Ruthenium-Catalyzed Hydroboration and Dehydrogenative Borylation of Linear and Cyclic Alkenes with Pinacolborane

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The bis(dihydrogen)ruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) catalyzes efficiently the borylation of linear and cyclic alkenes with pinacolborane. Similar results are obtained by using $RuH[(\mu\text{-}H)_2Bpin](\sigma\text{-}HBpin)(PCy_3)_2$ (**2**) as catalytic precursor. Selective hydroboration into the corresponding linear pinacol boronate is achieved in the case of 1-hexene, 1-octene, styrene, and allylbenzene. In the case of styrene, phenethyl pinacolboronate is isolated in 87% yield. Faster conversions of HBpin are obtained by increasing the alkene:borane ratio, with less than 10% of alkene hydrogenation. Isomerization into *trans*-β-methylstyrene is observed in the case of allylbenzene. Dehydrogenative borylation is competitive with ethylene and cyclic alkenes with large rings. Hydroboration of cyclohexene is highly favored, whereas for cyclodecene, vinylboronate is produced with only traces of allylboronate. Cyclooctene provides the two unsaturated boron-attached products, vinyl- and allylboronate in a 1:3 ratio, whereas only allylboronate is obtained from cycloheptene. The coupling of cyclodecenyl pinacolboronate with the aryl bromide $(CF_3)_2C_6H_3Br$, using standard catalytic Suzuki−Miyaura conditions, gives the corresponding product $(CF_3)_2C_6H_3(C_{10}H_{17})$ in 85% yield. Mechanistic investigations allow the characterization of the hydrido(boryl)(ethylene) complex $RuH(Bpin)(C_2H_4)(PCy_3)_2$ (**3**) as a key intermediate in the catalytic cycle.

Introduction

The synthetic utility of the hydroboration of carbon−carbon multiple bonds is well established.[1] Importantly, metal-catalyzed hydroborations are largely dominated by rhodium systems and catecholborane.[2] Alkene boronic esters have been of particular interest due to their potential to act as useful intermediates in organic synthesis, in particular for Suzuki−Miyaura cross-coupling.[3] They are usually prepared by hydroboration of alkynes.[1,2] The search for other synthetic routes toward alkene boronic esters using alkenes, which are easily prepared and commercially available with a wide variety of functionalities, is attractive.[4] Dehydrogenative borylation of alkenes, the competing reaction of catalyzed alkene hydroboration, represents an interesting alternative.[5,6] Recently, it was shown that rhodium-catalyzed dehydrogenative borylation of alkenes could be favored, leading to 1,1-disubstituted vinylboronates, without sacrificial hydrogenation of the alkene substrate.[7]

In view of the previous results we have obtained in hydrosilylation and dehydrogenative silylation of alkenes with the bis(dihydrogen) ruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) as an effective catalyst,[8] we have undertaken a similar study on pinacolborane activation, a reagent that has received little attention by comparison to catecholborane. The presence in **1** of two labile σ-dihydrogen ligands is a key feature allowing an easy access to formally a 14-electron intermediate. In the case of borane activation, we have shown that substitution of the two σ-ligands by pinacolborane leads to the formation of $RuH[(\mu\text{-}H)_2Bpin](\sigma\text{-}HBpin)(PCy_3)_2$ (**2**), a complex in which the two borane ligands are bonded to the metal in different modes, σ-coordination and dihydroborate ligation.[9] We now report that **1** and **2** serve as active catalyst precursors not only for hydroboration of various alkenes with pinacolborane but more interestingly for dehydrogenative borylation of ethylene and cyclic alkenes. Moreover, mechanistic investigations allow the characterization of a hydrido(boryl)(ethylene) complex, $RuH(Bpin)(C_2H_4)(PCy_3)_2$ (**3**), a key intermediate for catalyzed alkene hydroboration.

Results and Discussion

The catalytic experiments were performed at room temperature using a catalyst/pinacolborane ratio of 1:100 and an alkene ratio varying from 100 to 1000. The results are summarized in

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Table 1. Hydroboration of Alkenes with Pinacolborane[a]

entry	substrate	HBpin:substrate	time (min)[c]	RBpin selectivity saturated:unsaturated
1	1-hexene	100:100	10	>99:0
2	1-octene	100:100	10	>99:0
3	styrene	100:100	180	>99:0
4	styrene	100:200	150	>99:0
5	styrene	100:500	75	>99:0
6	allylbenzene	100:200	15	>99:0
7[b]	ethylene	100:3 bar	60	>99:0
8	ethylene	100:3 bar	60	82:18
9	*tert*-butylethylene	100:200	15	98:2
10	cyclohexene	100:100	70	96:4

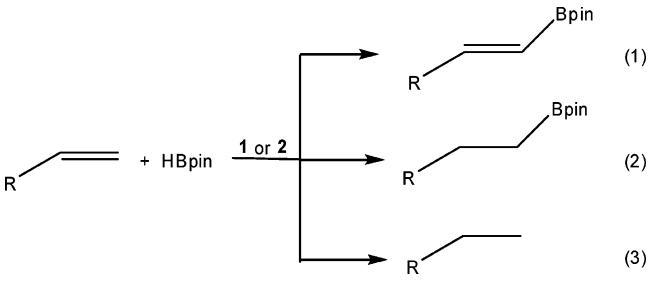
[a] Typical reaction conditions: a mixture of pinacolborane (100 equiv) and alkene (100 to 1000 equiv) was added to a solution of **1** or **2** (1 equiv) in 2 mL of THF and stirred at room temperature. The reaction was monitored by either GC-MS or a combination of GC-MS and NMR spectroscopy. [b]THF was replaced by toluene. [c]Time to achieve total conversion of HBpin. For entries 7 and 8, the reaction was only checked after 1 h.

Table 2. Dehydrogenative Borylation of Ethylene and Cyclic Alkenes with Pinacolborane[a]

entry	substrate	HBpin:substrate	time (min)[b]	RBpin selectivity saturated:unsaturated
1	ethylene	100:20 bar	15	44:56
2	cycloheptene	100:100	570	80:20
3	cycloheptene	100:200	360	70:30
4	cycloheptene	100:1000	420	47:53
5	*cis*-cyclooctene	100:100	240	57:43
6	*cis*-cyclooctene	100:200	120	30:70
7	*cis*-cyclooctene	100:1000	120	22:78
8	*trans*-cyclodecene	100:200	330	29:71
9	*trans*-cyclodecene	100:1000	60	20:80

[a] Typical reaction conditions: a mixture of pinacolborane (100 equiv) and alkene (100 to 1000 equiv) was added to a solution of **1** or **2** (1 equiv) in 2 mL of THF and stirred at room temperature. The reaction was monitored by either GC-MS or a combination of GC-MS and NMR spectroscopy. [b]Time to achieve total conversion of HBpin.

Scheme 1



Tables 1 and 2. The conditions were not optimized but serve as a guideline to investigate the catalytic activity of **1** or **2** on a variety of alkenes. A few linear and cyclic alkenes were selected. Access to boron-substituted cyclic olefins is highly desirable,[10] as they can serve as useful synthetic intermediates in particular for C−C bond formation through Suzuki coupling reactions. Moreover, the synthesis of cyclic 1-alkenylboron compounds cannot be easily performed by hydroboration of alkynes because of limited availability of the starting cycloalkynes.[11]

Total conversion of HBpin is observed within 15 min to a few hours depending on the alkene, and either one, two, or the three reactions depicted in Scheme 1 can be observed, i.e., dehydrogenative borylation (eq 1), hydroboration (eq 2), or hydrogenation (eq 3). We will also see that in some cases isomerization of the starting alkene can be observed, particularly when the alkene:HBpin ratio is higher than 1.

In the case of linear alkenes such as 1-hexene and 1-octene, selective hydroboration to the corresponding saturated alkyl pinacolboronate is achieved within 10 min (95% isolated yield). As shown by GC-MS and NMR, hydroboration of styrene leads exclusively to the formation of the linear product, and phenethyl pinacolboronate was isolated in 87% yield. Excess styrene significantly improves the activity (compare entries 3−5). Remarkably, hydrogenation of styrene into ethylbenzene remains a minor reaction (less than 10%).[7] Recent studies show that iridium catalyst precursors are also highly selective for the formation of the linear product (up to 99% with a 5% mixture of $[IrCl(COD)]_2$ and dppp), whereas the analogous rhodium system gave almost a 1:1 branched-to-linear ratio. Better results were obtained by using $RhCl(CO)(PPh_3)_2$ as catalyst precursor (76% of phenethyl pinacolboronate was obtained when using $RhCl(CO)(PPh_3)_2$/HBpin/styrene in a 1:40:33 ratio).[12,13] Using $[RhCl(cod)]_2$ as a catalyst precursor caused dehydrogenative coupling, but in that case styrene acted as a hydrogen acceptor with production of ethylbenzene in 46% yield.[14,6] The reaction of allybenzene with HBpin (Table 1, entry 6) led in our system to comparable results with styrene. In particular, when using 200 equiv of allylbenzene, conversion of HBpin was total within 15 min, with quantitative formation of the corresponding linear boronate. As shown by NMR and GC-MS measurements, excess olefin was isomerized into *trans*-β-methylstyrene and we detected only traces of the hydrogenated product, i.e., propylbenzene.

As expected, in the case of ethylene, an increase of pressure favored the dehydrogenative borylation process, and under 20 bar of ethylene (see Table 1, entries 7, 8, and Table 2, entry 1) up to 56% of vinylpinacolboronate was obtained. It should be noted in that case that the nature of the solvent had a slight effect on the selectivity, with dehydrogenative borylation favored

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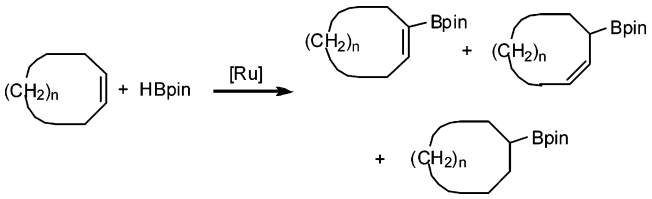
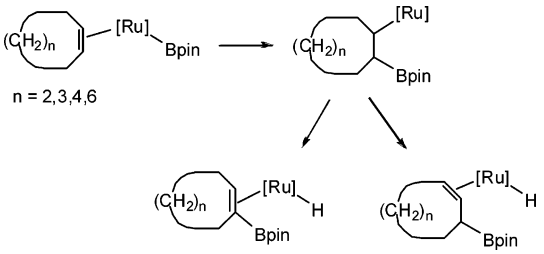
Scheme 2. Borylation of Cyclic Alkenes



Scheme 3. Proposed Pathway for the Formation of Vinylboronates and Allylboronates



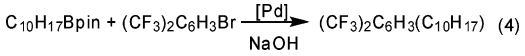
by using a polar solvent such as THF. Introduction of a bulky substituent on ethylene leads to selective hydroboration, as observed in the case of tertiobutylethylene (Table 1, entry 9).

The results on cyclic alkenes are listed in Table 2. The selectivity and activity depend on the size of the alkene cycle. Competitive dehydrogenative borylation can be achieved, leading to the formation of the corresponding vinylboronate or allylboronate (see Scheme 2). Using an excess of olefin versus HBpin led to partial hydrogenation (20 to 45% depending on the conditions) into the corresponding cyclic alkane. Hydroboration of cyclohexene (see Table 1, entry 10), is highly favored, whereas in the case of cyclodecene, vinylboronate was produced with only traces of allylboronate (see Table 2, entries 8, 9). Cyclooctene provided the two unsaturated boron-attached products, vinyl- and allylboronate in a 1:3 ratio, whereas only allylboronate was obtained from cycloheptene. It is noteworthy that allylboronate compounds are also versatile intermediates. Their stability allows them to be successfully applied in efficient catalytic enantioselective allylboration methods and in tandem reaction processes.[15,16]

It seems likely that, for the cyclic alkenes, selectivity depends on one of the key steps in the catalytic process, which is the formation of a boryl alkene species. Boryl migratory insertion would then result in a β-borylalkyl intermediate, which can undergo β-hydride elimination to produce either vinylboronate or allylboronate as depicted in Scheme 3, this step being controlled by conformational factors, or alternatively can undergo reductive elimination leading to the hydroboration product.

The usefulness of our method to produce boron-substituted cyclic olefins was demonstrated by the coupling of cyclodecenyl pinacolboronate with the aryl bromide $(CF_3)_2C_6H_3Br$, using standard catalytic Suzuki−Miyaura conditions (see eq 4 and Experimental Section).[17] The resulting coupling product $(CF_3)_2C_6H_3(C_{10}H_{17})$ was isolated in 85% yield and characterized by NMR and GC-MS.

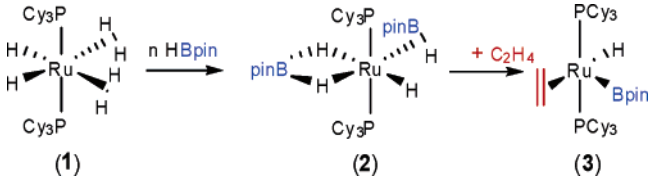
To gain some insight into the mechanism of our systems, the following stoichiometric and catalytic reactions were



investigated. The progress of the reactions was monitored by ^1H and ^{31}P NMR spectroscopies. In a first step, 10 equiv of HBpin was added to a C_7D_8 solution of **1**, leading as expected to **2** as the only organometallic species. Then 20 equiv of either cyclohexene or cyclooctene was added to the mixture. After 4 h of stirring, **2** remained the only organometallic species that could be detected by NMR and the catalysis proceeds.

In contrast, in the case of ethylene, a new organometallic complex was detected and formulated as $RuH(Bpin)(C_2H_4)(PCy_3)_2$ (**3**) on the basis of NMR data (see Scheme 4). **3** is characterized in ^1H NMR by a triplet at -5.77 ppm ($J_{PH} = 35$ Hz) for the hydride resonance and one singlet at 2.85 ppm for the ethylene resonance in free rotation. The two signals integrate in a 1:4 ratio. The ethylene resonance is observed in the $^{13}C\{^1H\}$ NMR spectrum at 42.0 ppm, and the assignment is confirmed by a HMQC experiment. The $^{11}B\{^1H\}$ NMR spectrum shows one singlet at 34.6 ppm, in the same range observed for related σ-pinacolborane ruthenium complexes. It is thus difficult to discriminate a boryl from a σ-borane formulation. A similar problem is found when comparing the ^{29}Si NMR chemical shift of silyl and σ-silane complexes.[18] However, the hydride signal is very sharp, in agreement with a hydrido(boryl) formulation with no sign of B−H interaction. Any attempt to isolate **3** was unsuccessful and led to decomposition and formation of the known ethylene complex $RuH(C_2H_4)\{P(\eta^3\text{-}C_6H_8)Cy_2\}(PCy_3)$ (**4**),[8a] together with the boronate products.

Scheme 4. Formation of the Hydrido(boryl)(ethylene) Complex $RuH(Bpin)(C_2H_4)(PCy_3)_2$ (3)



It is worth comparing these results with those we obtained when studying a similar process by replacing the borane reagent by a silane. Thus, bubbling ethylene to a solution of **1** with 2 equiv of $HSiMe_2Cl$ led to total conversion of the starting silane and formation of the corresponding chlorodimethylvinylsilane as a result of dehydrogenative silylation. The new ethylene complex $RuH(SiMe_2Cl)(C_2H_4)(PCy_3)_2$ (**5**), an analogous species of **3**, was detected.[8c] In the two systems, an unsaturated 16-electron species containing the three key ligands involved in the catalytic process, i.e., a hydride, an ethylene, and a boryl (or a silyl), is thus characterized. It is remarkable that **3** and **5** remain unsaturated even in the presence of an excess of ethylene or borane (or silane), respectively. This can be attributed to the strong trans influence of the boryl (or silyl) ligand. Such a strong trans influence of boryl ligands has been recently outlined by Lin and Marder.[19] It is noteworthy that five-coordinated boryl Ru species of general formula $RuCl(BR_2)(CO)(PPh_3)_2$ have been previously reported.[20] In our system, it is only when the two substrates, ethylene and pinacolborane, are both present in the

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reaction mixture that the reaction proceeds and the catalytic products are obtained. **3** can be considered as the catalyst resting state.

In summary, the nature of the olefin controls the selectivity toward hydroboration or dehydrogenative borylation. In the case of cyclic alkenes, conformational properties have a dramatic influence on both the rate and the selectivity of the reactions. Hydroboration of a C6 ring was selectively achieved, whereas allylboronate (for C7), a mixture of allylboronate and vinylboronate (for C8), and only vinylboronate (for C10) were isolated, respectively. Remarkably, using **2** as catalyst precursor instead of **1** for hydroboration or dehydrogenative borylation led to the same results (same activity and selectivity). We were able to characterize the hydrido(boryl)ethylene complex **3**, a complex incorporating the three key ligands necessary for the catalysis to proceed. It is remarkable that **3** is analogous to the silyl complex we previously identified. This encourages us to work on mapping out the similarity between silane and borane activation.

Experimental Section

General Methods. All preparations were carried out under an oxygen-free argon atmosphere using conventional Schlenk techniques. Solvents were dried and distilled prior to use. Alkenes and pinacolborane were purchased from a commercial supplier and employed without any further purification. The ruthenium complexes **1** and **2** were prepared following literature procedures.[8,9] GC data were collected with a HP 4890A instrument. GC-mass spectra were measured at 70 eV on a HP 5973 attached to a HP 6890, and NMR experiments were acquired on Bruker ARX250, AV400, and AV500 spectrometers.

General Catalytic Reaction of Alkenes and Pinacolborane. A mixture of pinacolborane (1.5 mmol) and alkene (1.5 to 15 mmol) was added to a solution of **1** or **2** (0.015 mmol) in 2 mL of THF and stirred at room temperature. The reaction was monitored by GC and stopped after total consumption of HBpin.

The solvent was removed under vacuum, and the products were purified by Kugelröhr distillation. The boronate products were characterized by GC-MS and NMR. Their NMR spectra agreed with those reported in the referenced papers.

The following blank experiments were performed: a mixture of pinacolborane (1.5 mmol), alkene (*tert*-butylethylene, 1-hexene, 1-octene, cyclohexene, styrene, or cyclooctene) (1.5 mmol-3 mmol), and cyclooctane or cyclohexane (0.32 mmol) as internal standard was dissolved in 2 mL of THF and stirred at room temperature for 30 min to 1 h. The reaction was monitored by GC. In each case, no reaction was observed.

2-(Hexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[21] ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.79 (t, 2H, $J = 7.6$ Hz), 0.89 (t, 3H, $J = 6.6$ Hz), 1.26 (s, 12H), 1.29 (m, 4H), 1.41 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 10.1, 14.1, 22.6, 23.9, 24.8, 31.6, 32.1, 82.8. EI-MS: *m*/*z* 212 (M^+), 197, 183, 169, 155, 128, 113, 98, 84, 69, 55, 41.

2-(Octyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[12] ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.76 (t, 2H, $J = 7.5$ Hz), 0.87 (t, 3H, $J = 6.8$ Hz), 1.24 (s, 12H), 1.21−1.29 (m, 10H), 1.38−1.41 (m, 2H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 62.89 MHz): δ 10.1, 14.1, 22.6, 23.9, 24.8, 29.2, 29.3, 31.8, 32.4, 82.8. EI-MS: *m*/*z* 240 (M^+), 225, 197, 183, 169, 154, 129, 111, 85, 69, 55, 43.

2-(2-Phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[12] ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 1.19 (t, 2H, $J = 8.1$ Hz), 1.26 (s, 12H), 2.80 (t, 2H, $J = 8.2$ Hz), 7.18 (m, 1 Ar−H), 7.27 (m, 2 Ar−H), 7.30 (m, 2 Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 13.0, 24.8, 30.0, 83.1, 125.5, 128.0, 128.2, 144.4. EI-MS: *m*/*z* 232 (M^+), 217, 203, 189, 175, 159, 133, 119, 105, 91, 77, 59, 41.

2-(3-Phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[12] ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.86 (t, 2H, $J = 8$ Hz), 1.27 (s, 12H), 1.76 (m, 2H), 2.64 (t, 2H, $J = 8$ Hz), 7.10−7.40 (m, 5 Ar−H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 62.89 MHz): δ 10.1, 24.8, 26.1, 38.6, 82.9, 125.5, 128.1, 128.5, 142.7. EI-MS: *m*/*z* 246 (M^+), 231, 189, 173, 127, 118, 105, 85, 77, 65, 55, 41.

2-(2-*tert*-Butylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[22] ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.72 (t, 2H, $J = 8$ Hz), 0.86 (s, 9H), 1.26 (s, 12H), 1.32 (t, 2H, $J = 8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 7.0, 24.8, 28.8, 30.8, 37.7, 82.8. EI-MS: *m*/*z* 212 (M^+), 197, 169, 157, 129, 113, 101, 83, 69, 57, 43.

2-(Cyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[12] ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.93−1.00 (m, 1H), 1.23 (s, 12H), 1.26−1.40 (m, 4H), 1.54−1.70 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 24.7, 26.7, 27.1, 27.9, 82.7. EI-MS: *m*/*z* 210 (M^+), 195, 167, 153, 139, 129, 124, 109, 85, 69, 55, 41.

2-(Cycloheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.80−1.05 (m, 1H), 1.19 (s, 12H), 1.40−2.20 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 24.5, 28.3, 28.9, 29.5, 82.7. EI-MS: *m*/*z* 224 (M^+), 209, 182, 167, 138, 123, 101, 96, 83, 55, 39.

2-(2-Cycloheptenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 1.21 (s, 12H), 1.40−2.20 (m, 9H), 5.71 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 24.7, 27.2, 28.8, 29.7, 33.1, 82.9, 132.2, 133.2. EI-MS: *m*/*z* 222 (M^+), 207, 181, 165, 138, 121, 101, 85, 67, 41.

2-(Cyclooctyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.80−1.05 (m, 1H), 1.21 (s, 12H), 1.40−2.40 (m, 14H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz) δ 24.5, 82.7. EI-MS: *m*/*z* 238 (M^+), 223, 209, 194, 180, 152, 124, 109, 84, 55, 41.

2-(2-Cyclooctenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 1.23 (s, 12H), 1.40−2.40 (m, 11H), 5.62 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 24.6, 83.0, 130.2, 130.4. EI-MS: *m*/*z* 236 (M^+), 221, 208, 194, 179, 165, 151, 135, 108, 84, 67, 41.

2-(1-Cyclooctenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[11] ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 1.26 (s, 12H), 1.35−1.50 (m, 8H), 2.20−2.40 (m, 4H), 6.56 (t, 1H, $J = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 24.7, 25.9, 26.2, 26.4, 27.1, 28.8, 29.6, 82.9, 145.9. EI-MS: *m*/*z* 236 (M^+), 221, 208, 194, 179, 165, 151, 135, 108, 84, 67, 41.

2-(Cyclodecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 0.80−1.05 (m, 1H), 1.25 (s, 12H), 1.40−3.00 (m, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 24.5, 82.7. EI-MS: *m*/*z* 266 (M^+), 251, 223, 209, 195, 180, 166, 152, 129, 101, 84, 69, 55, 41.

2-(1-Cyclodecenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 1.27 (s, 12H), 1.40−3.00 (m, 16H), 6.37 (t, 1H, $J = 8.3$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.89 MHz): δ 24.7, 82.8, 145.9. EI-MS: *m*/*z* 264 (M^+), 249, 221, 207, 179, 164, 136, 121, 101, 84, 69, 55, 41.

General Procedure for Intermolecular Cross-Coupling. The literature procedure was followed.[17] A solution of $PdCl_2$(dppf) (0.01mmol), 3,5-bis(trifluoromethyl)bromobenzene (0.3 mmol), cyclodecenyl pinacolboronate (0.3 mmol), and aqueous NaOH (2 mL of 0.5 M solution) in THF was refluxed overnight. After the reaction was completed, the product was extracted with ether, washed with brine, and dried over $MgSO_4$.

1-[3,5-Bis(trifluoromethyl)phenyl]cyclodecene. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 1.24−1.72 (m, 12H), 2.48 (q, 2H, $J = 7.0$ Hz), 2.79 (t, 2H, $J = 6.5$ Hz), 5.81 (t, 1H, $J = 8.3$ Hz), 7.76 (s, 1 Ar−H), 7.80 (s, 2 Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz): δ

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20.4, 21.3, 24.7, 25.7, 26.2, 26.5, 26.9, 27.4, 120.3, 126.4, 133.1, 137.6, 145.0. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 188.30 MHz): δ 13.2. EI-MS: *m*/*z* 350 (M^+), 331, 308, 293, 278, 254, 227, 212, 197, 177, 151, 128, 113, 96, 67, 41.

RuH(Bpin)(C_2H_4)(PCy_3)$_2$ (3). The reaction of **2** with ethylene was followed by NMR. Ethylene was bubbled for 1 min through a suspension of **2** (20 mg, 0.02 mmol) in 0.7 mL of C_7D_8 in a NMR tube. ^1H NMR (C_6D_6, 293 K, 500.33 MHz): δ −5.77 (t, 1H, $^2J_{PH}$ = 34.1 Hz, RuH), 1.12 (s, 12H, Bpin), 1.28−2.25 (m, 66H, PCy_3), 2.85 (pseudo t, 4H, ethylene). $^{11}B\{^1H\}$ NMR (C_6D_6, 293 K, 160.52 MHz): δ 34.6. $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K, 101.25 MHz): δ 59.7 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K, 125.80 MHz): δ 24.7 (br, CH_3), 42.0 (br, C ethylene), 82.5 (br, C). The HMQC $^1H-^{13}C$ (C_6D_6, 293 K) experiment shows a correlation between the signal at 2.85 ppm (C_2H_4 protons) and the signal at 42.0 ppm (C_2H_4 carbons) and a correlation between the signal at 1.12 ppm (Bpin protons) and the signal at 24.7 ppm (Bpin methyl carbons).

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Supporting Information Available: NMR spectra of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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