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Reaction Scope and Mechanism of Sterically Induced Ruthenium-Mediated Intramolecular Coupling of *o*-Carboranyl with Cyclopentadienyl. Synthesis and Structure of Ruthenium Complexes Incorporating Doubly Linked Cyclopentadienyl−Carboranyl Ligands

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Reactions of [Me(R^1)A(C$_5$H$_3$R^2)(C$_2$B$_{10}$H$_{10}$)]Li$_2$ (A = C, Si; R^1 = H, Me; R^2 = H, Me) with 1 equiv of RuCl$_2$(PPh$_3$)$_3$ in THF afforded the corresponding doubly linked cyclopentadienyl−carboranyl ruthenium(II) hydride complexes [η^5-Me$_2$C(C$_5$H$_3$)(C$_2$B$_{10}$H$_{10}$)]RuH(PPh$_3$)$_2$ (**6**), [η^5-MeHC(C$_5$H$_3$)(C$_2$B$_{10}$H$_{10}$)]RuH(PPh$_3$)$_2$ (**7**), [η^5-Me$_2$C(5-Me-C$_5$H$_2$)(C$_2$B$_{10}$H$_{10}$)]RuH(PPh$_3$)$_2$ (**8**), [η^5-Me$_2$C(3/4-Me-C$_5$H$_2$)(C$_2$B$_{10}$H$_{10}$)]RuH(PPh$_3$)$_2$ (**9a**/**9b**), and [η^5-Me$_2$Si(C$_5$H$_3$)(C$_2$B$_{10}$H$_{10}$)]RuH(PPh$_3$)$_2$ (**10**) in 72−85% isolated yields. On the other hand, interaction of [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$ with 1 equiv of RuCl$_2$[PPh$_2$(OEt)]$_3$ produced only [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru[PPh$_2$(OEt)]$_2$ (**14**). An equimolar reaction of [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$ with RuCl$_2$(PPh$_3$)$_3$ in the presence of dppe (dppe = 1,2-bis(diphenylphosphino)ethane) generated [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru(dppe) (**15**). No ruthenium hydride complexes were detected in the latter two cases. Treatment of [η^5-Me$_2$C(C$_5$H$_3$)(C$_2$B$_{10}$H$_{10}$)]RuH(PPh$_3$)$_2$ (**6**) with excess HBF$_4$·OEt$_2$ in toluene gave the neutral ligand Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$) (**12**). This work showed that such intramolecular coupling reactions were driven by steric factors. A possible reaction mechanism was proposed to account for these ruthenium-mediated coupling reactions. All new complexes were fully characterized by multinuclear NMR techniques and elemental analyses. Molecular structures of **6**, **7**, and **8** were further confirmed by single-crystal X-ray analyses.

Introduction

Ligands are an essential part of organometallic compounds. They impose a dominant control over both the chemical and the physical properties of the resulting metal complexes.[1] By taking the unique property of the carborane unit and the advantage of cyclic π ligands, a series of single-atom-bridged cyclopentadienyl−, indenyl−, and fluorenyl−carboranyl ligands, A(C$_5$H$_5$)(C$_2$B$_{10}$H$_{11}$) (A = Me$_2$C,[2] Me$_2$Si[3]), A′(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (A′ = Me$_2$C,[4] Me$_2$Si,[5] ^{i}Pr$_2$NB,[6] ^{i}Pr$_2$NP[7]), and A″(C$_{13}$H$_9$)(C$_2$B$_{10}$H$_{11}$) (A″ = H$_2$C,[8] Me$_2$Si[9]), have been developed. These ligands are finding many applications in organometallic chemistry.[1−10] Experimental results show that the bridging atom significantly influences the chemical and physical properties of the resulting organometallic complexes.[10] In this connection, we are interested in a doubly linked ligand system incorporating both carboranyl and cyclic π ligands.

A general method for the preparation of doubly bridged biscyclopentadienes is the reaction of [Me$_2$A(C$_5$H$_4$)$_2$]Li$_2$ with Me$_2$SiCl$_2$.[11] This methodology is, however, not applicable to the proposed system. For example, treatment of [Me$_2$A(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]M$_2$ (A = C, Si; M = Li, Na, K) with 1 equiv of Me$_2$SiCl$_2$ under various reaction conditions afforded a mixture of inseparable products. On the other hand, attempts to prepare [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru(PPh$_3$)$_2$ from the reaction of [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$ with RuCl$_2$(PPh$_3$)$_3$ under various conditions failed; instead, an unprecedented ruthenium hydride

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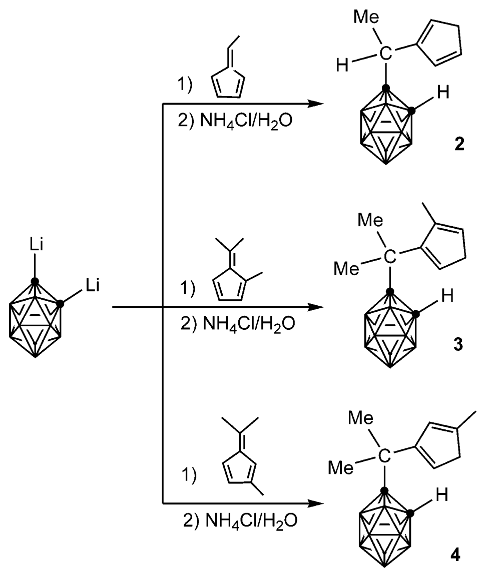
Scheme 1



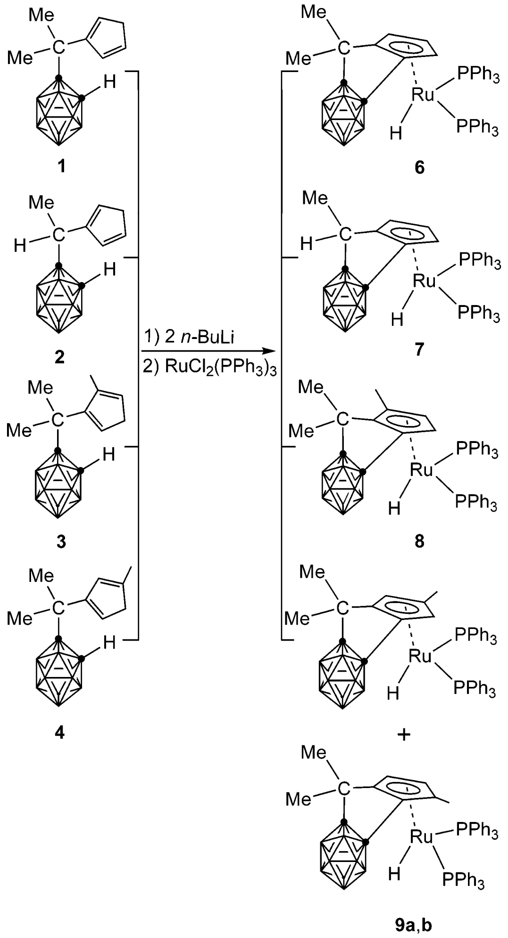
complex, [η^5-$Me_2C(C_5H_3)(C_2B_{10}H_{10})$]$RuH(PPh_3)_2$, containing the doubly linked ligand [$Me_2C(C_5H_3)(C_2B_{10}H_{10})$]$^-$ was isolated in 80% yield.[12] This result indicates that such an intramolecular coupling reaction is very efficient. An independent work was published soon after our communication,[13] in which the ruthenium complex [η^5-$(C_5H_4)(MeC_2B_{10}H_{10})$]$RuH(PPh_3)_2$ bearing a [$(C_5H_4)(MeC_2B_{10}H_{10})$]$^-$ ligand was prepared in 74% yield from the reaction of $CpRuCl(PPh_3)_2$ with $LiMeC_2B_{10}H_{10}$ in toluene. A metal-assisted nucleophilic attack on the Cp ring was proposed as a reaction pathway. These results prompted us to investigate the reaction scope and possible mechanism of ruthenium-mediated intramolecular coupling reaction of an *o*-carboranyl with a cyclopentadienyl. We report here a full account of our study on this subject.

Results and Discussion

Ligands. To study the reaction scope of the coupling reactions, several new carbon-bridged cyclopentadienyl−carboranyl ligands, $MeHC(C_5H_5)(C_2B_{10}H_{11})$ (**2**), $Me_2C(2\text{-}Me\text{-}C_5H_4)(C_2B_{10}H_{11})$ (**3**), and $Me_2C(3\text{-}Me\text{-}C_5H_4)(C_2B_{10}H_{11})$ (**4**), were synthesized from the reaction of $Li_2C_2B_{10}H_{10}$ with 1.1 equiv of 6-methylfulvene, 2,6,6-trimethylfulvene, or 3,6,6-trimethylfulvene in toluene/ether (2:1), followed by hydrolysis with a saturated NH_4Cl aqueous solution. They were isolated as a pale yellow solid in 80−90% yields (Scheme 1).

The ^1H NMR spectra showed that **2**−**4** are all mixtures of different isomers, with the linkage being bonded to either a sp^2- or sp^3-C of the five-membered ring. Several multiplets in the range 5.92−6.61 ppm attributable to the vinyl protons of cyclopentadiene, a broad singlet at about 3.4 ppm assignable to the cage CH proton, and several multiplets at about 3.0 ppm corresponding to the sp^3-CH_2 and sp^3-CH protons of the cyclopentadiene were observed. In addition, the linkage and methyl substituent on the Cp ring were also found in the ^1H NMR spectra of **2**−**4**. Their $^{13}C\{^1H\}$ NMR spectra were consistent with the ^1H NMR data. The $^{11}B\{^1H\}$ NMR spectrum of **2** displayed a 1:1:2:1:2:3 pattern, whereas those of **3** and **4** exhibited a 1:1:2:2:4 pattern. Compounds **2**−**4** were further characterized by high-resolution mass spectrometry.

Scheme 2



[η^5-$Me(R^1)A(C_5H_2R^2)(C_2B_{10}H_{10})$]$Ru(H)(PPh_3)_2$. The above carbon-bridged cyclopentadienyl−carboranyl ligands were easily converted into the corresponding dilithium salts [$Me(R^1)C(C_5H_3R^2)(C_2B_{10}H_{10})$]$Li_2$ by reaction with 2 equiv of *n*-BuLi. Treatment of these salts with 1 equiv of $RuCl_2(PPh_3)_3$ at room temperature in THF afforded, respectively, the ruthenium(II) hydride complexes [η^5-$Me_2C(C_5H_3)(C_2B_{10}H_{10})$]$RuH(PPh_3)_2$ (**6**),[12] [η^5-$MeHC(C_5H_3)(C_2B_{10}H_{10})$]$RuH(PPh_3)_2$ (**7**), [η^5-$Me_2C(5\text{-}Me\text{-}C_5H_2)(C_2B_{10}H_{10})$]$RuH(PPh_3)_2$ (**8**), and [η^5-$Me_2C(3/4\text{-}Me\text{-}C_5H_2)(C_2B_{10}H_{10})$]$RuH(PPh_3)_2$ (**9a**/**b**) as yellow crystals in 63−80% isolated yields (Scheme 2). A Me_2Si-linked analogue, [η^5-$Me_2Si(C_5H_3)(C_2B_{10}H_{10})$]$RuH(PPh_3)_2$ (**10**), was also prepared as yellow crystals in 67% isolated yield by the reaction of [$Me_2Si(C_5H_4)(C_2B_{10}H_{10})$]$Li_2$ with 1 equiv of $RuCl_2(PPh_3)_3$ in THF. Surprisingly, a few red crystals identified as the dinitrogen complex [$\{\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}Ru(PPh_3)$]$_2$($\mu$-$N_2$) (**11**) by single-crystal X-ray analyses (vide infra) were obtained from the mother liquor of the above reaction. Its spectroscopic data were not obtainable due to insufficient amount of materials (Scheme 3). It is noted that **9a** and **9b** were isolated as a 1:1 mixture, as shown by the ^1H NMR, which were inseparable by recrystallization. On the other hand, reaction of [$Me_2A(C_9H_6)(C_2B_{10}H_{10})$]$Li_2$ (A = C, Si) with 1 equiv of $RuCl_2(PPh_3)_3$ generated a mixture of inseparable products that did not contain any ruthenium hydride species, as indicated by the absence of the unique Ru-*H* resonance in the ^1H NMR spectra.

Complexes **6**−**10** are very soluble in polar organic solvents such as THF, CH_2Cl_2, $CHCl_3$, and toluene and barely soluble in hot *n*-hexane. They are stable for a few minutes in dry air in the solid state, but decompose in moist air.

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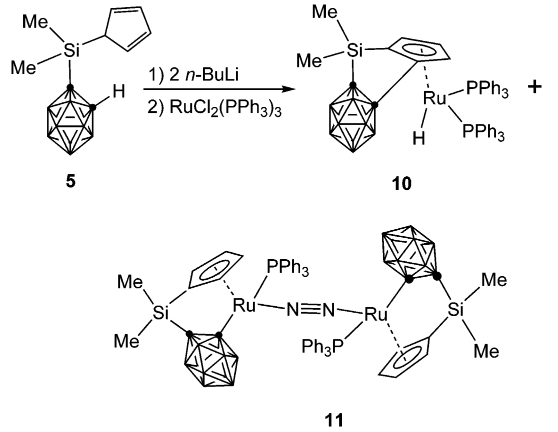
Scheme 3



The ${}^1H$ NMR spectra of **6**−**10** showed a unique doublet of doublets at about −10 ppm with ${}^2J_{HP} \approx 30$ and 40 Hz assignable to the Ru-*H* proton, several multiplets of aromatic protons in the range 7.65−6.81 ppm, and two singlets of Me_2C or Me_2Si methyl protons (or a doublet of MeHC methyl protons in **7**). In addition, the CH and CMe protons of the five-membered ring were also observed in the ${}^1H$ NMR spectra. The ${}^{11}B\{{}^1H\}$ NMR spectra exhibited a 1:2:1:1 pattern for **6**−**10**. Two singlets at about 70 and 65 ppm were found in the ${}^{31}P\{{}^1H\}$ NMR spectra of **6**−**10**, indicating the presence of planar chirality in all those ruthenium hydride complexes. Their solid-state IR spectra all displayed a characteristic terminal B-H absorption at around 2550 cm^{-1} and the frequency of a Ru-H stretch at around 1970 cm^{-1}.[14] The composition of **6**−**10** was confirmed by elemental analyses. The presence of **9a**,**b** isomers was supported by the existence of two sets of NMR data (except for ${}^{11}B\{{}^1H\}$ NMR), in particular, two doublets of doublets of two Ru-*H* protons and two singlets and two doublets of the Cp protons corresponding to **9a** and **9b**, respectively, observed in the ${}^1H$ NMR spectrum and four singlets found in the ${}^{31}P\{{}^1H\}$ NMR. It is noted that, except for the Cp protons, a full assignment of the resonances to **9a**,**b** is not possible. The ratio of **9a**,**b** did not change as shown by the ${}^1H$ NMR even after heating the NMR solution at 80 °C for 4 h.

The molecular structures of **6**−**8** were further confirmed by single-crystal X-ray analyses. Figures 1 and 2 show the representative structures of **7** and **8**, respectively. Selected bond distances and angles are listed in Table 1 for comparison. They have similar solid-state structures in which the Ru(II) ion is η^5-bound to a cyclopentadienyl ring and σ-bound to a hydrogen atom and coordinated to two phosphorus atoms in a three-legged piano stool geometry. The Ru−Cent distances of 1.910 Å in **6**, 1.916 Å in **7**, and 1.922 Å in **8** are close to that of 1.907 Å in $[\eta^5\text{-}C_5D_4\text{-}(MeC_2B_{10}H_{10})]RuD(PPh_3)_2$,[13] but are longer than that of 1.889 Å in $CpRuH(PPh_3)_2$,[15] 1.847 Å in $CpRuCl(PPh_3)_2$,[16] and 1.848 Å in $CpRuBr(PPh_3)_2$.[17] The P(1)−Ru−P(2) angle of 96.0(1)° in **6**, 97.6(1)° in **7**, and 97.2(1)° in **8** are almost the same as that of 97.4(1)° in $[\eta^5\text{-}C_5D_4\text{-}(MeC_2B_{10}H_{10})]RuD(PPh_3)_2$,[13] but are significantly smaller than that of 101.4(1)° in $CpRuH(PPh_3)_2$,[15] 104.0(1)° in $CpRuCl(PPh_3)_2$,[16] and 103.2(1)° in $CpRuBr(PPh_3)_2$,[17] indicating the steric effect of the carboranyl moiety. The Ru−P distances in **6**−**8** are very similar to those observed in $CpRuX(PPh_3)_2$ (X = Cl, Br, H).[15−17] The Ru−H distances of 1.54(1) Å in **6**, 1.53(5) Å in **7**, and 1.54(3) Å in **8** are within the range reported for other Ru−H complexes, for example, 1.55(3) Å in $(C_5H_4CH_2CH_2NMe_2)RuH(PPh_3)_2$,[14a] 1.52(4) Å in $[(\eta^6\text{-cot})Ru((-)\text{-Me-DuPHOS})(H)][BF_4]$ (cot = 1,3,5-cyclooctatriene, (−)-Me-DuPHOS = (−)-1,2-bis((2*R*,5*R*)-2,5-dimethylphospholanyl)benzene),[14d] and 1.51(4) Å in $CpRuH(PPh_3)_2$.[15] The C(2)−C(15) distances of 1.490(2) Å in **6**, 1.495(6) Å in **7**, and 1.486(4) Å in **8** are very close to the corresponding values found in directly linked cyclopentadienyl−carboranes, for example, 1.492(2) Å in $[\eta^5\text{-}C_5D_4\text{-}(MeC_2B_{10}H_{10})]RuD(PPh_3)_2$,[13] 1.491(5) Å in $1\text{-}(4\text{-}C_7H_7)\text{-}12\text{-}[C_5H_3\text{-}3,4\text{-}(CH_3)_2]\text{-}C_2B_{10}H_{10}$,[18] and 1.489(2) Å in 2-(*o*-carboranyl)indene.[19] The newly formed five-membered rings (C(2)C(1)C(11)C(14)C(15))

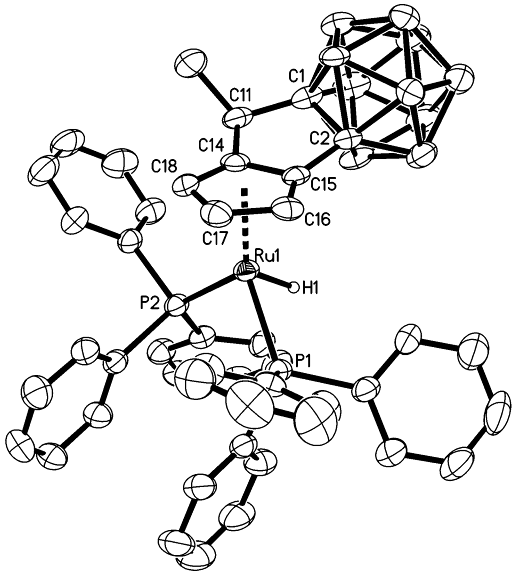


Figure 1. Molecular structure of $[\eta^5\text{-}MeHC(C_5H_3)(C_2B_{10}H_{10})]RuH(PPh_3)_2$ (**7**).

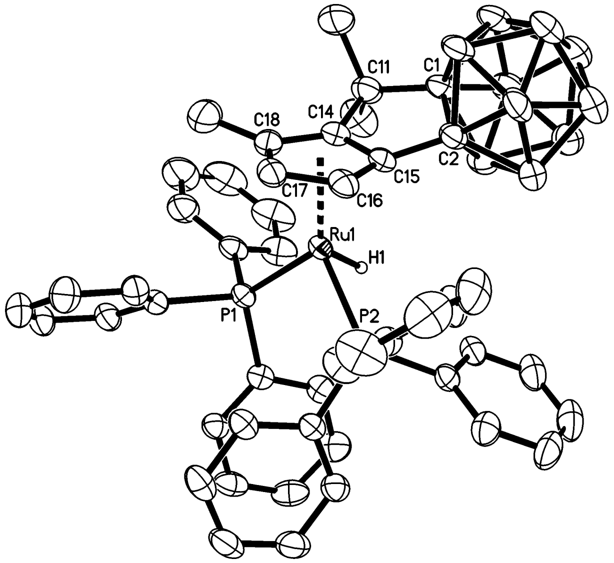


Figure 2. Molecular structure of $[\eta^5\text{-}Me_2C(5\text{-}Me\text{-}C_5H_2)(C_2B_{10}H_{10})]RuH(PPh_3)_2$ (**8**).

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 6, 7, and 8[a]

	6·0.5THF[b]	**7**	**8**
Ru−H	1.54(1)	1.53(5)	1.54(3)
av Ru−C_{ring}	2.263(2) [2.266(2)]	2.262(5)	2.269(3)
Ru−Cent	1.910	1.916	1.922
Ru−P(1)	2.291(1) [2.289(1)]	2.279(1)	2.280(1)
Ru−P(2)	2.282(1) [2.283(1)]	2.261(1)	2.280(1)
C(1)−C(2)	1.671(2) [1.674(2)]	1.679(6)	1.652(4)
C(2)−C(15)	1.490(2) [1.482(2)]	1.495(6)	1.486(4)
C(15)−C(14)	1.442(2) [1.422(2)]	1.412(6)	1.416(4)
C(14)−C(11)	1.516(2) [1.539(2)]	1.527(6)	1.534(4)
C(11)−C(1)	1.571(2) [1.569(2)]	1.543(6)	1.560(4)
P(1)−Ru−P(2)	96.0(1) [96.5(1)]	97.6(1)	97.2(1)
C(1)−C(11)−C(14)	101.1(1) [101.0(1)]	102.7(3)	101.6(2)
C(15)−C(2)−C(1)	102.5(1) [102.5(1)]	103.0(3)	103.0(2)
C(2)−C(1)−C(11)	109.1(1) [108.7(1)]	107.6(4)	108.7(2)

[a] Cent: the centroid of the five-membered ring. [b] Distances and angles in brackets are those of a second molecule.

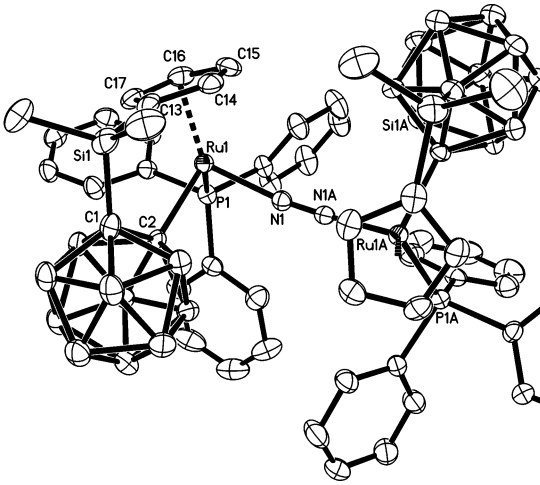
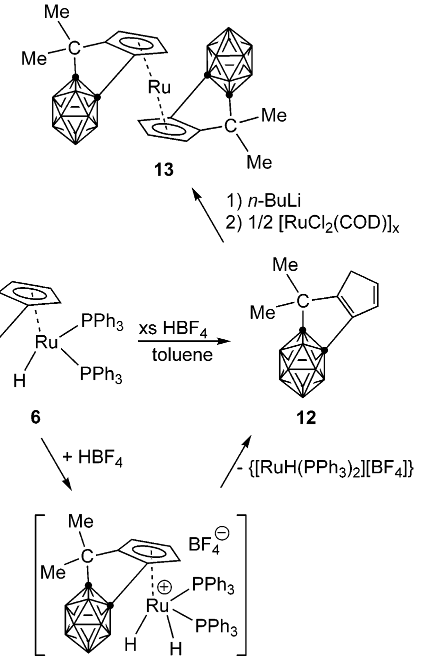


Figure 3. Molecular structure of $[\{\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{Ru}(\text{PPh}_3)]_2(\mu\text{-N}_2)$ (**11**). Selected distances [Å] and angles [deg]: Ru1−C2 = 2.165(6), Ru1−C13 = 2.224(7), Ru1−C14 = 2.241(7), Ru1−C15 = 2.253(7), Ru1−C16 = 2.205(7), Ru1−C17 = 2.173(7), Ru1−P1 = 2.331(2), Ru1−Cent = 1.860, Ru1−N1 = 2.014(5), N1−N1A = 1.099(10), C13−Si1−C1 = 103.2(3), Ru1−N1−N1A = 167.2(2).

in **6**−**8** are almost coplanar. The B−B, B−C, and C−C distances of the cage are very comparable to those observed in other carboranyl complexes.[10]

Scheme 4



A single-crystal X-ray diffraction study revealed that **11** is a centrosymmetrical dinuclear complex in which the two $[\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Ru}(\text{PPh}_3)$ moieties are connected by a dinitrogen molecule, as shown in Figure 3. The crystallographic center of symmetry lies at the midpoint of the N≡N bond, and each ruthenium atom adopts the typical three-legged piano stool geometry. The bridging N−N distance of 1.099(10) Å and the Ru−N distance of 2.014(5) Å can be compared to the corresponding values found in other ruthenium dinitrogen complexes, for example, 1.110(3) and 1.955(2) Å in [*mer,trans*-RuCl_2-(NN′N)$]_2(\mu\text{-N}_2)$ (NN′N = 2,6-bis[(dimethylamino)methyl]-pyridine),[20a] 1.134(6) and 2.038(4) Å in $[\text{RuH(PCP)}]_2(\mu\text{-N}_2)$ (PCP = $[2,6\text{-}(\text{CH}_2\text{PBu}^t{}_2)_2\text{C}_6\text{H}_3]^-$),[20b] and 1.119(4) and 1.965(4) Å in $[(\text{PNP})\text{RuCl}_2]_2(\mu\text{-N}_2)$ (PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine).[20c] The dinitrogen molecule in **11** just serves as a bridging donor, and its triple bond character remains unchanged. The Ru−C(cage) and Ru−C (ring) distances are very close to those observed in $[\eta^5:\sigma\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Ru}(\text{L}_2)$ (L = Lewis bases) complexes.[21]

Doubly Linked Compound $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})$. Complexes **6**−**10** contain doubly linked cyclopentadienyl−carboranyl ligands. We wondered whether the free ligands could be released from these ruthenium complexes. In general, the Cp−Ru π bonds are very strong and rather inert, which remain intact in catalysis.[22] There is no method to effectively break the Cp−Ru π bonds. We attempted to reduce the Ru(II) to Ru(0) using group 1 metals in the hope of releasing the free ligands. This reduction was unfortunately coupled with cage-opening, leading to a mixture of products. To our surprise, a free ligand was isolated during the protonation of **6**. Treatment of **6** with excess $\text{HBF}_4\cdot\text{OEt}_2$ in toluene at −78 °C gave, after quenching with a saturated NaHCO_3 aqueous solution, a doubly linked compound, $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})$ (**12**), as a white solid in 65% isolated yield (Scheme 4).

The mechanism of this process is not clear. But the ^{1}H NMR experiments in C_6D_6 suggested the presence of a cationic ruthenium dihydride intermediate, as deduced from the observation of a triplet at −6.50 ppm ($^2J_{\text{HP}}$ = 23.4 Hz) assignable to the RuH_2 protons and three multiplets at 6.76, 4.36, and 3.33 ppm corresponding to the Cp protons in the ^{1}H NMR spectrum and only one singlet at 59.3 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. These characteristic NMR data are very similar to those

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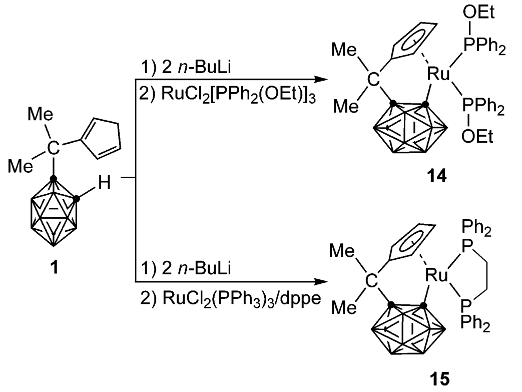
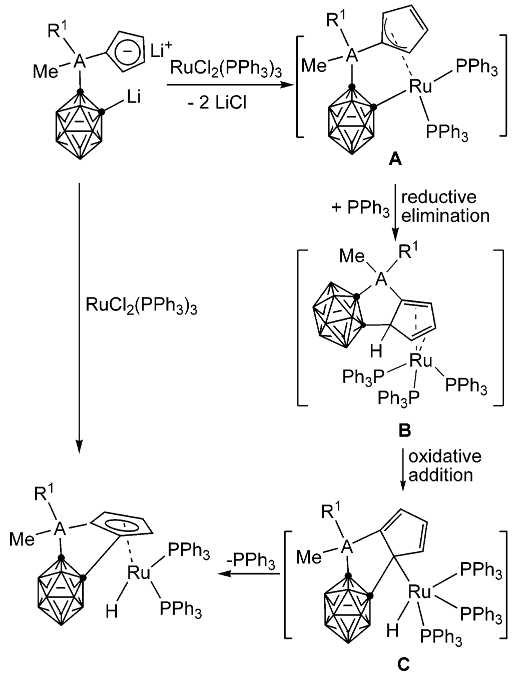
Scheme 5



Scheme 6



A = C, Si; R^1 = H, Me

observed in $[(Cp\text{-}NH)RuH_2(PPh_3)_2][PF_6]_2$ (Cp-NH = $C_5H_4CH_2CH_2NHMe_2$),[14a] $[Cp^*RuH_2(dppm)][BF_4]$ (dppm = bis(diphenylphosphino)methane),[14b] and $[CpRuH_2(PPh_3)_2][BF_4]$.[14c] Hence, it is proposed that $[\{\eta^5\text{-}Me_2C(C_5H_3)(C_2B_{10}H_{10})\}RuH_2(PPh_3)_2][BF_4]$ might serve as an intermediate, followed by reductive elimination to generate **12**, as shown in Scheme 4.

The ^1H NMR spectrum of **12** showed two multiplets of the vinyl protons at 6.04 and 5.91 ppm, one multiplet of $sp^3\text{-}CH_2$ protons of the cyclopentadiene at 3.30 ppm, and one singlet of the two methyl protons at 1.53 ppm. Its $^{13}C\{^1H\}$ NMR spectrum was consistent with the ^1H NMR data. The $^{11}B\{^1H\}$ NMR spectrum exhibited a 1:1:2:2:4 pattern. Its composition was further confirmed by high-resolution mass spectrometry. Compound **12** was conveniently converted into the monolithium salt by reacting with 1 equiv of *n*-BuLi in THF. Interaction of this salt with 0.5 equiv of $[RuCl_2(COD)]_x$ in THF afforded, after workup, the ruthenocene $[\eta^5\text{-}Me_2C(C_5H_3)(C_2B_{10}H_{10})]_2Ru$ (**13**) in 42% isolated yield. It was fully characterized spectroscopically.

Mechanism. The above results clearly show that the coupling reaction of the cyclopentadienyl with an *o*-carboranyl proceeds efficiently to form a new C(cage)−C(ring) bond as long as there is no substituent on one of the α-carbon atoms of the Cp ring. The unprecedented isolation of **11** indicates the importance of the steric factors. If the coupling reactions were induced by the steric forces, phosphines with smaller cone angles would disfavor the coupling reactions. In fact, reaction of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$ with 1 equiv of $RuCl_2[PPh_2(OEt)]_3$ (cone angles are 133° for $PPh_2(OEt)$ and 145° for PPh_3)[23] in THF gave the salt metathesis product $[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[PPh_2(OEt)]_2$ (**14**) in 55% isolated yield (Scheme 5). In the presence of dppe, the complex $[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(dppe)$ (**15**) was isolated in 62% yield from the reaction of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$ with 1 equiv of $RuCl_2(PPh_3)_3$ (Scheme 5). No ruthenium hydride complex was isolated from the above two reactions. These results further support the argument of a sterically induced coupling reaction.[24] The presence of PPh_3 in the reaction system is essential for such a coupling reaction.

Therefore, a possible reaction pathway for the formation of **6**−**10** is proposed and shown in Scheme 6. Reaction of $[Me(R^1)A(C_5H_4)(C_2B_{10}H_{10})]Li_2$ with $RuCl_2(PPh_3)_3$ gives the first intermediate, **A**. Coordination of PPh_3 induces reductive elimination, leading to the formation of the intermediate **B** with a new C(cage)−C(ring) bond. Oxidative addition produces the species **C**, followed by the dissociation of PPh_3 and haptotropic shift from η^1 to η^5 to yield the final product. This proposed mechanism can also explain why no ruthenium hydride complexes were detected from the reaction of $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]Li_2$ (A = C, Si) with $RuCl_2(PPh_3)_3$. For indenyl, the rearrangement of the double bonds within the C_5 ring can destroy the aromaticity, which is energically highly unfavorable.

Conclusion

This work shows that intramolecular couplings of a cyclopentadienyl with an *o*-carboranyl unit are driven by steric factors. Both carboranyl and phosphines with large cone angles are crucial components for such coupling reactions. Sterically less demanding phosphines such as $PPh_2(OEt)$ and dppe lead to the formation of $[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]RuL_2$ (L_2 = $[PPh_2(OEt)]_2$, dppe), rather than ruthenium hydride complexes.

The doubly linked cyclopentadienyl−carboranyl compound can be prepared by treatment of the corresponding ruthenium hydride complexes with excess $HBF_4{\cdot}OEt_2$, followed by hydrolysis. These ligands are not accessible by any other known methods.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. THF, toluene, diethyl ether, and *n*-hexane were freshly distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 was freshly distilled from CaH_2 and P_2O_5, respectively, immediately prior to use. 6-Methylfulvene,[25] 2,6,6-trimethylfulvene,[26] 3,6,6-trimethylfulvene,[27] $Me_2C(C_5H_5)(C_2B_{10}H_{11})$,[2b] $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$,[3c] $RuCl_2(PPh_3)_3$,[28] $RuCl_2[P(OEt)Ph_2]_3$,[29] and [RuCl2-

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(COD)]$_x$[30] were prepared according to literature methods. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 and 162 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3 \cdot OEt_2$ (0.0 ppm) for boron chemical shifts, and to external 85% H_3PO_4 (0.0 ppm) for phosphorus chemical shifts. Mass spectra were obtained on a ThermoFinnigan MAT 95 XL mass spectrometer. Elemental analyses were performed by either MEDAC Ltd. U.K. or Shanghai Institute of Organic Chemistry, CAS, China. Melting points were determined on an Electrothermal digital melting point apparatus M-IA9100 and were uncorrected.

Preparation of $MeHC(C_5H_5)(C_2B_{10}H_{11})$ (2). To a solution of *o*-$C_2B_{10}H_{12}$ (1.00 g, 6.90 mmol) in a dry toluene/diethyl ether (2:1, 15 mL) mixture was added dropwise a 1.60 M solution of *n*-BuLi in *n*-hexane (8.70 mL, 13.90 mmol) at −78 °C with stirring, and the mixture was warmed to room temperature and stirred for 3 h. The resulting solution ($Li_2C_2B_{10}H_{10}$) was then cooled to 0 °C, and a solution of 6-methylfulvene (0.70 g, 7.60 mmol) in a toluene/diethyl ether (2:1, 15 mL) mixture was slowly added. The reaction mixture was stirred at 80 °C overnight, quenched with 20 mL of a saturated NH_4Cl aqueous solution at 0 °C, transferred to a separatory funnel, and then diluted with 30 mL of diethyl ether. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined ether solutions were dried over anhydrous Na_2SO_4 and concentrated to give a crude yellow solid, which was purified by column chromatography (SiO_2, hexane) to yield **2** as a pale yellow solid (1.47 g, 90%). ^{1}H NMR ($CDCl_3$): δ 6.51−6.19 (m, 3H, vinyl *H*), 3.57 (m, 1H, C*H*CH$_3$), 3.39 (br s, 1H, C*H* of cage), 3.02 (m, 2H, sp^3-C*H*$_2$ in C_5H_5), 1.41 (d, $^3J = 7.2$ Hz, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.6, 135.4, 131.8, 130.8 (*C*$_5$H$_4$), 79.2 (cage *C*), 60.8 (sp^3-*C* in C_5H_5), 41.2 (*C*HCH$_3$), 20.7 (CH*C*H$_3$). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −3.1 (1B), −5.1 (1B), −9.2 (2B), −11.1 (1B), −11.9 (2B), −13.7 (3B). IR (KBr, cm^{-1}): ν 2574 (vs) (B-H). HRMS: *m*/*z* calcd for $C_9H_{20}{}^{11}B_8{}^{10}B_2{}^+$ 236.2563, found 236.2563.

Preparation of $Me_2C(2\text{-}Me\text{-}C_5H_4)(C_2B_{10}H_{11})$ (3). This compound was prepared as a pale yellow solid from *o*-$C_2B_{10}H_{12}$ (1.00 g, 6.90 mmol), *n*-BuLi in *n*-hexane (1.60 M, 8.70 mL, 13.90 mmol), and 2,6,6-trimethylfulvene (0.91 g, 7.60 mmol) in a toluene/diethyl ether (2:1) mixture using the identical procedures reported for **2**: yield 1.55 g (80%). ^{1}H NMR ($CDCl_3$): δ 6.61−6.42 (m, 2H, vinyl *H*), 3.44 (br s, 1H, C*H* of cage), 3.03 (m, 2H, sp^3-C*H*$_2$ in C_5H_4), 2.15 (s, 3H, C*H*$_3$−C$_5$H$_4$), 1.61 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 135.1, 134.6, 130.5, 129.9 (*C*$_5$H$_4$), 86.0 (cage *C*), 63.7 (sp^3-*C* in C_5H_4), 46.1 (*C*H$_3$−C$_5$H$_4$), 42.5 (*C*(CH$_3$)$_2$), 32.7 (C(*C*H$_3$)$_2$). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −4.1 (2B), −9.2 (2B), −11.7 (2B), −13.9 (4B). IR (KBr, cm^{-1}): ν 2587 (vs) (B-H). HRMS: *m*/*z* calcd for $C_{11}H_{24}{}^{11}B_8{}^{10}B_2{}^+$ 264.2876, found 264.2870.

Preparation of $Me_2C(3\text{-}Me\text{-}C_5H_4)(C_2B_{10}H_{11})$ (4). This compound was prepared as a pale yellow solid from *o*-$C_2B_{10}H_{12}$ (1.00 g, 6.90 mmol), *n*-BuLi in *n*-hexane (1.60 M, 8.70 mL, 13.90 mmol), and 3,6,6-trimethylfulvene (0.91 g, 7.60 mmol) in a toluene/diethyl ether (2:1) mixture using the identical procedures reported for **2**: yield 1.53 g (79%). ^{1}H NMR ($CDCl_3$): δ 6.11−5.98 (m, 2H, vinyl *H*), 3.44 (br s, 1H, C*H* of cage), 2.89 (m, 2H, sp^3-C*H*$_2$ in C_5H_4), 2.05 (s, 3H, C*H*$_3$−C$_5$H$_4$), 1.50 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.4, 146.9, 127.2, 126.9 (*C*$_5$H$_4$), 84.7 (cage *C*), 64.0 (sp^3-*C* in C_5H_4), 44.5 (*C*H$_3$−C$_5$H$_4$), 41.2 (*C*(CH$_3$)$_2$), 30.9 (C(*C*H$_3$)$_2$). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −4.1 (2B), −9.2 (2B), −11.7 (2B), −13.9 (4B). IR (KBr, cm^{-1}): ν 2588 (vs) (B-H). HRMS: *m*/*z* calcd for $C_{11}H_{24}{}^{11}B_8{}^{10}B_2{}^+$ 264.2876, found 264.2872.

Preparation of $[\eta^5\text{-}Me_2C(C_5H_3)(C_2B_{10}H_{10})]RuH(PPh_3)_2 \cdot 0.5THF$ (6·0.5THF). A 1.60 M solution of *n*-BuLi in *n*-hexane (1.25 mL, 2.00 mmol) was slowly added to a THF solution (15 mL) of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.25 g, 1.00 mmol) at −78 °C with stirring. The mixture was warmed to room temperature and stirred for 3 h. The powder of $RuCl_2(PPh_3)_3$ (0.96 g, 1.00 mmol) was added to the resulting solution, and the mixture was stirred at room temperature for 24 h. After removal of the solvent and addition of CH_2Cl_2 (20 mL), the precipitate was filtered off, and the solvent was removed under vacuum. The resulting red solid was recrystallized from a THF solution to give **6**·0.5THF as yellow crystals (0.73 g, 80%), mp 156−157 °C. ^{1}H NMR (C_6D_6): δ 7.60−6.81 (m, 30H, aryl *H*), 4.83 (m, 1H, C$_5$*H*$_3$), 3.71 (m, 1H, C$_5$*H*$_3$), 3.65 (m, 1H, C$_5$*H*$_3$), 3.55 (m, 2H, THF), 1.42 (m, 2H, THF), 1.14 (s, 3H, C(C*H*$_3$)$_2$), 0.92 (s, 3H, C(C*H*$_3$)$_2$), −10.14 (dd, $^2J_{HP} = 39.3$ and 31.5 Hz, 1H, Ru-*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 140.6 (d, $^1J_{CP} = 40.0$ Hz, aryl *C*), 140.0 (d, $^1J_{CP} = 40.0$ Hz, aryl *C*), 134.4 (d, $^2J_{CP} = 10.8$ Hz, aryl *C*), 134.2 (d, $^2J_{CP} = 10.8$ Hz, aryl *C*), 128.5 (d, $^3J_{CP} = 6.5$ Hz, aryl *C*), 127.4 (d, $^4J_{CP} = 3.6$ Hz, aryl *C*), 127.3 (d, $^4J_{CP} = 3.6$ Hz, aryl *C*), 98.9, 89.9, 82.8, 82.1, 75.8 (*C*$_5$H$_3$), 67.8 (THF), 42.2 (*C*(CH$_3$)$_2$), 36.2 (C(*C*H$_3$)$_2$), 30.0 (C(*C*H$_3$)$_2$), 25.8 (THF), cage carbons were not observed. ^{31}P{^{1}H} NMR (C_6D_6): δ 71.9, 65.2. ^{11}B{^{1}H} NMR (C_6D_6): δ −5.4 (2B), −7.7 (4B), −10.1 (2B), −14.1 (2B). IR (KBr, cm^{-1}): ν 2568 (vs) (B-H), 1970 (s) (Ru-H). Anal. Calcd for $C_{46}H_{50}B_{10}P_2Ru$ (**6**): C, 63.21; H, 5.77. Found: C, 63.00; H, 5.80.

Preparation of $[\eta^5\text{-}MeHC(C_5H_3)(C_2B_{10}H_{10})]RuH(PPh_3)_2$ (7). This complex was prepared as yellow crystals from $MeHC(C_5H_5)(C_2B_{10}H_{11})$ (0.24 g, 1.00 mmol), *n*-BuLi in *n*-hexane (1.60 M, 1.25 mL, 2.00 mmol), and $RuCl_2(PPh_3)_3$ (0.96 g, 1.00 mmol) in THF using the identical procedures reported for **6**: yield 0.67 g (78%), mp 145−146 °C. ^{1}H NMR (C_6D_6): δ 7.53−6.89 (m, 30H, aryl *H*), 4.29 (m, 1H, C$_5$*H*$_3$), 4.18 (m, 1H, C$_5$*H*$_3$), 3.78 (m, 1H, C$_5$*H*$_3$), 2.10 (m, 1H, C*H*CH$_3$), 0.63 (d, $^3J = 6.9$ Hz, 3H, CHC*H*$_3$), −10.43 (dd, $^2J_{HP} = 35.7$ Hz, 1H, Ru-*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 140.3 (d, $^1J_{CP} = 40.0$ Hz, aryl *C*), 139.5 (d, $^1J_{CP} = 40.0$ Hz, aryl *C*), 134.1 (d, $^2J_{CP} = 11.0$ Hz, aryl *C*), 133.9 (d, $^2J_{CP} = 11.0$ Hz, aryl *C*), 127.5 (d, $^3J_{CP} = 6.0$ Hz, aryl *C*), 127.3 (d, $^3J_{CP} = 6.0$ Hz, aryl *C*), 110.3 (d, $^4J_{CP} = 3.6$ Hz, aryl *C*), 108.6 (d, $^4J_{CP} = 3.6$ Hz, aryl *C*), 94.9, 83.1, 82.9, 82.3, 77.8 (*C*$_5$H$_3$), 38.6 (*C*HCH$_3$), 19.2 (CH*C*H$_3$), cage carbons were not observed. ^{31}P{^{1}H} NMR (C_6D_6): δ 69.6, 64.6. ^{11}B{^{1}H} NMR (C_6D_6): δ −4.3 (2B), −5.4 (4B), −8.5 (2B), −11.7 (2B). IR (KBr, cm^{-1}): ν 2584 (vs) (B-H), 1944 (s) (Ru-H). Anal. Calcd for $C_{45}H_{48}B_{10}P_2Ru$: C, 62.85; H, 5.63. Found: C, 63.13; H, 5.68.

Preparation of $[\eta^5\text{-}Me_2C(5\text{-}Me\text{-}C_5H_2)(C_2B_{10}H_{10})]RuH(PPh_3)_2$ (8). This complex was prepared as yellow crystals from $Me_2C(2\text{-}Me\text{-}C_5H_4)(C_2B_{10}H_{11})$ (0.26 g, 1.00 mmol), *n*-BuLi in *n*-hexane (1.60 M, 1.25 mL, 2.00 mmol), and $RuCl_2(PPh_3)_3$ (0.96 g, 1.00 mmol) in THF using the identical procedures reported for **6**: yield 0.56 g (63%), mp 168−170 °C. ^{1}H NMR (C_6D_6): δ 7.65−6.85 (m, 30H, aryl *H*), 4.85 (d, $^3J = 2.1$ Hz, 1H, C$_5$*H*$_2$), 3.45 (d, $^3J = 2.1$ Hz, 1H, C$_5$*H*$_2$), 2.11 (s, 3H, C*H*$_3$−C$_5$H$_2$), 1.18 (s, 3H, C(C*H*$_3$)$_2$), 0.97 (s, 3H, C(C*H*$_3$)$_2$), −10.04 (dd, $^2J_{HP} = 42.3$ and 29.1 Hz, 1H, Ru-*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 140.7 (d, $^1J_{CP} = 40.0$ Hz, aryl *C*), 138.7 (d, $^1J_{CP} = 40.0$ Hz, aryl *C*), 134.9 (d, $^2J_{CP} = 10.8$ Hz, aryl *C*), 134.5 (d, $^2J_{CP} = 10.8$ Hz, aryl *C*), 127.4 (d, $^3J_{CP} = 6.5$ Hz, aryl *C*), 127.2 (d, $^4J_{CP} = 3.6$ Hz, aryl *C*), 93.5, 82.6, 82.1, 76.4, 75.9 (*C*$_5$H$_2$), 43.2 (*C*H$_3$−C$_5$H$_2$), 41.6 (*C*(CH$_3$)$_2$), 32.9 (C(*C*H$_3$)$_2$), 29.4 (C(*C*H$_3$)$_2$),

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cage carbons were not observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 69.7, 66.5. $^{11}B\{^1H\}$ NMR (C_6D_6): δ −5.4 (2B), −7.2 (4B), −9.8 (2B), −13.8 (2B). IR (KBr, cm^{-1}): ν 2576 (vs) (BH), 1928 (s) (Ru-H). Anal. Calcd for $C_{47}H_{52}B_{10}P_2Ru$: C, 63.57; H, 5.90. Found: C, 63.36; H, 5.93.

Preparation of [η^5-$Me_2C(3/4\text{-}Me\text{-}C_5H_2)(C_2B_{10}H_{10})$]RuH($PPh_3$)$_2$ (9a/b). These mixtures of complexes were prepared as yellow crystals from $Me_2C(3\text{-}Me\text{-}C_5H_4)(C_2B_{10}H_{11})$ (0.26 g, 1.00 mmol), *n*-BuLi in *n*-hexane (1.60 M, 1.25 mL, 2.00 mmol), and $RuCl_2(PPh_3)_3$ (0.96 g, 1.00 mmol) in THF using the identical procedures reported for **6**: yield 0.64 g (72%), mp 195 °C dec. ^1H NMR (C_6D_6): δ 7.60−6.81 (m, 60H, aryl *H*), 4.82 (d, ^3J = 2.1 Hz, 1H, C_5H_2), 3.67 (s, 1H, C_5H_2), 3.41 (s, 1H, C_5H_2), 3.45 (d, ^3J = 2.1 Hz, 1H, C_5H_2), 2.11 (s, 3H, $CH_3{-}C_5H_2$), 2.08 (s, 3H, $CH_3{-}C_5H_2$), 1.36 (s, 3H, $C(CH_3)_2$), 1.17 (s, 6H, $C(CH_3)_2$), 1.02 (s, 3H, $C(CH_3)_2$), −10.41 (dd, $^2J_{HP}$ = 37.2 and 32.7 Hz, 1H, Ru-*H*), −10.62 (dd, $^2J_{HP}$ = 39.6 and 31.7 Hz, 1H, Ru-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.3 (d, $^1J_{CP}$ = 40.0 Hz, aryl *C*), 139.0 (d, $^1J_{CP}$ = 40.0 Hz, aryl *C*), 135.0 (d, $^2J_{CP}$ = 12.2 Hz, aryl *C*), 134.7 (d, $^2J_{CP}$ = 12.2 Hz, aryl *C*), 128.0 (d, $^3J_{CP}$ = 6.6 Hz, aryl *C*), 127.4 (d, $^3J_{CP}$ = 6.6 Hz, aryl *C*), 110.2 (d, $^4J_{CP}$ = 4.0 Hz, aryl *C*), 99.1, 98.7, 91.8, 90.7, 89.3, 88.0, 86.7, 84.3, 82.4, 77.0 (C_5H_2), 42.6, 42.0 ($CH_3{-}C_5H_2$), 41.3, 41.1 ($C(CH_3)_2$), 32.4, 31.9, 30.1, 30.0 ($C(CH_3)_2$), cage carbons were not observed. $^{11}B\{^1H\}$ NMR (C_6D_6): δ −4.5 (2B), −6.6 (4B), −8.6 (2B), −13.1 (2B). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 69.9, 69.2, 66.8, 63.5. IR (KBr, cm^{-1}): ν 2576 (s) (B-H), 1940 (vs) (Ru-H). Anal. Calcd for $C_{47}H_{52}B_{10}P_2Ru$: C, 63.57; H, 5.90. Found: C, 63.70; H, 6.42.

Preparation of [η^5-$Me_2Si(C_5H_3)(C_2B_{10}H_{10})$]RuH($PPh_3$)$_2$ (10) and [{η^5:σ-$Me_2Si(C_5H_4)(C_2B_{10}H_{10})$}Ru($PPh_3$)]$_2$($\mu$-$N_2$) (11). Complex **10** was prepared as yellow crystals from $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ (0.27 g, 1.00 mmol), *n*-BuLi in *n*-hexane (1.60 M, 1.25 mL, 2.00 mmol), and $RuCl_2(PPh_3)_3$ (0.96 g, 1.00 mmol) in THF using the identical procedures reported for **6**: yield 0.60 g (67%), mp 204 °C dec. Slow evaporation of the mother liquor at room temperature gave a few red crystals identified as **11**. For **10**, ^1H NMR (C_6D_6): δ 7.59−6.82 (m, 30H, aryl *H*), 4.97 (m, 1H, C_5H_3), 4.11 (m, 1H, C_5H_3), 3.79 (m, 1H, C_5H_3), 0.13 (s, 3H, $Si(CH_3)_2$), 0.05 (s, 3H, $Si(CH_3)_2$), −9.97 (dd, $^2J_{HP}$ = 37.0 and 32.2 Hz, 1H, Ru-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.7 (d, $^1J_{CP}$ = 40.0 Hz, aryl *C*), 140.3 (d, $^1J_{CP}$ = 40.0 Hz, aryl *C*), 134.3 (d, $^2J_{CP}$ = 10.8 Hz, aryl *C*), 134.2 (d, $^2J_{CP}$ = 10.8 Hz, aryl *C*), 127.3 (d, $^3J_{CP}$ = 9.6 Hz, aryl *C*), 111.1 (d, $^4J_{CP}$ = 4.4 Hz, aryl *C*), 93.1, 92.0, 81.3, 80.0, 78.3 (C_5H_3), 0.1 (CH_3), −2.8 (CH_3), cage carbons were not observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 71.6, 64.1. $^{11}B\{^1H\}$ NMR (C_6D_6): δ −4.3 (2B), −8.9 (4B), −10.8 (2B), −13.8 (2B). IR (KBr, cm^{-1}): ν 2572 (vs) (B-H), 1975 (s) (Ru-H). Anal. Calcd for $C_{45}H_{50}B_{10}P_2RuSi$: C, 60.72; H, 5.66. Found: C, 61.24; H, 6.11.

Preparation of $Me_2C(C_5H_4)(C_2B_{10}H_{10})$ (12). A solution of HBF_4 in diethyl ether (54% wt, 0.10 mL, 1.00 mmol) was slowly added to a toluene solution (5 mL) of **6** (0.15 g, 0.17 mmol) at −78 °C with stirring, and the mixture was warmed to room temperature and stirred for 3 h. Then the reaction was quenched with 10 mL of a saturated $NaHCO_3$ aqueous solution, transferred to a separatory funnel, and diluted with 10 mL of diethyl ether. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined ether solutions were dried over anhydrous Na_2SO_4. Removal of solvent gave a crude brown solid, which was purified by column chromatography (SiO_2, hexane) to yield **12** as a white solid (0.027 g, 65%). ^1H NMR ($CDCl_3$): δ 6.04 (m, 1H, vinyl *H*), 5.91 (m, 1H, vinyl *H*), 3.30 (m, 2H, sp^3-CH_2 in C_5H_4), 1.53 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 180.5, 162.4, 123.1, 120.3 (C_5H_4), 96.4 (cage *C*), 46.7 (sp^3-*C* in C_5H_4), 43.3 ($C(CH_3)_2$), 30.1 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −5.5 (1B), −6.1 (1B), −7.7 (2B), −9.1 (2B), −12.5 (4B). IR (KBr, cm^{-1}): ν 2588 (vs) (B-H). HRMS: *m/z* calcd for $C_{10}H_{20}{}^{11}B_8{}^{10}B_2{}^+$ 248.2563, found 248.2561.

Preparation of [η^5-$Me_2C(C_5H_3)(C_2B_{10}H_{10})$]$_2$Ru (13). A 1.60 M solution of *n*-BuLi in *n*-hexane (63 μL, 0.10 mmol) was slowly added to a THF solution (5 mL) of $Me_2C(C_5H_4)(C_2B_{10}H_{10})$ (**12**; 25 mg, 0.10 mmol) at −78 °C with stirring, and the mixture was warmed to room temperature and stirred for 2 h. The powder of $[RuCl_2(COD)]_x$ (14 mg, 0.05 mmol) was added to the resulting solution, and the mixture was stirred at room temperature for 12 h. After removal of the solvent, the resulting yellow solid was recrystallized from an ether solution to give **13** as a pale yellow solid (13 mg, 42%). ^1H NMR ($CDCl_3$): δ 4.57 (m, 2H, C_5H_3), 3.45 (m, 2H, C_5H_3), 3.29 (m, 2H, C_5H_3), 1.40 (s, 6H, $C(CH_3)_2$), 1.38 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 102.1, 85.8, 76.6, 65.2 (C_5H_3), 37.7 ($C(CH_3)_2$), 30.6, 29.9 ($C(CH_3)_2$), cage carbons were not observed. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −4.5 (4B), −9.5 (8B), −11.5 (4B), −13.7 (4B). IR (KBr, cm^{-1}): ν 2562 (vs) (B-H). HRMS: *m/z* calcd for $C_{20}H_{38}{}^{11}B_{16}{}^{10}B_4Ru^+$ 596.4018, found 596.4019.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$PPh_2(OEt)$]$_2$ (14). This complex was prepared as yellow crystals from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.25 g, 1.00 mmol), *n*-BuLi in *n*-hexane (1.60 M, 1.25 mL, 2.00 mmol), and $RuCl_2[PPh_2(OEt)]_3$ (0.86 g, 1.00 mmol) in THF using the identical procedures reported for **6**: yield 0.45 g (55%), mp 269−270 °C. ^1H NMR (C_6D_6): δ 7.56−7.03 (m, 20H, aryl *H*), 4.13 (m, 2H, C_5H_4), 3.72 (m, 2H, C_5H_4), 3.23 (m, 2H, OCH_2), 3.07 (m, 2H, OCH_2), 1.32 (s, 6H, $C(CH_3)_2$), 0.99 (t, ^3J = 6.9 Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.3, 139.1, 136.3, 133.2, 132.3, 129.9, 129.7, 127.4 (aryl *C*), 84.2, 77.0 (C_5H_4), 63.8 (OCH_2), 39.7 ($C(CH_3)_2$), 31.7 ($C(CH_3)_2$), 16.1 (CH_2CH_3), cage carbons were not observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 135.4. $^{11}B\{^1H\}$ NMR (C_6D_6): δ −3.4 (2B), −7.3 (8B). IR (KBr, cm^{-1}): ν 2584 (vs) (B-H). These data were identical with those reported in the literature.[21]

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(dppe) (15). A 1.60 M solution of *n*-BuLi in *n*-hexane (1.25 mL, 2.00 mmol) was slowly added to a THF solution (15 mL) of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.25 g, 1.00 mmol) at −78 °C with stirring, the mixture was warmed to room temperature. To the resulting solution was slowly added a THF solution (10 mL) containing dppe (0.40 g, 1.00 mmol) and $RuCl_2(PPh_3)_3$ (0.96 g, 1.00 mmol), and the mixture was stirred at room temperature for 24 h. After removal of the solvent and addition of CH_2Cl_2 (20 mL), the precipitate was filtered off. The clear solution was concentrated to dryness. The resulting yellow solid was recrystallized from a CH_2Cl_2 solution to give **15** as yellow crystals (0.46 g, 62%), mp 162−163 °C. ^1H NMR ($CDCl_3$): δ 7.92−6.74 (m, 20H, aryl *H*), 5.32 (m, 2H, C_5H_4), 4.30 (m, 2H, C_5H_4), 2.87 (t, ^3J = 9.0 Hz, 2H, CH_2), 2.48 (t, ^3J = 9.0 Hz, 2H, CH_2), 1.48 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.4, 131.6, 130.8, 129.5, 128.9, 128.4, 128.0, 127.6 (aryl *C*), 82.7, 74.6 (C_5H_4), 39.8 ($C(CH_3)_2$), 31.6 (CH_3), 24.6 (d, J_{CP} = 21.2 Hz, PCH_2CH_2P), cage carbons were not observed. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −4.2 (2B), −7.5 (4B), −9.6 (4B). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 81.1. IR (KBr, cm^{-1}): ν 2563 (s) (B-H). These data were identical with those reported in the literature.[8]

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 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.[31] 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

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[31] Sheldrick, G. M. *SADABS*: *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen: Germany, 1996.

Table 2. Crystal Data and Summary of Data Collection and Refinement for 6−8 and 11

	6·0.5THF	**7**	**8**	**11**
formula	$C_{48}H_{54}B_{10}O_{0.5}P_2Ru$	$C_{45}H_{48}B_{10}P_2Ru$	$C_{47}H_{52}B_{10}P_2Ru$	$C_{54}H_{70}B_{20}N_2P_2Ru_2Si_2$
cryst size (mm)	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.20	0.40 × 0.40 × 0.20	0.25 × 0.20 × 0.10
fw	910.0	860.0	888.0	1283.6
cryst syst	triclinic	triclinic	monoclinic	tetragonal
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P4_32_12$
a, Å	13.317(3)	10.335(1)	17.534(1)	14.762(2)
b, Å	16.389(3)	12.577(2)	12.296(1)	14.762(2)
c, Å	23.527(5)	16.789(2)	21.374(1)	31.863(3)
α, deg	93.51(3)	81.82(1)	90	90
β, deg	100.28(3)	81.23(1)	102.50(1)	90
γ, deg	109.95(3)	84.43(1)	90	90
V, Å^3	4708(2)	2128.4(5)	4499.1(4)	6943.1(9)
Z	4	2	4	4
D_{calcd}, Mg/m^3	1.284	1.342	1.311	1.228
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
$2\theta_{max}$, deg	50.0	50.0	50.0	50.0
μ, mm^{-1}	0.436	0.477	0.453	0.551
F(000)	1880	884	1832	2616
no. of obsd reflns	13 317	7463	7916	6117
no. of params refnd	1116	527	545	371
goodness of fit	1.035	1.007	1.001	1.134
R1	0.048	0.052	0.033	0.046
wR2	0.131	0.111	0.081	0.135

the SHELXTL program package.[32] For the noncentrosymmetric structure of **11**, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[33] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 2.

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Supporting Information Available: X-ray crystallographic data in CIF format for **6**, **7**, **8**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0604122

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