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Reaction of Zirconocene−Carboryne with Alkenes: Synthesis and Structure of Zirconacyclopentanes with a Carborane Auxiliary

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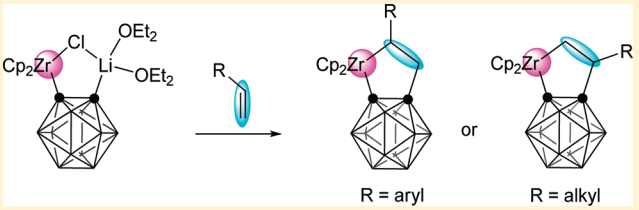
Supporting Information

ABSTRACT: Reaction of zirconocene−carboryne in situ generated from $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ with various alkenes $RCH{=}CH_2$ in refluxing toluene gave the monoinsertion products 1,2-$[Cp_2ZrCH(R)CH_2]$-1,2-$C_2B_{10}H_{10}$ (R = aryl) or 1,2-$[Cp_2ZrCH_2CH(R)]$-1,2-$C_2B_{10}H_{10}$ (R = alkyl) in good to high isolated yields with very high regioselectivity, depending on the polarity of the alkenes. This reaction offered an efficient route to zirconacyclopentanes with a carborane auxiliary, which can be viewed as a carborane version of zirconacyclopentanes. They are thermally very stable and chemically inert toward unsaturated organic molecules such as alkenes, alkynes, nitriles, CO, and CO_2. All complexes have been fully characterized by various spectroscopic techniques. Some have been further confirmed by single-crystal X-ray analyses.



INTRODUCTION

The reactivity patterns of carboryne (1,2-dehydro-*o*-carborane)[1] can be modified and controlled by the formation of metal−carboryne complexes whose chemical properties are dominated by the nature of transition metals.[2] For example, Ni-carboryne complex $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$[3] can undergo coupling reaction with alkenes to generate alkenylcarboranes,[4] two-component [2+2+2] cycloaddition with 2 equiv of alkynes to afford benzocarboranes,[5] and three-component [2+2+2] cyclotrimerization with activated alkene and alkyne to give dihydrobenzocarboranes.[6] The reaction of carboryne with alkynes can also proceed in a catalytic manner using Ni species as catalyst.[7] In contrast, the zirconium−carboryne, in situ generated from $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**1**), reacts with polar unsaturated organic substrates such as isonitrile, nitrile, and azide to give monoinsertion products[8] and with alkynes to give the corresponding zirconacyclopentenes,[9] which is a very useful intermediate for the synthesis of a variety of benzocarboranes.[10] We have very recently communicated that transmetalation of zirconacyclopentanes with a carborane auxiliary to nickel allows the insertion of alkyne into the resultant Ni−C bond, leading to the formation of a series of dihydrobenzocarboranes.[11] In this connection, we explored the generality of the reaction of **1** with various kinds of alkenes. The results show that the prepared zirconacyclopentanes with a carborane auxiliary are thermally very stable and chemically inert. In sharp contrast, zirconacyclopentanes without a carborane unit are very unstable and reactive and can undergo ring-contraction to give alkene−zirconocene complexes or ligand exchange with alkynes to afford the corresponding zirconacyclopentenes and zirconacyclopentadienes.[12] These findings are reported in this article.

RESULTS AND DISCUSSION

Synthesis. Treatment of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**1**)[8a] with 1.2−2 equiv of terminal alkenes $RCH{=}CH_2$ in refluxing toluene gave 1,2-$[Cp_2ZrCH(R)CH_2]$-1,2-$C_2B_{10}H_{10}$ (**3**; R = aryl) or 1,2-$[Cp_2ZrCH_2CH(R)]$-1,2-$C_2B_{10}H_{10}$ (**4**; R = alkyl) in 59−91% isolated yields (Scheme 1). No double-insertion products were observed. An excess amount of alkenes was used to ensure the full consumption of **1**, facilitating the isolation of the products. Both solvents and temperatures were crucial to this reaction. Complexes **3** or **4** were not observed if donor solvents such as Et_2O and THF were used instead of toluene, suggesting that the coordination of alkene to the Zr atom was essential for the subsequent insertion. High temperature was required, as it not only can promote the dissociation of LiCl from **1** forming the zirconocene−carboryne intermediate but may also facilitate the coupling reaction between carboryne and the coordinated alkene via the intermediates **A**/**B** (Scheme 1). However, disubstituted alkenes such as α-methylstyrene and cyclohexene did not react with **1** even after prolonged heating in toluene probably due to steric reasons.

As shown in Table 1, a variety of styrenes inserted effectively into the Zr−C(cage) bond of the Zr-carboryne intermediate to form zirconacyclopentanes **3** in 67−91% isolated yields (entries 1−12). It was noted that a small amount of another regioisomer, 1-$CH_3CH(R)$-1,2-$C_2B_{10}H_{11}$ (R = aryl), was observed by GC-MS analyses of the quenched reaction mixture. However, no pure 1,2-$[Cp_2ZrCH_2CH(R)]$-1,2-$C_2B_{10}H_{10}$ (R = aryl) was isolated. The results showed that the electronic nature

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Scheme 1. Reaction of 1 with Alkenes

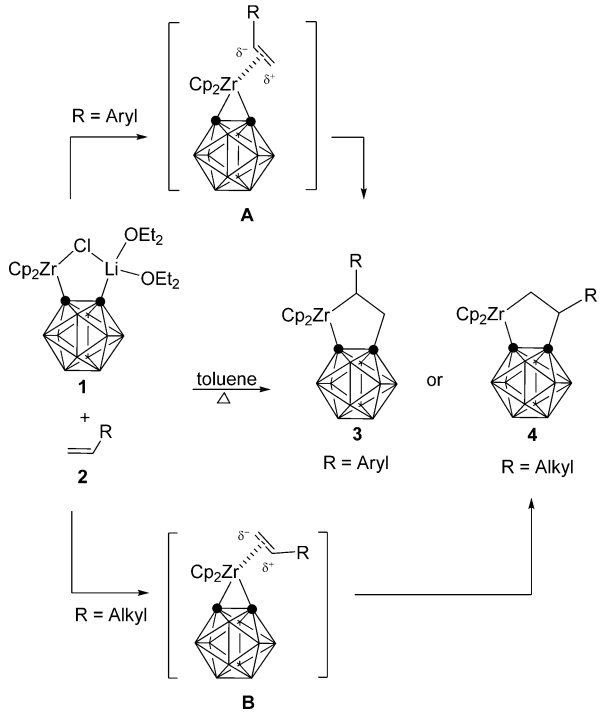


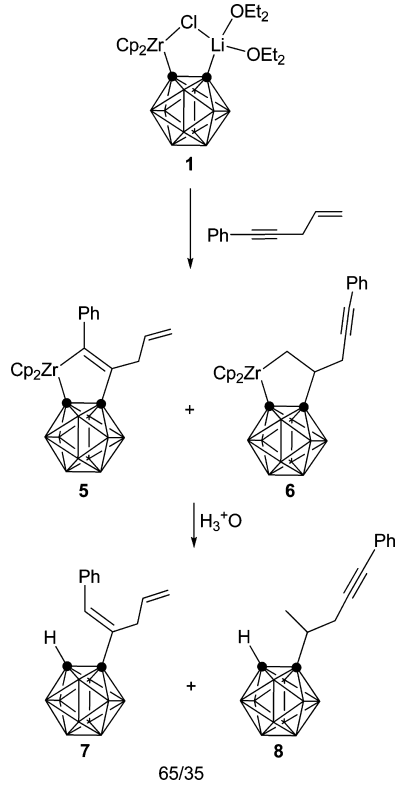
Table 1. Reaction of 1 with Alkenes

entry	alkene (2)	R	product (3) or (4)		isolated yield (%)
1	**2a**	Ph	**3a**	-	87
2	**2b**	4-$CH_3C_6H_4$	**3b**	-	75
3	**2c**	4-$CH_3OC_6H_4$	**3c**	-	78
4	**2d**	4-$C(CH_3)_3OC_6H_4$	**3d**	-	67
5	**2e**	2-ClC_6H_4	**3e**	-	85
6	**2f**	3-ClC_6H_4	**3f**	-	84
7	**2g**	4-ClC_6H_4	**3g**	-	86
8	**2h**	2-$CF_3C_6H_4$	-	-	none
9	**2i**	3-$CF_3C_6H_4$	**3i**	-	91
10	**2j**	4-$CF_3C_6H_4$	**3j**	-	73
11	**2k**	4-BrC_6H_4	**3k**	-	82
12	**2l**	4-FC_6H_4	**3l**	-	81
13	**2m**	TMS	**3m**	-	78
14	**2n**	Ph_2P	**3n**	-	59
15	**2o**	H	**3o**	-	45
16	**2p**	2-C_5H_4N	**3p**	-	trace
17	**2q**	^{n}Bu	-	**4q**	88
18	**2r**	Ph_2PCH_2	-	**4r**	59

of the substituents on the phenyl ring had little effect on the reaction yields, and on the other hand, the bulkiness of substituents on the phenyl ring influenced largely the insertion of alkenes. For example, 2-trifluoromethylstyrene did not react with **1**, whereas 3- and 4-trifluoromethylstyrene reacted well to give **3i** and **3j** in 91% and 73% yield, respectively (entries 8–10). $TMSCH{=}CH_2$ also generated the monoinsertion product **3m** in good yield (78%, entry 13). The reaction of $CH_2{=}CH_2$ and $Ph_2PCH{=}CH_2$ resulted in much lower yields (45–59%, entries 14 and 15) probably due to the low concentration of ethylene in solution or the large steric effect of the Ph_2P unit. On the other hand, ^{n}BuCH=CH_2 and $Ph_2PCH_2CH{=}CH_2$ afforded another kind of regioisomeric insertion products, **4q** and **4r**, in 88% and 59% yield, respectively (entries 17 and 18), and no other regioisomer was observed by GC-MS analyses of the quenched reaction mixture. These data suggest that the regioselectivity of the reactions is mainly controlled by the polarity of the alkenes.[13] In general, the electron-donating substituents on vinyl carbon give complexes **4** via intermediate **B**, whereas the electron-withdrawing substituents offer complexes **3** via intermediate **A** (Scheme 1).

To investigate the relative reactivity between alkene and alkyne, $PhC{\equiv}CCH_2CH{=}CH_2$ was treated with **1** to afford a mixture of alkyne insertion product 1,2-[$Cp_2ZrC(Ph){=}C(CH_2CH{=}CH_2)$]-1,2-$C_2B_{10}H_{10}$ (**5**) and alkene insertion product 1,2-[$Cp_2ZrCH_2CH(CH_2C{\equiv}CPh)$]-1,2-$C_2B_{10}H_{10}$ (**6**) in a ratio of 65 to 35 based on the GC-MS analyses of the hydrolysis products (Scheme 2).

Scheme 2. Reaction of 1 with Eneyne



Complexes **3**–**6** are very soluble in donor solvents, but are insoluble in hexane. Complexes **3b**–**g**,**i**,**j**,**l**,**m**,**o** and **4q**,**r** are also soluble in hot aromatic solvents, whereas **3a**,**k**,**n** and **5**/**6** are only barely soluble. They are stable in air for a few minutes in the solid state, while their solutions are moisture-sensitive. They are chemically inert toward alkenes, alkynes, nitriles, CO, and CO_2. In sharp contrast, zirconacyclopentanes without a carborane unit are reactive and can undergo ring-contraction in the presence of phosphine ligands to give alkene–zirconocene complexes, ligand exchange with alkynes to afford the

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corresponding zirconacyclopentenes and zirconacyclopentadienes, and insertion reaction with CO, cyanides, azides, or diazomethanes.[14]

Complexes **3**−**6** were fully characterized by various spectroscopic techniques and elemental analyses. Two distinct cage carbons were found at ∼92 and ∼90 ppm, respectively, in the ^{13}C NMR spectra. The unique Cp carbons at ∼115 and ∼116 ppm and protons at 5 to 6 ppm as two singlets were also observed. For complexes **3a**−**n**, the protons on the zirconacyclopentane rings were observed as an AMX pattern in the range 2 to 4 ppm in their ^1H NMR spectra. For **3o**, two triplets at 0.82 and 2.76 ppm corresponding to the α- and β-H, respectively, were observed, which compares to those of 0.91 ppm (α-H) and 1.70 ppm (β-H) in $Cp_2Zr(1,4\text{-}C_4H_8)$,[15] 0.39/1.34 ppm ($\alpha$-H) and 1.83/1.95 ppm ($\beta$-H) in *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]$Zr(1,4\text{-}C_4H_8)$,[15] 1.25 ppm (α-H) and 3.25 ppm (β-H) in $Cp_2Zr[CH_2CH_2(1,2\text{-}C_6H_4)]$,[16] and 0.81/1.39 ppm (α-H) and 2.11/2.27 ppm (β-H) in $Cp_2Zr[1,4\text{-}CH_2CH_2CH_2CH(2\text{-}C_5H_4N)]$.[17] On the other hand, the two α-H and one β-H were observed at −0.43/0.16, 2.12/2.41, and 3.03/3.12 ppm, respectively, in the ^1H NMR spectrum of **4q**/**4r**, which are very similar to that of 0.25, 2.15, and 3.50 ppm in $Cp_2Zr[CH_2CH(Me)(1,2\text{-}C_6H_4)]$.[16] The characteristic α- and β-carbons of zirconacyclopentane rings were observed at about 40 and 60 ppm in their ^{13}C NMR spectra, respectively. The ^{11}B NMR spectra of **3**−**6** exhibited different patterns spanning the range 0 to −12 ppm.

Structure. Molecular structures of **3a**,**e**,**l**,**m**,**n**,**o**, **4q**, and **4r** were further confirmed by single-crystal X-ray analyses, and their representative structures are shown in Figures 1−6,

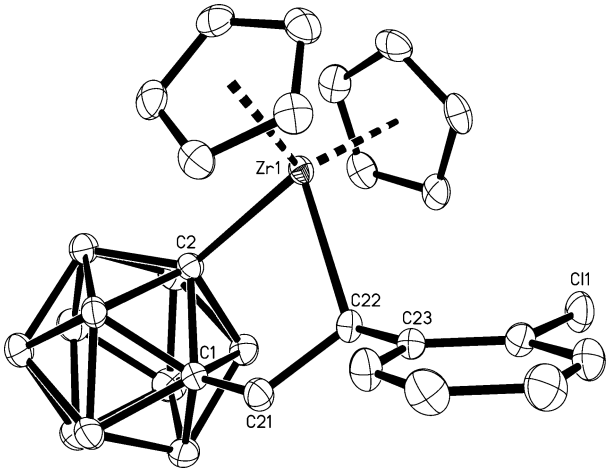

Figure 1. Molecular structure of 1,2-$[Cp_2ZrCH(2\text{-}Cl\text{-}C_6H_4)CH_2]$-1,2-$C_2B_{10}H_{10}$ (**3e**).

respectively. Selected bond distances and angles are summarized in Table 2. Except for **3n** (Figure 4), in which an additional coordination bond between the Zr and P atoms with a Zr−P distance of 2.670(1) Å is observed, all other complexes adopt a distorted-tetrahedral coordination environment. As shown in Table 2, the Zr−C(1) distance of 2.502(4) Å in **3n** is much longer than those (2.389(3)−2.434(2) Å) observed in its analogues, whereas the C(3)−C(4) distance of 1.323(6) Å in **3n** is significantly shorter than the corresponding values (1.493(8)−1.552(3) Å) found in its analogues. Such differences should result from the additional coordination of the P to the Zr atom. The C(3)−C(4) and C(2)−C(3) distances of ca. 1.51 Å clearly suggest their single-bond characters. The C(1)−C(2) distance of ca. 1.69 Å is a typical value found in *o*-carboranes.[18] The Zr−C(1) distances (2.389(3)−2.502(4) Å) are very close to the corresponding values observed in zirconocene−carboranyl complexes.[19] The Zr−C(4) distances fall in the range 2.268(8)−2.401(2) Å, which are comparable to the corresponding values of 2.289(4)/2.307(4) Å in *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]$Zr(C_4H_8)$,[15] 2.302(2)/2.307(2) Å in $(\eta^5\text{-menthyl-}C_5H_4)_2Zr(C_4H_8)$,[20] and 2.275 (2)/2.286(2) Å in $Cp_2Zr[1,4\text{-}(2,3\text{-}C_3H_6)C_4H_8]$.[21] On the other hand, the sum of five interior angles on the five-membered zirconacyclopentane ring falls in the range 527.6−529.4° (Table 2), suggestive of a nonplanar geometry, which is different from those of zirconacyclopentenes incorporating a carboranyl unit.[9]

■ CONCLUSION

We have developed an efficient and practical method for the preparation of a new class of zirconacyclopentanes incorporating a carboranyl unit from the reaction of zirconocene−carboryne precursor **1** with terminal alkenes. High regioselectivity is observed for different alkenes depending upon the polarity of the C═C double bond. In general, aryl substituents go to the α position (**3** in Scheme 1), whereas the alkyl substituents prefer the β position (**4** in Scheme 1). These carborane-functionalized zirconacycles are very thermally stable and chemically inert, which is significantly different from those without a carboranyl moiety.[12] However, after transmetalation to nickel, they become useful intermediates for the synthesis of functional carboranes, as evidenced by our preliminary results.[11]

■ EXPERIMENTAL SECTION

General Procedures. All 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.[9a] ^1H NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 300 MHz or a Bruker DPX 400 spectrometer at 400 MHz. $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Bruker DPX 400 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 were reported in δ units with references 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. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences, China. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**1**) was prepared according to the reported procedure.[8a] Complexes **3a** and **4q** were communicated earlier.[11] Other chemicals were purchased from either Sigma-Aldrich or Acros Chemical Co. and used as received unless otherwise specified.

Preparation of 1,2-$[Cp_2ZrCH(4\text{-}Me\text{-}C_6H_4)CH_2]$-1,2-$C_2B_{10}H_{10}$ (3b). To a toluene solution (20 mL) of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})$-$Li(OEt_2)_2$ (**1**; 554 mg, 1.0 mmol) was added 4-methylstyrene (**2b**; 236 mg, 2.0 mmol), and the reaction mixture was heated to reflux for 48 h. After removal of the precipitate (LiCl) by filtration, the clear solution was concentrated to about 5 mL, from which **3b** was isolated as red crystals after the solution stood at room temperature overnight (359 mg, 75%). ^1H NMR (400 MHz, benzene-d_6): δ 6.83 (d, J = 7.2 Hz,

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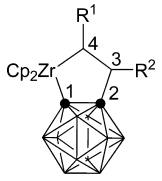
Table 2. Selected Bond Lengths (Å) and Angles (deg)



compd	3a	3e[b]	3l	3m	3n	3o	4q[b]	4r
av Zr−Cent[a]	2.216	2.212	2.209	2.228	2.220	2.212	2.222	2.217
av Zr−C (C_5 ring)	2.516(2)	2.513(3)	2.503(5)	2.524(2)	2.501(5)	2.506(3)	2.498(10)	2.513(3)
Zr−C(1)	2.434(2)	2.398(3)	2.399(4)	2.406(2)	2.502(4)	2.401(2)	2.391(7)	2.389(3)
Zr−C(4)	2.352(2)	2.375(3)	2.367(5)	2.308(2)	2.357(4)	2.401(2)	2.268(8)	2.294(3)
C(1)−C(2)	1.700(3)	1.690(5)	1.683(6)	1.691(3)	1.687(5)	1.689(3)	1.679(10)	1.700(3)
C(2)−C(3)	1.520(3)	1.523(5)	1.531(7)	1.534(3)	1.521(6)	1.534(4)	1.539(11)	1.546(3)
C(3)−C(4)	1.520(3)	1.547(5)	1.532(7)	1.552(3)	1.323(6)	1.541(4)	1.493(8)	1.540(4)
Cent−Zr−Cent	128.0	128.2	128.7	128.4	127.4	128.4	130.0	130.3
C(1)−Zr−C(4)	74.2(1)	78.8(1)	77.3(2)	78.3(1)	69.2(1)	77.7(1)	76.8(3)	76.4(1)
Zr−C(1)−C(2)	111.2(1)	108.3(2)	109.4(3)	108.4(1)	112.6(2)	109.3(1)	111.0(4)	110.5(1)
C(3)−C(4)−Zr	117.4(2)	109.5(3)	111.6(3)	111.8(1)	130.0(3)	113.8(2)	119.3(6)	115.6(2)
C(1)−C(2)−C(3)	114.7(2)	115.7(3)	115.3(4)	114.9(2)	112.9(3)	114.6(2)	114.1(6)	113.8(2)
C(2)−C(3)−C(4)	112.7(2)	115.7(3)	114.0(4)	114.5(2)	115.0(4)	114.0(2)	115.5(7)	111.7(2)

[a]Cent = the centroid of Cp ring. [b]Average values of two independent molecules in the unit cell.

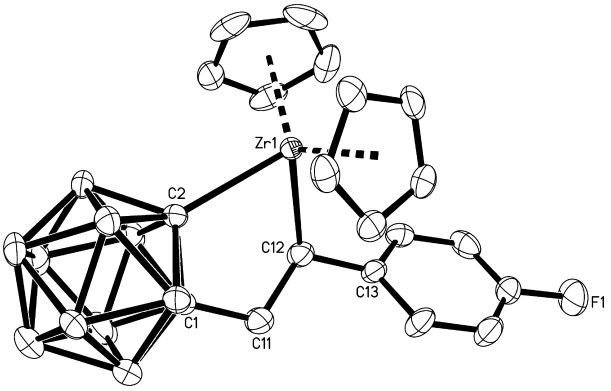


Figure 2. Molecular structure of 1,2-[$Cp_2ZrCH(4\text{-}F\text{-}C_6H_4)CH_2$]-1,2-$C_2B_{10}H_{10}$ (**3l**).

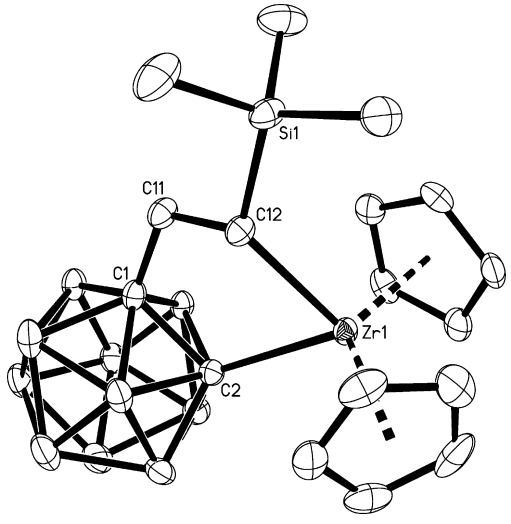


Figure 3. Molecular structure of 1,2-[$Cp_2ZrCH(TMS)CH_2$]-1,2-$C_2B_{10}H_{10}$ (**3m**).

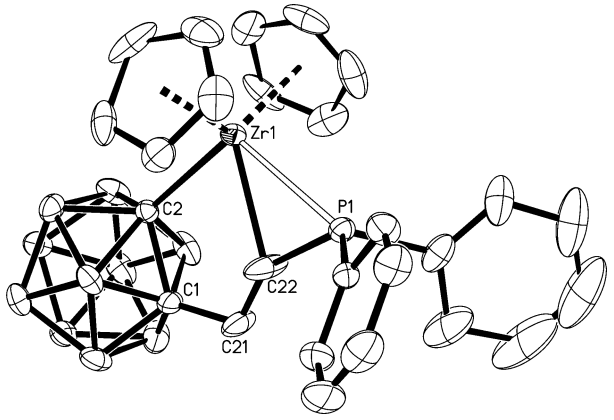


Figure 4. Molecular structure of 1,2-[$Cp_2ZrCH(PPh_2)CH_2$]-1,2-$C_2B_{10}H_{10}$ (**3n**).

2H), 5.82 (d, J = 7.2 Hz, 2H) (aromatic H), 5.78 (s, 5H), 5.01 (s, 5H) (C_5H_5), 3.32 (m, 1H, CH), 3.15 (m, 1H, CHH), 2.95 (dd, J = 6.0, 13.6 Hz, 1H, CHH), 2.10 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 138.2, 132.2, 132.0, 119.1 (aromatic C), 115.3, 114.1 (C_5H_5), 94.3, 90.4 (cage C), 66.5 (CH), 41.9 (CH_2), 20.6 (CH_3).

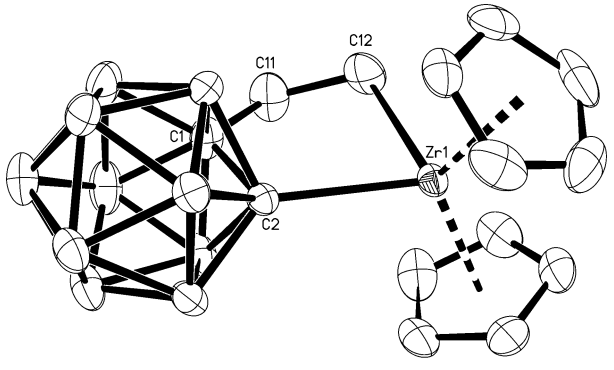


Figure 5. Molecular structure of 1,2-[$Cp_2ZrCH_2CH_2$]-1,2-$C_2B_{10}H_{10}$ (**3o**).

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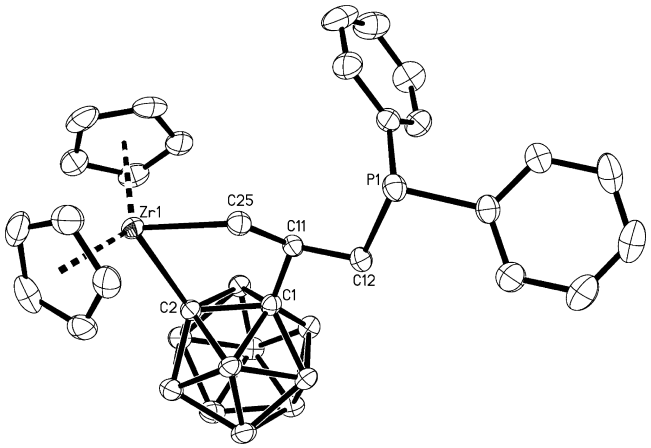

Figure 6. Molecular structure of 1,2-[$Cp_2ZrCH_2CH(CH_2PPh_2)$]-1,2-$C_2B_{10}H_{10}$ (**4r**).

$^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ 0.66 (1B), −4.0 (1B), −5.6 (5B), −8.7 (3B). IR (KBr, cm^{-1}): ν 2567 (BH). Anal. Calcd for $C_{21}H_{30}B_{10}Zr$ (**3b**): C, 52.35; H, 6.28. Found: C, 52.53; H, 6.44.

Preparation of 1,2-[Cp_2ZrCH(4-MeO-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3c). This complex was prepared as a purple solid from **1** (554 mg, 1.0 mmol) and 4-methoxystyrene (**2c**; 270 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 387 mg (78%). ^1H NMR (400 MHz, pyridine-d_5): δ 7.09 (d, J = 8.4 Hz, 2H, aromatic *H*), 6.54 (m, 7H, aromatic *H* and C_5H_5), 5.64 (s, 5H, C_5H_5), 3.71 (s, 3H, OCH_3), 3.55 (m, 2H, C*H* and CH*H*), 3.09 (dd, J = 5.6, 13.2 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 156.2, 131.8, 119.8, 116.8, 112.2 (aromatic *C*), 114.9, 113.8 (C_5H_5), 95.3, 91.1 (cage *C*), 66.0 (*C*H), 54.7 (OCH_3), 41.3 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ −1.2 (1B), −5.3 (1B), −6.2 (2B), −7.2 (2B), −9.9 (4B). IR (KBr, cm^{-1}): ν 2562 (BH). Anal. Calcd for $C_{21}H_{30}B_{10}OZr$ (**3c**): C, 50.67; H, 6.07. Found: C, 50.39; H, 6.01.

Preparation of 1,2-[Cp_2ZrCH(4-^{t}BuO-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3d). This complex was prepared as red crystals from **1** (554 mg, 1.0 mmol) and 4-*tert*-butoxystyrene (**2d**; 352 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 362 mg (67%). ^1H NMR (400 MHz, benzene-d_6): δ 6.80 (d, J = 8.4 Hz, 2H, aromatic *H*), 5.73 (m, 7H, aromatic *H* and C_5H_5), 4.99 (s, 5H, C_5H_5), 3.28 (dd, J = 6.4, 12.0 Hz, 1H, C*H*), 3.07 (m, 1H, CH*H*), 2.93 (dd, J = 6.4, 14.0 Hz, 1H, C*H*H), 1.24 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 150.8, 134.9, 128.3, 126.0, 124.6, 118.9 (aromatic *C*), 114.3, 113.1 (C_5H_5), 93.0, 89.1 (cage *C*), 77.2 ($OC(CH_3)_3$), 64.8 (*C*H), 41.1 (CH_2), 27.9 ($OC(CH_3)_3$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ 0.2 (1B), −4.2 (2B), −5.0 (1B), −6.2 (2B), −9.3 (4B). IR (KBr, cm^{-1}): ν 2571 (BH). Anal. Calcd for $C_{24}H_{36}B_{10}OZr$ (**3d**): C, 53.39; H, 6.72. Found: C, 53.51; H, 6.65.

Preparation of 1,2-[Cp_2ZrCH(2-Cl-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3e). This complex was prepared as purple crystals from **1** (554 mg, 1.0 mmol) and 2-chlorostyrene (**2e**; 277 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 378 mg (75%). ^1H NMR (400 MHz, benzene-d_6): δ 7.05 (d, J = 8.0 Hz, 1H), 6.95 (m, 2H), 6.54 (m, 1H) (aromatic *H*), 5.99 (s, 5H), 5.53 (s, 5H) (C_5H_5), 3.83 (m, 1H, *C*H), 3.02 (dd, J = 9.4, 15.0 Hz, 1H, CH*H*), 2.84 (dd, J = 7.6, 15.0 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 149.2, 129.9, 129.1, 127.3, 126.0, 123.2 (aromatic *C*), 117.6, 116.7 (C_5H_5), 88.8, 84.5 (cage *C*), 58.0 (*C*H), 44.4 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ 0.45 (1B), −5.4 (2B), −6.4 (3B), −7.8 (2B), −9.6 (2B). IR (KBr, cm^{-1}): ν 2566 (BH). Anal. Calcd for $C_{21.75}H_{29}B_{10}ClZr$ (**3e** + 0.25 toluene): C, 49.74; H, 5.57. Found: C, 49.85; H, 5.64.

Preparation of 1,2-[Cp_2ZrCH(3-Cl-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3f). This complex was prepared as purple crystals from **1** (554 mg, 1.0 mmol) and 3-chlorostyrene (**2f**; 277 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 440 mg (84%). ^1H NMR (400 MHz, benzene-d_6): δ 6.71 (m, 2H), 5.95 (s, 1H), 5.86 (d, J = 7.6 Hz, 1H) (aromatic *H*), 5.78 (s, 5H), 5.12 (s, 5H) (C_5H_5), 3.42 (dd, J = 6.0, 12.2 Hz, 1H, C*H*), 3.01 (m, 1H, CH*H*), 2.74 (dd, J = 6.0 and 14.2 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 145.8, 136.7, 131.9, 121.9, 120.0, 118.3 (aromatic *C*), 116.1, 115.1 (C_5H_5), 92.2, 87.9 (cage *C*), 63.6 (*C*H), 41.8 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ −0.3 (1B), −5.0 (3B), −7.0 (3B), −10.2 (3B). IR (KBr, cm^{-1}): ν 2568 (BH). Anal. Calcd for $C_{20}H_{27}B_{10}ClZr$ (**3f**): C, 47.83; H, 5.42. Found: C, 48.07; H, 5.68.

Preparation of 1,2-[Cp_2ZrCH(4-Cl-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3g). This complex was prepared as purple crystals from **1** (554 mg, 1.0 mmol) and 4-chlorostyrene (**2g**; 277 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 430 mg (86%). ^1H NMR (400 MHz, benzene-d_6): δ 6.99 (d, J = 8.4 Hz, 2H), 5.78 (d, J = 8.4 Hz, 2H) (aromatic *H*), 5.74 (s, 5H), 5.16 (s, 5H) (C_5H_5), 3.58 (dd, J = 6.4, 12.8 Hz, 1H, C*H*), 3.01 (m, 1H, CH*H*), 2.72 (dd, J = 6.4, 14.4 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 142.9, 129.8, 127.4, 123.4 (aromatic *C*), 116.6, 115.5 (C_5H_5), 91.2, 86.6 (cage *C*), 62.6 (*C*H), 42.4 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ 0.27 (1B), −5.0 (2B), −6.6 (3B), −10.3 (4B). IR (KBr, cm^{-1}): ν 2574 (BH). Anal. Calcd for $C_{20}H_{27}B_{10}ClZr$ (**3g**): C, 47.83; H, 5.42. Found: C, 48.23; H, 5.11.

Preparation of 1,2-[Cp_2ZrCH(3-CF_3-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3i). This complex was prepared as a pale white solid from **1** (554 mg, 1.0 mmol) and 3-trifluoromethylstyrene (**2i**; 344 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 490 mg (91%). ^1H NMR (400 MHz, benzene-d_6): δ 6.89 (m, 2H), 6.25 (s, 1H), 6.24(d, J = 8.8 Hz, 1H) (aromatic *H*), 5.79 (s, 5H), 5.16 (s, 5H) (C_5H_5), 3.67 (dd, J = 6.0, 12.6 Hz, 1H, C*H*), 3.13 (m, 1H, CH*H*), 2.73 (dd, J = 6.0, 14.2 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 146.0, 130.4, 129.3, 126.1, 118.2 (aromatic *C*), 116.8, 115.9 (C_5H_5), 90.8, 86.0 (cage *C*), 61.9 (*C*H), 42.2 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ 0.7 (1B), −2.0 (1B), −4.8 (2B), −6.4 (3B), −8.7 (1B), −10.1 (2B). IR (KBr, cm^{-1}): ν 2566 (BH). Anal. Calcd for $C_{24.5}H_{31}B_{10}F_3Zr$ (**3i** + 0.5 toluene): C, 50.58; H, 5.37. Found: C, 50.52; H, 5.43.

Preparation of 1,2-[Cp_2ZrCH(4-CF_3-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3j). This complex was prepared as a pale white solid from **1** (554 mg, 1.0 mmol) and 4-trifluoromethylstyrene (**2j**; 344 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 391 mg (73%). ^1H NMR (400 MHz, benzene-d_6): δ 7.26 (d, J = 8.0 Hz, 2H), 5.93 (d, J = 8.0 Hz, 2H) (aromatic *H*), 5.75 (s, 5H), 5.15 (s, 5H) (C_5H_5), 3.76 (dd, J = 5.6, 12.4 Hz, 1H, C*H*), 3.11 (m, 1H, CH*H*), 2.71 (dd, J = 5.6, 14.0 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 149.3, 129.3, 126.4, 122.3 (aromatic *C*), 116.9, 116.0 (C_5H_5), 90.6, 85.8 (cage *C*), 62.2 (*C*H), 42.1 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ 0.6 (1B), −4.7 (3B), −6.4 (3B), −8.8 (1B), −10.1 (2B). IR (KBr, cm^{-1}): ν 2573 (BH). Anal. Calcd for $C_{21}H_{27}B_{10}F_3Zr$ (**3j**): C, 47.08; H, 5.08. Found: C, 46.72; H, 4.94.

Preparation of 1,2-[Cp_2ZrCH(4-Br-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3k). This complex was prepared as purple crystals from **1** (554 mg, 1.0 mmol) and 4-bromostyrene (**2k**; 366 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 364 mg (82%). ^1H NMR (400 MHz, pyridine-d_5): δ 7.47 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H) (aromatic *H*), 6.71 (s, 5H), 6.00 (s, 5H) (C_5H_5), 4.10 (dd, J = 6.0, 12.6 Hz, 1H, C*H*), 3.68 (m, 1H, CH*H*), 2.96 (dd, J = 6.0, 14.2 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 143.1, 132.4, 123.6, 114.4 (aromatic *C*), 116.8, 115.9 (C_5H_5), 91.6, 86.9 (cage *C*), 62.2 (*C*H), 41.7 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ −0.6 (2B), −2.5 (1B), −5.5 (4B), −9.2 (3B). IR (KBr, cm^{-1}): ν 2571 (BH). Anal. Calcd for $C_{20}H_{27}B_{10}BrZr$ (**3k**): C, 43.94; H, 4.98. Found: C, 44.20; H, 5.10.

Preparation of 1,2-[Cp_2ZrCH(4-F-C_6H_4)CH_2]-1,2-$C_2B_{10}H_{10}$ (3l). This complex was prepared as purple crystals from **1** (554 mg, 1.0 mmol) and 4-fluorostyrene (**2l**; 244 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 393 mg (81%). ^1H NMR (400 MHz, benzene-d_6): δ 6.69 (t, J = 8.4 Hz, 2H), 5.81 (dd, J = 5.2, 8.4 Hz, 2H) (aromatic *H*), 5.75 (s, 5H), 5.17 (s, 5H) (C_5H_5), 3.60 (dd, J = 6.4, 12.6 Hz, 1H, C*H*), 3.04 (m, 1H, CH*H*), 2.76 (dd, J = 6.4, 14.2 Hz, 1H, C*H*H). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 140.3, 123.5 (J = 6.8 Hz), 116.4, 115.5 (aromatic *C*), 116.5, 115.5 (C_5H_5), 86.7 (cage *C*), 62.5 (*C*H), 42.8 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ 0.4

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(1B), −5.0 (3B), −6.4 (3B), −9.1 (1B), −10.3 (2B). IR (KBr, cm^{-1}): ν 2569 (BH). Anal. Calcd for $C_{20}H_{27}B_{10}FZr$ (**3l**): C, 49.45; H, 5.60. Found: C, 49.73; H, 5.56.

Preparation of 1,2-[$Cp_2ZrCH(TMS)CH_2$]-1,2-$C_2B_{10}H_{10}$ (3m). This complex was prepared as light brown crystals from **1** (554 mg, 1.0 mmol) and TMSCH═CH_2 (**2m**; 200 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 364 mg (78%). ^{1}H NMR (300 MHz, benzene-d_6): δ 5.83 (s, 5H), 5.81 (s, 5H) (C_5H_5), 3.30 (dd, J = 5.1, 13.2 Hz, 1H, C*H*), 3.00 (m, 1H, CH*H*), 2.62 (dd, J = 5.1, 14.7 Hz, 1H, C*H*H), −0.36 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 116.0, 115.3 (C_5H_5), 89.7, 88.4 (cage *C*), 64.7 (CH), 42.9 (CH_2), 0.28 (TMS). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ −0.0 (1B), −5.6 (4B), −7.8 (2B), −9.6 (1B), −11.4 (2B). IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{17}H_{32}B_{10}SiZr$ (**3m**): C, 44.02; H, 6.95. Found: C, 43.82; H, 6.85.

Preparation of 1,2-[$Cp_2ZrCH(PPh_2)CH_2$]-1,2-$C_2B_{10}H_{10}$ (3n). This complex was prepared as black crystals from **1** (554 mg, 1.0 mmol) and diphenylvinylphosphine (**2n**; 424 mg, 2.0 mmol) using the same procedures reported for **3b**: yield 405 mg (59%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.92 (m, 4H), 7.40 (m, 6H) (aromatic *H*), 6.03 (s, 5H), 5.82 (s, 5H) (C_5H_5), 3.90 (m, 1H, C*H*), 2.64 (m, 1H, CH*H*), 2.18 (m, 1H, C*H*H). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 137.1 (d, J = 7.7 Hz), 133.3 (d, J = 10.0 Hz), 131.7 (d, J = 13.1 Hz), 130.3 (d, J = 22.5 Hz), 129.2 (d, J = 9.2 Hz), 129.1 (d, J = 9.5 Hz) (aromatic *C*), 107.9, 107.4 (C_5H_5), 101.0 (d, J = 9.9 Hz), 95.2 (d, J = 23.0 Hz) (cage *C*), 41.7 (CH_2), 23.3 (d, J = 34.8 Hz, *C*H). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ −1.7 (1B), −5.8 (4B), −7.3 (2B), −9.4 (2B), −11.3 (1B). IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{26}H_{33}B_{10}PZr$ (**3n**): C, 54.23; H, 5.78. Found: C, 53.87; H, 5.92.

Preparation of 1,2-[$Cp_2ZrCH_2CH_2$]-1,2-$C_2B_{10}H_{10}$ (3o). This complex was prepared as light brown crystals from **1** (554 mg, 1.0 mmol) and excess ethylene (1 atom) (**2o**) using the same procedures reported for **3b**, but the reaction mixture was stirred for 3 d at room temperature: yield 176 mg (45%). ^{1}H NMR (400 MHz, benzene-d_6): δ 5.72 (s, 10H, C_5H_5), 2.76 (t, J = 7.2 Hz, 2H, CH_2), 0.82 (t, J = 7.2 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 115.5 (C_5H_5), 90.2, 88.1 (cage *C*), 44.6, 41.1 (CH_2). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ 0.4 (1B), −5.6 (4B), −7.2 (1B), −8.8 (4B). IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{14}H_{24}B_{10}Zr$ (**3o**): C, 42.93; H, 6.18. Found: C, 42.86; H, 6.17.

Preparation of 1,2-[$Cp_2ZrCH_2CH(CH_2PPh_2)$]-1,2-$C_2B_{10}H_{10}$ (4r). This complex was prepared as colorless crystals from **1** (554 mg, 1.0 mmol) and allyldiphenylphosphine (**2r**; 271 mg, 1.2 mmol) using the same procedures reported for **3b**: yield 350 mg (59%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.61 (m, 2H), 7.40 (m, 2H), 7.15 (m, 3H), 7.07 (m, 3H) (aromatic *H*), 5.76 (s, 5H), 5.60 (s, 5H) (C_5H_5), 3.10 (m, 1H, C*H*), 2.76 (m, 1H, C*H*HP), 2.38 (t, J = 12.8 Hz, 1H, CH*H*), 2.07 (m, 1H, CH*H*P), 0.16 (m, 1H, C*H*H). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 140.8 (d, J = 13.3 Hz), 138.3 (d, J = 16.2 Hz), 134.4 (d, J = 20.5 Hz), 132.0 (d, J = 17.0 Hz), 129.8, 129.0 (d, J = 7.4 Hz), 128.7 (d, J = 5.3 Hz), 128.2 (aromatic *C*), 115.7, 115.4 (C_5H_5), 93.5 (d, J = 8.2 Hz), 90.8 (cage *C*), 56.1 (d, J = 7.1 Hz, CH_2), 47.9 (d, J = 14.7 Hz, CH_2P), 43.1 (d, J = 10.3 Hz, *C*H). ^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ −0.1 (1B), −5.5 (3B), −7.9 (3B), −11.9 (3B). IR (KBr, cm^{-1}): ν 2560 (BH). Anal. Calcd for $C_{27}H_{35}B_{10}PZr$ (**4r**): C, 54.89; H, 5.98. Found: C, 54.80; H, 6.37.

Preparation of 1,2-[$Cp_2ZrC(Ph)$═$C(CH_2CH$═$CH_2)$]-1,2-$C_2B_{10}H_{10}$ (5) and 1,2-[$Cp_2ZrCH_2CH(CH_2C$≡$CPh)$]-1,2-$C_2B_{10}H_{10}$ (6). Complexes **5** and **6** were prepared as a yellow solid mixture (65/35) from **1** (554 mg, 1.00 mmol) and PhC≡CCH_2CH═CH_2 (170 mg, 1.20 mmol) using the same procedures reported for **3b**: yield 415 mg (82%). They were inseparable by recrystallization. The molar ratio of **5**/**6** was determined by GC-MS analyses after hydrolysis. ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.38 (m), 7.31 (m), 7.10 (t, J = 7.5 Hz), 6.97 (d, J = 7.5 Hz) (aromatic *H*), 6.61 (s, C_5H_5), 5.95 (m), 5.80 (m), 5.21 (m), 4.96 (m) (C═*C*H), 3.17 (d, J = 3.4 Hz, CH_2), 2.85 (d, J = 6.0 Hz, CH_2). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 196.9, 143.7, 139.2, 135.7, 128.7, 128.4, 128.2, 128.0,127.9, 126.1, 124.1 (aromatic *C*), 117.0, 114.6 (C_5H_5), 91.3, 87.9 (cage *C*), 65.1, 61.1(CH), 41.7, 38.1, 34.9, 14.8 (CH_2). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ −0.9 (1B), −3.3 (1B), −5.0 (1B), −7.4 (2B), −9.7 (2B), −11.0 (2B), −13.4 (1B). IR (KBr, cm^{-1}): ν 2557 (BH). Anal. Calcd for $C_{23}H_{30}B_{10}Zr$ (**5**/**6**): C, 54.62; H, 5.98. Found: C, 54.62; H, 5.97.

Preparation of 1-[PhCH═C(CH_2CH═CH_2)]-1,2-$C_2B_{10}H_{11}$ (7) and 1-[$CH_3CH(CH_2C$≡$CPh)$]-1,2-$C_2B_{10}H_{11}$ (8). A solution of the above mixture (**5** + **6**) obtained from the reaction of **1** (277 mg, 1.00 mmol) with PhC≡CCH_2CH═CH_2 (85 mg, 1.20 mmol) was treated with 1 M HCl aqueous solution (10 mL). The organic layer was separated, and the aqueous solution was extracted twice with diethyl ether (10 mL × 2). The organic phases were combined, washed with saturated brine aqueous solution (20 mL), and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was subjected to flash column chromatography on silica gel using hexane as eluent to give **7** as a white solid (79 mg, 55%) and **8** as a colorless oil (35 mg, 24%). For **7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 3H), 7.27 (m, 2H) (aromatic *H*), 7.04 (s, 1H, C═*C*HPh), 5.89 (m, 1H, C*H*═CH_2), 5.24 (dd, J = 1.3 and 10.3 Hz, 1H, CH═CH*H*), 5.16 (dd, J = 1.3 and 17.2 Hz, 1H, CH═C*H*H), 3.92 (brs, 1H, cage *H*), 3.11 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 136.4, 135.2, 135.0, 131.2, 128.5, 128.3, 117.9 (aromatic and olefinic *C*), 79.1, 59.2 (cage *C*), 35.3 (CH_2). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −4.0 (1B), −5.4 (1B), −10.4 (2B), −11.6 (2B), −12.9 (2B), −14.4 (2B). HRMS: m/z calcd for $C_{13}H_{22}B_8{}^{10}B_2{}^+$ (**7**) 286.2719, found 286.2713. For **8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.31 (m, 3H) (aromatic *H*), 3.94 (brs, 1H, cage *H*), 2.75 (dd, J = 5.2 and 16.4 Hz, 1H, CH*H*), 2.66 (m, 1H, C*H*), 2.52 (dd, J = 7.2 and 16.4 Hz, 1H, C*H*H), 1.33 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 131.5, 128.4, 128.3, 122.8 (aromatic *C*), 85.8, 83.8 (*C*≡*C*), 79.3, 60.0 (cage *C*), 38.8 (*C*H), 27.1 (CH_2), 20.3 (CH_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ −4.0 (1B), −5.8 (1B), −10.4 (2B), −12.5 (2B), −14.4 (4B). HRMS: m/z calcd for $C_{13}H_{22}B_8{}^{10}B_2{}^+$ (**8**) 286.2719, found 286.2712.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under nitrogen in thin-walled glass capillaries. 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.[22] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.[23] Structures of **3e** and **3n** showed one-quarter and one toluene of solvation, respectively. All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data and summary of data collection and refinement as well as crystallographic data in CIF format for **3a**, **3e**, **3l**, **3m**, **3n**, **3o**, **4q**, and **4r**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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