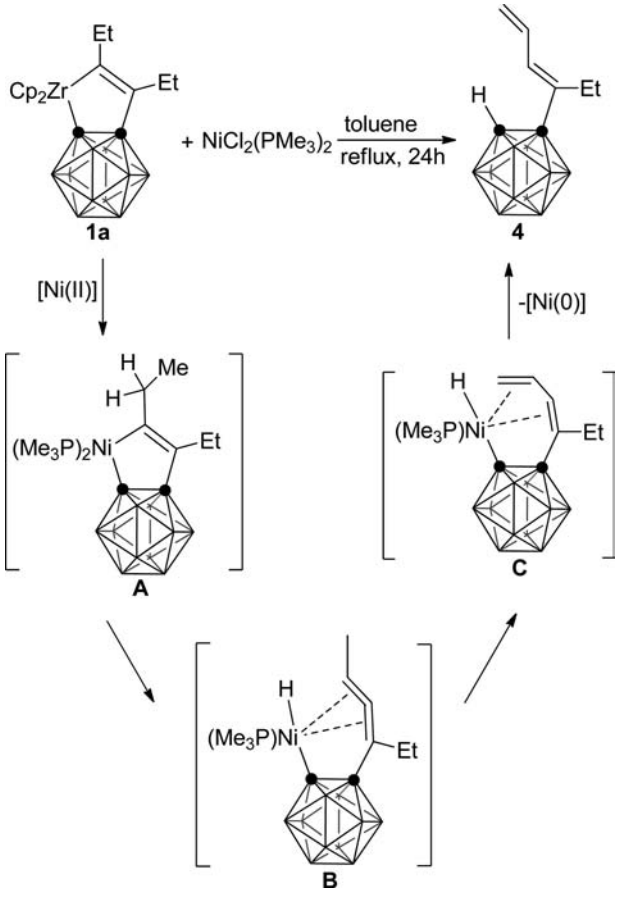
All of the new benzocarboranes were characterized by ^{1}H, ^{13}C, and ^{11}B NMR techniques as well as high-resolution mass spectrometry (HRMS). The molecular structures of **3p** and **3q** were further confirmed by X-ray analyses and are shown in Figure 2. Selected bond lengths and angles are summarized in Table 6 for comparison; they are similar to those observed for other benzocarboranes.[10]

Reaction Mechanism. An early attempt to prepare nickelacyclopentene from the reaction of **1a** with $NiCl_2(PMe_3)_2$ failed. However, we isolated a new compound, 1-[C(Et)=CHCH=CH_2]-1,2-$C_2B_{10}H_{11}$ (**4**), from this reaction. A possible pathway for the formation of **4** is depicted in Scheme 1. After transmetalation of **1a** to Ni(II), the resultant nickelacyclopentene complex (**A**) undergoes β-H elimination to give **B**, which isomerizes to form intermediate **C**. Reductive elimination affords the product **4**. This reaction offers strong evidence for the transmetalation to Ni(II).

Scheme 1. Reaction of 1a with $NiCl_2(PMe_3)_2$



To avoid the β-H elimination and stabilize the intermediate, the complex 1,2-[$Cp_2ZrC(Ph)$=$C(Ph)$]-1,2-$C_2B_{10}H_{10}$ (**1b**) and $NiCl_2$(dppe) were chosen as the reactants. The expected nickelacyclopentene complex 1,2-[(dppe)NiC(Ph)=C(Ph)]-1,2-$C_2B_{10}H_{10}$ (**5**) was isolated as light-brown crystals in 69% yield from the reaction of **1b** with $NiCl_2$(dppe) in refluxing toluene for 24 h (Scheme 2).

Complex **5** was fully characterized by various NMR techniques and elemental analyses. The characteristic vinyl and cage carbons were observed at 164.5/147.3 and 90.4/74.7 ppm, respectively, in its ^{13}C NMR spectrum. The characteristic phosphines were observed at 53.9 and 44.6 ppm in its ^{31}P NMR spectrum.

The molecular structure of **5** was further confirmed by single-crystal X-ray diffraction studies, which showed an essentially planar configuration about the Ni atom (Figure 3). This further supports the previous hypothesis. The Ni−C_{vinyl} and Ni−C_{cage} bond distances of 1.963(4) and 1.950(4) Å are close to the corresponding Ni−C distances of 1.928(8) and 1.901(8) Å in [{2-[C(Bu^n)=C(*o*-C_5H_4N)]-1,2-$C_2B_{10}H_{10}$}Ni][μ-Cl][Li-$(THF)_4$].[10b] Further reaction of **5** with $^nBuC{\equiv}CBu^n$ gave the cycloaddition product **3r** in 85% yield, providing support that **5** is the intermediate.

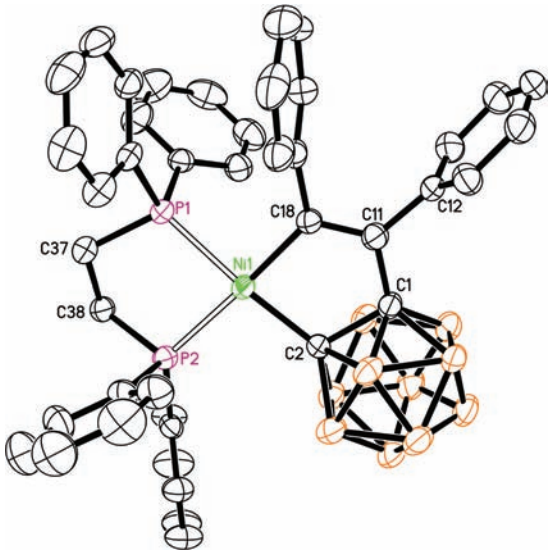
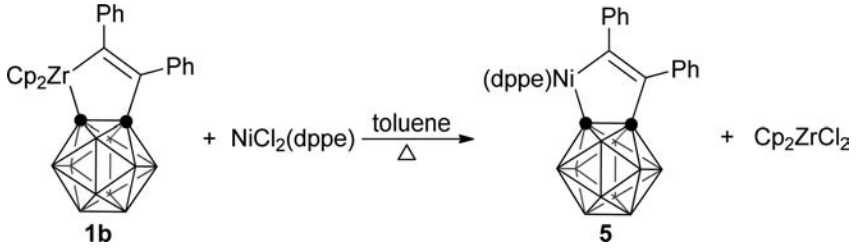


Figure 3. Molecular structure of **5**.

On the basis of these experimental results and those of earlier reports,[10,12] a possible mechanism is proposed in Scheme 3. Transmetalation of zirconacyclopentene to nickel gives nickelacyclopentene intermediate **5′**, and this is followed by the alkyne insertion to form another intermediate, **D**. Reductive elimination affords the final product benzocarborane **3** and

Scheme 2. Nickelacyclopentene Incorporating a Carboranyl Unit



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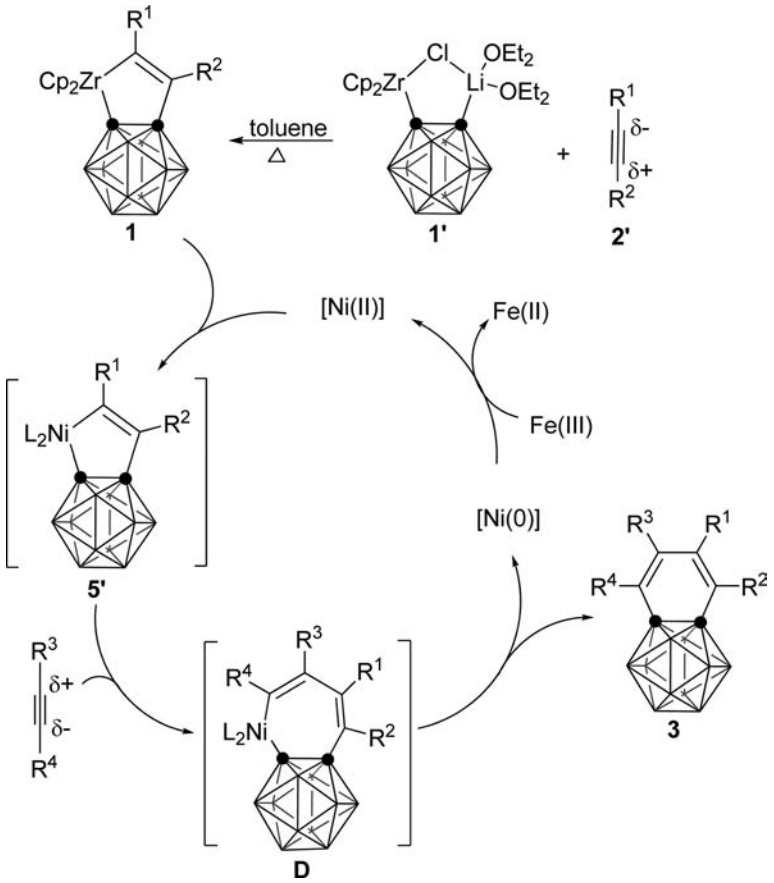
Scheme 3. Proposed Mechanism for the Formation of Benzocarborane



Ni(0). The regioselectivity in the insertion is controlled by the polarity of the unsymmetrical alkynes. Oxidation of Ni(0) by Fe(III) regenerates Ni(II) to complete the catalytic cycle. As both $FeCl_2$ and $FeCl_3$ are also able to promote the cycloaddition reactions, although they are less reactive than $NiCl_2$, they may be involved in the insertion reaction via transmetalation of zirconacycles to iron.

CONCLUSION

We have developed an efficient three-component [2 + 2 + 2] cycloaddition protocol for the preparation of a new class of highly substituted benzocarboranes in a one-pot or two-step manner via transmetalation of zirconacyclopentenes incorporating a carboranyl unit to nickel or iron. A reaction mechanism has been proposed after the isolation and full characterization of the key intermediate nickelacycle. The results show that both electronic and steric factors play a role in the regioselective formation of benzocarboranes. Using a catalytic amount of nickel can dramatically reduce the formation of alkyne homotrimerization products, allowing the insertion of activated alkynes such as DMAD. Transmetalation to iron makes the cycloaddition reaction tolerant to substrates such as DMAD and TMS-substituted alkynes. On the other hand, the catalytic version of this transmetalation of zirconacycles to nickel represents an important advance in the development of zirconacycle-based methodologies. This sets an example for the conversion of traditional zirconocene-based stoichiometric reactions into catalytic ones.

EXPERIMENTAL SECTION

General Procedures. All of the reactions were performed under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. ^1H NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 300 MHz or a Varian Inova 400 spectrometer at 400 MHz. $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Varian Inova 400 spectrometer at 100 MHz. $^{11}B\{^1H\}$ NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 96 MHz or a Varian Inova 400 spectrometer at 128 MHz. ^{31}P NMR spectra were recorded on a Bruker DPX 300 spectrometer at 121 MHz. All chemical shifts are reported in δ units with reference to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts, and to external 85% H_3PO_4 (0.00 ppm) for phosphorus chemical shifts. IR spectra were obtained from KBr pellets prepared in the glovebox on a PerkinElmer 1600 Fourier transform IR spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry (Chinese Academy of Sciences, China). Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. All of the organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. All of the alkynes were freshly distilled from CaH_2 prior to use. The alkynes $^nBuC{\equiv}CBu^t$ (**2h**),[24] $PhC{\equiv}CCH_2N(CH_3)_2$ (**2l**),[25] $PhC{\equiv}CCH_2OMe$ (**2m**),[26] $PhC{\equiv}CCH_2CH{=}CH_2$(**2n**),[27] $TMSC{\equiv}CBu^n$ (**2p**),[28] and $TMSC{\equiv}CPh$ (**2q**)[29] were prepared according to literature methods. The zirconocene complexes were prepared according to the reported procedure.[13] Other chemicals were purchased from either Aldrich or Acros and used as received unless otherwise specified.

Preparation of Benzocarboranes 3. *Method A.* To a suspension of zirconacyclopentene **1** (0.20 mmol) in toluene (10 mL) were added $NiCl_2(PMe_3)_2$ (62 mg, 0.21 mmol) and

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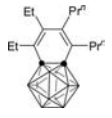
alkyne **2** (0.70 mmol), and the reaction vessel was closed and heated at 110 °C for 2 days. The reaction mixture was then cooled to room temperature and treated with 1 M HCl (10 mL). The organic layer was separated, and the aqueous solution was extracted with diethyl ether (20 mL × 2). The organic portions were combined and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was subjected to column chromatographic separation (silica gel, 300−400 mesh) using hexane as the eluent to give **3** as an oil, white solid, or colorless crystals.

Method B. To a suspension of zirconacyclopentene **1** (0.20 mmol) in 2:1 (v/v) toluene/THF (10 mL) were added $FeCl_3$ (65 mg, 0.40 mmol) or $FeCl_2$ (51 mg, 0.40 mmol) and alkyne **2** (0.40 mmol), and the reaction vessel was closed and heated at 110 °C for 2 days. Using the same workup procedures as above afforded **3** as an oil, white solid, or colorless crystals.

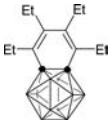
Method C. Alkyne (0.30 mmol) was added to a solution of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (111 mg, 0.20 mmol) in toluene (10 mL), and the mixture was heated to reflux for 2 days. After the excess alkyne and toluene were removed under reduced pressure, toluene (10 mL), the second alkyne **2** (0.70 mmol), and $NiCl_2(PMe_3)_2$ (62 mg, 0.21 mmol) were added to the residue, and the reaction vessel was closed and heated at 110 °C for 2 days. Using the same workup procedures as above afforded **3** as an oil, white solid, or colorless crystals.

3a: Method A, yield 84%. Method C, yield 82%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (q, J = 7.4 Hz, 2H, CH_2), 2.50 (m, 2H, CH_2), 2.32 (q, J = 7.4 Hz, 2H, CH_2), 2.25 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.42 (m, 4H, CH_2), 1.31 (m, 2H, CH_2), 1.18 (t, J = 7.4 Hz, 3H, CH_3), 1.02 (t, J = 7.4 Hz, 3H, CH_3), 0.97 (t, J = 7.2 Hz, 3H, CH_3), 0.95 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.9, 134.3, 134.1, 132.6 (olefinic *C*), 77.2, 76.3 (cage *C*), 33.4, 32.7, 32.6, 28.9, 26.3, 23.1, 23.0, 22.1, 15.0, 14.8, 14.0, 13.8, 13.7 (Et and ^{n}Bu). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −7.2 (2B), −10.1 (6B), −12.9 (2B). HRMS (*m*/*z*): Calcd for $C_{18}H_{38}{}^{11}B_8{}^{10}B_2{}^+$: 362.3971. Found: 362.3974.

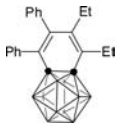
3b: Method A, yield 81%. Method C, 80%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (q, J = 7.4 Hz, 2H, CH_2), 2.48 (m, 2H, CH_2), 2.32 (q, J = 7.4 Hz, 2H, CH_2), 2.23 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.36 (m, 2H, CH_2), 1.05 (t, J = 7.4 Hz, 3H, CH_3), 1.01 (m, 9H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.9, 134.4, 134.1, 132.6 (olefinic *C*), 77.2, 76.3 (cage *C*), 35.8, 31.2, 26.3, 23.9, 22.1, 15.3, 15.0, 14.8, 14.4, 14.3 (Et and ^{n}Pr). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −7.4 (2B), −10.3 (6B), −13.2 (2B). HRMS (*m*/*z*): Calcd for $C_{16}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 334.3658. Found: 334.3659.



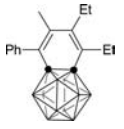
3c: Method A, yield 78%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (q, J = 7.6 Hz, 4H, CH_2), 2.34 (q, J = 7.6 Hz, 4H, CH_2), 1.18 (t, J = 7.6 Hz, 6H, CH_3), 1.03 (t, J = 7.6 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.2, 133.9 (olefinic *C*), 76.3 (cage *C*), 26.3, 22.0, 15.0, 14.8 (Et). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −7.1 (2B), −10.0 (6B), −12.9 (2B). These data are in agreement with the literature.[10a]



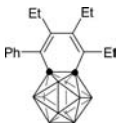
3d: Method A, 70% yield for the reaction of **1a** with **2d** and 81% yield for the reaction of **1b** with **2c**. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (m, 6H, aromatic *H*), 6.93 (m, 2H, aromatic *H*), 6.86 (d, J = 6.5 Hz, 2H, aromatic *H*), 2.72 (q, J = 7.4 Hz, 2H, CH_2), 2.12 (q, J = 7.4 Hz, 2H, CH_2), 1.29 (t, J = 7.4 Hz, 3H, CH_3), 0.76 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.0, 137.7, 137.3, 136.9, 136.3, 133.7, 130.8, 129.6, 127.3, 127.0, 126.7 (aromatic and olefinic *C*), 76.2, 74.6 (cage *C*), 26.4, 23.3, 14.9, 13.8 (Et). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −6.9 (2B), −10.2 (5B), −12.8 (3B). HRMS (*m*/*z*): Calcd for $C_{22}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 402.3345. Found: 402.3347.



3e: Method A, yield 76%. Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H, aromatic *H*), 7.12 (m, 2H, aromatic *H*), 2.68 (q, J = 7.4 Hz, 2H, CH_2), 2.42 (q, J = 7.4 Hz, 2H, CH_2), 1.66 (s, 3H, CH_3), 1.25 (t, J = 7.4 Hz, 3H, CH_3), 1.07 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 138.4, 136.2, 134.3, 130.3, 130.1, 128.1, 128.0 (aromatic and olefinic *C*), 75.8, 74.7 (cage *C*), 26.3, 22.6, 18.2, 14.9, 14.0 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −7.1 (2B), −10.3 (5B), −13.0 (3B). HRMS (*m*/*z*): Calcd for $C_{17}H_{28}{}^{11}B_8{}^{10}B_2{}^+$: 340.3189. Found: 340.3194.



3f: Method A, yield 81%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 3H, aromatic *H*), 7.16 (m, 2H, aromatic *H*), 2.68 (q, J = 7.4 Hz, 2H, CH_2), 2.40 (q, J = 7.4 Hz, 2H, CH_2), 2.01 (q, J = 7.4 Hz, 2H, CH_2), 1.25 (t, J = 7.4 Hz, 3H, CH_3), 1.08 (t, J = 7.4 Hz, 3H, CH_3), 0.84 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.6, 137.2, 135.9, 134.3, 133.7, 130.4, 128.0, 127.7 (aromatic and olefinic *C*), 75.8, 74.7 (cage *C*), 26.4, 23.8, 22.0, 15.0, 14.8 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −8.1 (2B), −11.2 (5B), −14.0 (3B). HRMS (*m*/*z*): Calcd for $C_{18}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 354.3345. Found: 354.3340.



3f′: Method B, yield 22%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H, aromatic *H*), 7.09 (m, 2H, aromatic *H*), 2.62 (q, J = 7.4 Hz, 2H, CH_2), 2.44 (q, J = 7.4 Hz, 2H, CH_2), 1.99 (q, J = 7.4 Hz, 2H, CH_2), 1.20 (t, J = 7.4 Hz, 3H, CH_3), 0.86 (t, J = 7.4 Hz, 3H, CH_3), 0.70 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2, 137.4, 136.0, 134.8, 133.8, 129.3, 128.1, 127.4 (aromatic *C*), 75.8 (cage *C*), 27.3, 26.2, 23.1, 14.8, 14.3, 13.7 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ −6.4 (2B), −9.4 (5B), −12.2 (3B). HRMS (*m*/*z*): Calcd for $C_{18}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 354.3345. Found: 354.3334.

3g: Method A, yield 83%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 3H, aromatic *H*), 7.14 (m, 2H, aromatic *H*), 2.67 (q, J = 7.4 Hz, 2H, CH_2), 2.37 (q, J = 7.4 Hz, 2H, CH_2), 1.92 (m, 2H, CH_2), 1.25 (t, J = 7.4 Hz, 3H, CH_3), 1.18 (m, 2H, CH_2), 1.08 (m, 2H, CH_2), 1.06 (t, J = 7.4 Hz, 3H, CH_3), 0.70 (t, J = 7.2 Hz, 3H, CH_3).

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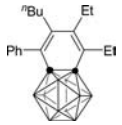
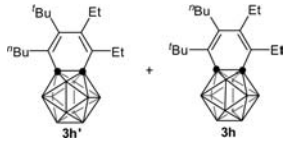
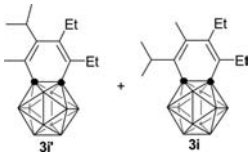
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.6, 136.9, 134.8, 134.3, 133.9, 130.4, 128.0, 127.7 (aromatic and olefinic *C*), 75.8, 74.7 (cage *C*), 32.6, 30.5, 26.4, 22.8, 22.1, 15.0, 14.7, 13.4 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −7.2 (2B), −10.4 (5B), −13.1 (3B). HRMS (*m*/*z*): Calcd for $C_{20}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 382.3658. Found: 382.3652.



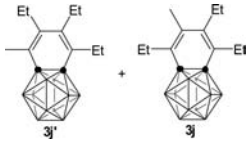
3h + **3h′**: Method A, yield 71%. **3h**/**3h′** = 83:17 by GC−MS. Fractional recrystallization gave **3h** in 31% isolated yield as colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 2.58 (m, 2H, CH_2), 2.29 (m, 4H, CH_2), 1.51 (s, 9H, CH_3), 1.40 (m, 2H, CH_2), 1.15 (t, *J* = 7.6 Hz, 3H, CH_3), 1.11 (m, 2H, CH_2), 0.96 (t, *J* = 7.6 Hz, 3H, CH_3), 0.92 (t, *J* = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.2, 138.5, 135.6, 133.5 (olefinic *C*), 81.2, 77.6 (cage *C*), 39.7 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 33.9, 32.6, 27.0, 23.1, 22.8, 15.2, 14.6, 13.9 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −6.4 (1B), −7.9 (1B), −9.8 (2B), −11.6 (3B), −13.0 (3B). HRMS (*m*/*z*): Calcd for $C_{18}H_{38}{}^{11}B_8{}^{10}B_2{}^+$: 362.3971. Found: 362.3975.



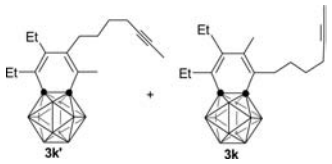
3i + **3i′**: Method A, yield 67%. White solid. An inseparable mixture was formed (**3i**/**3i′** = 81:19 by GC−MS). The pure product was not obtained by recrystallization. Compound **3i** was isolated as a major product contaminated with **3i′**. ^1H NMR (400 MHz, $CDCl_3$) (**3i**): δ 3.25 (m, 1H, *CH*), 2.57 (q, *J* = 7.6 Hz, 2H, CH_2), 2.35 (q, *J* = 7.6 Hz, 2H, CH_2), 2.03 (s, 3H, CH_3), 1.30 (d, *J* = 7.2 Hz, 6H, CH_3), 1.18 (t, *J* = 7.6 Hz, 3H, CH_3), 1.03 (t, *J* = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (**3i** + **3i′**): δ 138.9, 135.1, 134.3, 128.3 (olefinic *C*), 75.9 (cage *C*), 34.5 (*CH*), 26.2, 22.0, 20.9, 20.7, 17.0, 14.7, 14.1 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −8.1 (2B), −11.0 (6B), −14.3 (2B). HRMS (*m*/*z*): Calcd for $C_{14}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 306.3345. Found: 306.3335.



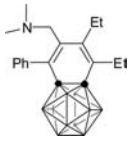
3j + **3j′**: Method A, yield 33%. White solid. An inseparable mixture was formed (**3j**/**3j′** = 57:43 by GC−MS). Compound **3j** was isolated as a major product contaminated with **3j′**. ^1H NMR (400 MHz, $CDCl_3$) (**3j**): δ 2.61 (m, 2H, CH_2), 2.37 (m, 4H, CH_2), 1.96 (s, 3H, CH_3), 1.18 (t, *J* = 7.6 Hz, 3H, CH_3), 1.09 (t, *J* = 7.4 Hz, 3H, CH_3), 1.03 (t, *J* = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (**3j** + **3j′**): δ 135.2, 134.7, 134.5, 134.2, 133.6, 129.3, 128.0 (olefinic *C*), 76.1 (cage *C*), 27.2, 26.3, 26.2, 22.6, 22.5, 22.1, 19.2, 15.9, 14.9, 14.8, 14.5, 14.0, 13.3 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −7.9 (2B), −10.8 (4B), −11.5 (2B), −13.7 (2B). HRMS (*m*/*z*): Calcd for $C_{13}H_{28}{}^{11}B_8{}^{10}B_2{}^+$: 292.3189. Found: 292.3197.



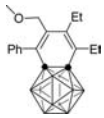
3k + **3k′**: Method A, yield 29%. Colorless oil. An inseparable mixture was formed (**3k**/**3k′** = 66:34 by GC). Compound **3k** was isolated as a major product contaminated with **3k′**. ^1H NMR (400 MHz, $CDCl_3$) (**3k**): δ 2.59 (m, CH_2), 2.36 (m, CH_2), 2.20 (m, CH_2), 2.18 (m, CH_2), 1.96 (s, 3H, CH_3), 1.79 (m, CH_2), 1.55 (m, CH_2), 1.40 (m, CH_2), 1.16 (t, *J* = 7.2 Hz, CH_3), 1.02 (t, *J* = 7.2 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (**3k** + **3k′**): δ 134.6, 134.5, 134.3, 133.8, 132.2, 129.6, 128.2 (olefinic *C*), 78.7, 78.5, 76.2, 76.0 (cage and alkyne *C*), 33.8, 29.7, 28.8, 28.1, 27.8, 26.3, 26.2, 22.5, 22.2, 19.5, 18.3, 16.0, 14.9, 14.8, 14.5, 14.0, 3.4, 1.0 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −8.4 (2B), −11.4 (5B), −14.2 (3B). HRMS (*m*/*z*): Calcd for $C_{18}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 358.3658. Found: 358.3655.



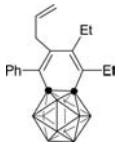
3l: Method A, yield 21%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H, aromatic *H*), 7.11 (m, 2H, aromatic *H*), 2.78 (s, 2H, NCH_2), 2.66 (q, *J* = 7.6 Hz, 2H, CH_2), 2.63 (q, *J* = 7.6 Hz, 2H, CH_2), 2.01 (s, 6H, NCH_3), 1.26 (t, *J* = 7.6 Hz, 3H, CH_3), 1.08 (t, *J* = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.2, 137.0, 136.9, 135.0, 131.1, 128.2, 127.5 (aromatic and olefinic *C*), 76.1, 74.4 (cage *C*), 58.2, 44.8, 26.1, 21.3, 15.1, 14.9 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −6.9 (2B), −10.2 (5B), −12.9 (3B). HRMS (*m*/*z*): Calcd for $C_{19}H_{33}{}^{11}B_8{}^{10}B_2N^+$: 383.3611. Found: 383.3619.



3m: Method A, yield 31%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H, aromatic *H*), 7.18 (m, 2H, aromatic *H*), 3.68 (s, 2H, OCH_2), 3.05 (s, 3H, OCH_3), 2.66 (q, *J* = 7.4 Hz, 2H, CH_2), 2.47 (q, *J* = 7.4 Hz, 2H, CH_2), 1.25 (t, *J* = 7.4 Hz, 3H, CH_3), 1.10 (t, *J* = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.0, 137.4, 136.7, 133.6, 130.7, 130.3, 128.4, 127.6 (aromatic and olefinic *C*), 76.2, 74.2 (cage *C*), 69.6, 58.0, 26.1, 21.8, 14.8, 14.7 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −6.7 (2B), −10.2 (5B), −12.9 (3B). HRMS (*m*/*z*): Calcd for $C_{18}H_{30}{}^{11}B_8{}^{10}B_2O^+$: 370.3294. Found: 370.3292.



3n: Method A, yield 35% [the yield increased to 74% when 2 equiv of $NiCl_2(PMe_3)_2$ and 1.5 equiv of $PhC{\equiv}CCH_2(CH{=}CH_2)$ were used]. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 3H, aromatic *H*), 7.14 (m, 2H, aromatic *H*), 5.70 (m, 1H, vinyl *H*), 5.00 (dd, *J* = 1.6 and 10.4 Hz, 1H, vinyl *H*), 4.73 (dd, *J* = 1.6 and 17.3 Hz, 1H, vinyl *H*), 2.74 (m, 2H, CH_2), 2.68 (q, *J* = 7.4 Hz, 2H, CH_2), 2.36 (q, *J* = 7.4 Hz, 2H, CH_2), 1.25 (t, *J* = 7.4 Hz, 3H, CH_3), 1.06 (t, *J* = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.5, 137.1, 136.1, 135.9, 134.0, 131.6, 130.0, 128.2, 127.6, 115.6 (aromatic and olefinic *C*), 75.9, 74.6 (cage *C*), 34.4, 26.3, 22.3, 14.9, 14.8 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −7.0 (2B), −10.2 (5B), −12.9 (3B). HRMS (*m*/*z*): Calcd for $C_{19}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 366.3345. Found: 366.3345.



3o: Method B, yield 20%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 2.69 (q, *J* = 7.4

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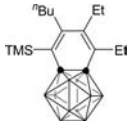
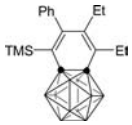
Hz, 2H, CH_2), 2.37 (q, J = 7.4 Hz, 2H, CH_2), 1.22 (t, J = 7.4 Hz, 3H, CH_3), 1.01 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.7, 163.8 (CO_2Me), 143.3, 136.2, 129.5, 128.3 (olefinic C), 69.1 (cage C), 53.0, 52.9 (OCH_3), 26.7, 22.9, 14.6, 13.9 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −6.0 (1B), −6.7 (1B), −9.8 (2B), −11.2 (2B), −12.9 (4B). HRMS (m/z): Calcd for $C_{14}H_{26}{}^{11}B_8{}^{10}B_2O_4{}^+$: 366.2829. Found: 366.2833.

3p: Method B, yield 53%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 2.63 (q, J = 7.4 Hz, 2H, CH_2), 2.40 (m, 2H, CH_2), 2.34 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.21 (m, 5H, CH_2 + CH_3), 0.96 (m, 6H, CH_3), 0.41 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.3, 138.4, 135.5, 133.5 (olefinic C), 78.4, 78.1 (cage C), 34.0, 33.6, 26.8, 22.9, 21.8, 15.1, 14.8, 13.9 (CH_2 and CH_3), 4.6 (TMS). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −8.2 (2B), −10.2 (2B), −11.7 (3B), −13.7 (3B). HRMS (m/z): Calcd for $C_{17}H_{38}{}^{11}B_8{}^{10}B_2Si^+$: 378.3740. Found: 378.3727.

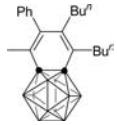


3q: Method B, yield 59%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 3H, aromatic H), 7.06 (m, 2H, aromatic H), 2.61 (q, J = 7.4 Hz, 2H, CH_2), 1.84 (q, J = 7.4 Hz, 2H, CH_2), 1.20 (t, J = 7.4 Hz, 3H, CH_3), 0.69 (t, J = 7.4 Hz, 3H, CH_3), −0.10 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.5, 139.9, 138.8, 137.3, 133.2, 130.1, 127.9, 127.8 (aromatic and olefinic C), 78.8, 77.6 (cage C), 26.7, 22.7, 14.6, 14.0 (CH_2 and CH_3), 3.8 (TMS). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ −8.2 (2B), −10.4 (2B), −12.0 (3B), −13.9 (3B). HRMS (m/z): Calcd for $C_{19}H_{34}{}^{11}B_8{}^{10}B_2Si^+$: 398.3427. Found: 398.3419.

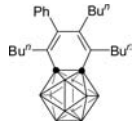


3r: Method A, yield 83%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (m, 6H, aromatic H), 6.94 (m, 2H, aromatic H), 6.85 (d, J = 8.0 Hz, 2H, aromatic H), 2.63 (m, 2H, CH_2), 2.03 (m, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.14 (m, 2H, CH_2), 1.01 (t, J = 7.2 Hz, 3H, CH_3), 0.97 (m, 2H, CH_2), 0.62 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.1, 137.9, 137.3, 136.0, 132.5, 130.8, 129.6, 127.3, 127.0, 126.7 (aromatic and olefinic C), 76.4, 74.7 (cage C), 33.5, 32.6, 31.3, 30.0, 23.1, 22.5, 13.8, 13.3 (^{n}Bu). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −7.6 (2B), −10.9 (5B), −13.4 (3B). HRMS (m/z): Calcd for $C_{20}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 458.3971. Found: 458.3966.

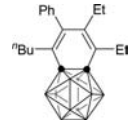
3s: Method A, yield 85%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H, aromatic H), 7.01 (m, 2H, aromatic H), 2.53 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 1.84 (s, 3H, CH_3), 1.53 (m, 2H, CH_2), 1.44 (m, 2H, CH_2),1.06 (m, 2H, CH_2), 0.98 (m, 2H, CH_2), 0.95 (t, J = 7.2 Hz, 6H, CH_3), 0.63 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 139.1, 135.5, 133.5, 132.3, 131.4, 128.8, 128.3, 127.3 (aromatic and olefinic C), 77.2, 75.9 (cage C), 33.2, 32.5, 31.2, 30.0, 23.1, 22.6, 21.1, 13.7, 13.3 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −7.0 (2B), −10.3 (5B), −12.8 (3B). HRMS (m/z): Calcd for $C_{21}H_{36}{}^{11}B_8{}^{10}B_2{}^+$: 396.3815. Found: 396.3805.



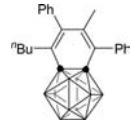
3t: Method A, yield 81%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 3H, aromatic H), 7.06 (m, 2H, aromatic H), 2.51 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.28 (m, 2H, CH_2), 1.04 (m, 9H, CH_2 and CH_3), 0.64 (t, J = 7.2 Hz, 3H, CH_3), 0.61 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.2, 136.2, 136.1, 133.7, 132.5, 129.4, 128.0, 127.4 (aromatic and olefinic C), 77.0, 76.0 (cage C), 34.0, 33.3, 32.5, 31.6, 31.2, 29.8, 23.1, 22.6, 22.5, 13.7, 13.3, 13.2 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −7.2 (2B), −10.2 (5B), −12.9 (3B). HRMS (m/z): Calcd for $C_{24}H_{42}{}^{11}B_8{}^{10}B_2{}^+$: 438.4284. Found: 438.4277.



3u: Method A, yield 80%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H, aromatic H), 7.08 (d, J = 8.0 Hz, 2H, aromatic H), 2.62 (q, J = 7.6 Hz, 2H, CH_2), 2.18 (m, 2H, CH_2), 2.01 (q, J = 7.4 Hz, 2H, CH_2), 1.29 (m, 2H, CH_2), 1.20 (t, J = 7.4 Hz, 3H, CH_3), 1.03 (m, 2H, CH_2), 0.69 (t, J = 7.4 Hz, 3H, CH_3), 0.65 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.2, 136.5, 135.9, 134.7, 133.8, 129.4, 128.0, 127.4 (aromatic and olefinic C), 76.8, 76.0 (cage C), 34.0, 31.7, 26.2, 23.1, 22.7, 14.9, 13.7, 13.3 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −7.1 (2B), −10.2 (5B), −12.9 (3B). HRMS (m/z): Calcd for $C_{20}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 382.3658. Found: 382.3645.



3v: Method A, yield 36% (the yield increased to 73% when the reaction was extended to 5 days). Colorless crystals. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 6H, aromatic H), 7.15 (d, J = 8.0 Hz, 2H, aromatic H), 7.09 (d, J = 8.0 Hz, 2H, aromatic H), 2.31 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.19 (s, 3H, CH_3), 1.10 (q, J = 7.2 Hz, 2H, CH_2), 0.69 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.4, 137.9, 137.7, 135.9, 133.5, 130.5, 130.2, 130.0, 129.4, 128.8, 128.4, 128.1, 127.7, 127.5 (aromatic and olefinic C), 75.7, 75.3 (cage C), 34.0, 31.9, 22.7, 20.6, 13.3 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −6.8 (2B), −10.1 (5B), −12.6 (3B). HRMS (m/z): Calcd for $C_{23}H_{32}{}^{11}B_8{}^{10}B_2{}^+$: 416.3502. Found: 416.3487.



3w: Method A, yield 77%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H, aromatic H), 7.07 (d, J = 8.0 Hz, 2H, aromatic H), 3.19 (t, J = 6.6 Hz, 2H, CH_2), 2.63 (q, J = 7.4 Hz, 2H, CH_2), 2.36 (m, 2H, CH_2), 2.01 (q, J = 7.4 Hz, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.19 (t, J = 7.4 Hz, 3H, CH_3), 0.70 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.8, 137.0, 135.5, 134.5, 133.7, 129.1, 128.3, 127.7 (aromatic and olefinic C), 76.8, 75.5 (cage C), 44.2, 32.2, 31.9, 26.3, 23.1, 14.8, 13.7 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −6.9 (2B), −10.2 (5B), −12.9 (3B). HRMS (m/z): Calcd for $C_{19}H_{31}{}^{11}B_8{}^{10}B_2Cl^+$: 402.3112. Found: 402.3119.

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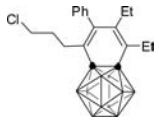

3x: Method B, yield 44%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (m, 4H, CH_2), 2.20 (m, 4H, CH_2), 1.59 (m, 4H, CH_2), 1.35 (m, 4H, CH_2), 1.00 (t, J = 7.4 Hz, 6H, CH_3), 0.98 (t, J = 7.4 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.1, 132.8 (olefinic *C*), 76.4 (cage *C*), 35.8, 31.4, 23.9, 23.8, 14.4, 14.3 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ −8.5 (2B), −11.3 (6B), −14.2 (2B). These data are in agreement with the literature.[10a]

Preparation of 1-[C(Et)═CH−CH═CH$_2$]-1,2-C$_2$B$_{10}$H$_{11}$ (4). To a suspension of 1,2-[$Cp_2ZrC(Et)$═$C(Et)$]-1,2-$C_2B_{10}H_{10}$ (**1a**) (89 mg, 0.20 mmol) in toluene (10 mL) was added $NiCl_2(PMe_3)_2$ (62 mg, 0.21 mmol). The mixture was heated to reflux for 2 days. The reaction mixture was concentrated and subjected to column chromatography on silica gel using hexane as the eluent to give **4** as a colorless oil (21 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51 (dt, J = 10.8 and 16.7 Hz, 1H, vinyl *H*), 6.25 (d, J = 10.8 Hz, 1H, vinyl *H*), 5.41 (dd, J = 0.8, 16.7 Hz, 1H, vinyl *H*), 5.33 (dd, J = 0.8, 10.8 Hz, 1H, vinyl *H*), 3.78 (brs, 1H, cage C*H*), 2.36 (q, J = 7.6 Hz, 2H, CH_2), 1.08 (t, J = 7.6 Hz, 2H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.9, 132.1, 131.3, 122.2 (olefinic *C*), 78.4, 59.8 (cage *C*), 24.5, 14.2 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −2.7 (1B), −4.4 (1B), −9.2 (2B), −11.2 (4B), −13.2 (2B). HRMS (*m*/*z*): Calcd for $[C_8H_{10}{}^{11}B_8{}^{10}B_2{}^+ - 2H]$: 222.2406. Found: 222.2396.

Preparation of 1,2-[(dppe)NiC(Ph)═C(Ph)]-1,2-C$_2$B$_{10}$H$_{10}$ (5). A suspension of 1,2-[$Cp_2ZrC(Ph)$═$C(Ph)$]-1,2-$C_2B_{10}H_{10}$ (**1b**) (108 mg, 0.20 mmol) and $NiCl_2$(dppe) (110 mg, 0.20 mmol) in toluene (10 mL) was heated to reflux for 24 h with stirring. The mixture was filtered to yield a hot brown solution from which the product **5** was isolated as brown crystals after this solution was allowed to stand for 2 days at room temperature (120 mg, 69%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 8.09 (m, 1H), 7.66 (m, 1H), 7.53 (m, 1H), 7.46 (m, 6H), 7.30 (m, 12H), 7.22 (m, 1H), 7.12 (t, J = 7.5 Hz, 2H), 7.02 (m, 1H), 6.93 (m, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.61 (t, J = 7.5 Hz, 2H), 6.52 (m, 1H) (aromatic *H*), 2.31 (t, J = 4.2 Hz, 4H, CH_2). ^{13}C{^{1}H} NMR data were not obtained because of the poor solubility of **5**. ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ −1.7 (3B), −4.7 (2B), −7.5 (4B), −10.3 (1B). ^{31}P{^{1}H} NMR (121 MHz, pyridine-d_5): δ 53.9 (d, J = 2.4 Hz), 44.6 (d, J = 2.4 Hz). IR (KBr) ν (cm^{-1}): 2563 (B−H), 1595 (C═C). Anal. Calcd for $C_{49}H_{52}B_{10}NiP_2$ (**5** + toluene): C, 67.67; H, 6.03. Found: C, 67.41; H, 5.95.

X-ray Structure Determination. Single-crystals of **3e**, **3h**, **3m**, **3n**, **3p**, **3q**, **3v**, and **5** were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. All data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[30] 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 calculations on F^2 using the SHELXTL program package.[31] Complex **5** showed one toluene of solvation. All of the H atoms were geometrically fixed using the riding model.

■ ASSOCIATED CONTENT

Supporting Information

Table of crystal data, details of data collection and refinement, and crystallographic data in CIF format for **3e**, **3h**, **3m**, **3n**, **3p**, **3q**, **3v**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

zxie@cuhk.edu.hk

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