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4,4,5,5-Tetraphenyl-1,3,2-dioxaborolane: A Bulky Borane for the Transition Metal Catalysed Hydroboration of Alkenes

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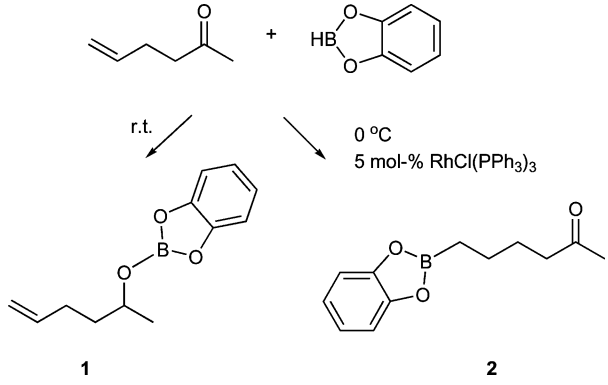
Dedicated to the memory of Professor Yoshihiko Ito

Keywords: Boranes / Catalysis / Hydroboration / Organoboronate esters / Borylrhodium complexes

4,4,5,5-Tetraphenyl-1,3,2-dioxaborolane (HBBzpin, **3**) has been prepared in high yield by the addition of $H_3B{\cdot}SMe_2$ to benzopinacol. HBBzpin is a relatively stable solid that reacts with a variety of alkenes under catalytic conditions to give air- and chromatography-stable organoboronate esters. Reactions of vinylarenes in the presence of catalytic amounts of $[Cp^*IrCl_2]_2$ gave the corresponding terminal products selectively. Addition of HBBzpin to $RhCl(PPh_3)_3$ gave Rh(H)Cl(BzBpin)$(PPh_3)_2$ (**11**) as the only new rhodium-containing product. The complex **11** has been characterized by a number of physical and analytical methods, including a single-crystal X-ray diffraction study.

Introduction

There has been considerable recent interest in the use of transition metals to catalyse the hydroboration of alkenes and alkynes.[1] Products obtained from these reactions can have complementary or opposite chemo-, regio-, and/or stereoselectivity to those generated by the uncatalysed variant. For instance, an elegant study by Männig and Nöth demonstrated that the addition of catecholborane (HBcat; cat = 1,2-$O_2C_6H_4$) to 5-hexen-2-one proceeded readily at room temperature to give the expected borate product **1** (Scheme 1), where addition of the borane has occurred at the more reactive ketone functionality.[2] However, if the reaction was carried out at lower temperatures in the presence of a rhodium catalyst, e.g. $RhCl(PPh_3)_3$, they were able to facilitate selective addition of HBcat to the less reactive alkene group to give the corresponding alkylboronate ester **2**. Since this seminal discovery, a considerable amount of research has focussed on investigating the mechanism and scope of catalysed hydroboration reactions.[3] Much less studied, however, is the use of alternate borane sources for catalysed hydroboration reactions.[4] Indeed, pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane or HBpin) is occasionally used as a replacement for HBcat as the resulting organoborane products are stable to air and chromatography.[5] Unfortunately, these reactions can suffer from poor selectivities or competing pathways (i.e. hydrogenation or dehydrogenative borylations[6]). As such, we have investigated the synthesis and use of bulky 4,4,5,5-tetraphenyl-1,3,2-dioxaborolane (**3**) for its use in the catalysed hydroboration of alkenes in order to circumvent these shortcomings.



Scheme 1. Hydroboration of 5-hexen-2-one with catecholborane (HBcat).

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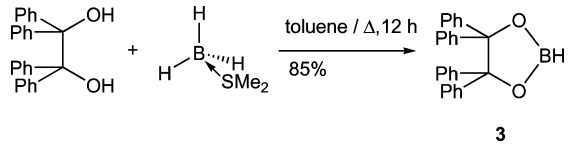
Results and Discussion

Synthesis

Compound **3** (HBBzpin) was prepared in 85% yield by the addition of benzopinacol to a solution of $H_3B{\cdot}SMe_2$ in toluene heated at reflux for 12 h and characterized by multinuclear NMR spectroscopy (Scheme 2). HBBzpin is a white solid that can be kept indefinitely at room temperature under nitrogen. A broad peak in the ^{11}B NMR spectrum at δ = 27 ppm and a broad singlet at δ = 4.95 ppm in the ^1H NMR spectrum are consistent with chemical shifts found for other bulky diorganyloxyboranes. Interestingly, attempts to prepare this compound using $H_3B{\cdot}THF$ resulted in a mixture of products.[4a] Compound **3** is remarkably stable, and all attempts to add this borane to a number of unsaturated molecules at room temperature proved unsuccessful.



Scheme 2. Synthesis of 4,4,5,5-tetraphenyl-1,3,2-dioxaborolane (**3**).

Catalysed Hydroborations

We therefore decided to examine the metal-catalysed hydroboration of **3** in the presence of the metal complexes $RhCl(PPh_3)_3$, Rh(acac)(dppb), $[Rh(cod)(dppb)]BF_4$, and $[Cp^*IrCl_2]_2$ [acac = acetylacetonato, cod = 1,5-cyclooctadiene, dppb = 1,4-bis(diphenylphosphanyl)butane] with a number of alkenes. Although $RhCl(PPh_3)_3$ is frequently used to catalyse hydroborations with HBcat and HBpin, all efforts to use this complex to facilitate the addition of HBBzpin to 4-vinylanisole (4-$MeOC_6H_4CH{=}CH_2$) at room temperature failed. Reactions with Rh(acac)(dppb) gave a mixture of branched [4-$MeOC_6H_4CH(BzBpin)CH_3$ (**4**), 20%] and linear [4-$MeOC_6H_4CH_2CH_2$(BzBpin) (**5**), 45%] hydroboration products, as well as a small amount of the corresponding alkenyl boronate ester [4-MeO-$C_6H_4CH{=}CH$(BzBpin) (**6**), 15%] and the hydrogenation product (4-$MeOC_6H_4CH_2CH_3$, 20% Scheme 3). Compound **6** presumably arises from a dehydrogenative borylation pathway, commonly observed as a competing reaction in catalysed hydroborations. While reactions using $[Rh(cod)(dppb)]BF_4$ also gave a mixture of products, the linear organoboronate compound **5** was the sole product (100% conversion) generated in reactions using catalytic amounts (5 mol-%) of $[Cp^*IrCl_2]_2$.[7] Related allenes containing this tetraphenylethylene glycol ester have been used recently in the enantioselective synthesis of 1,5-*anti*- and 1,5-*syn*-diols.[8]

Similar selectivities were observed in reactions with 4-F-$C_6H_4CH{=}CH_2$ where the corresponding linear product 4-F-$C_6H_4CH_2CH_2$BzBpin (**7**) was the only organoboronate ester generated in the presence of $[Cp^*IrCl_2]_2$. Compound **7** has been characterized by a number of physical methods including a single-crystal X-ray diffraction study, and the molecular structure is shown in Figure 1. The B–O bond lengths of 1.361(3) and 1.371(3) Å are typical for three-coordinate diorganyloxyboranes.[9] Indeed, the two short bonds indicate that π-bonding between the oxygen lone pairs and the empty p-orbital of the boron atom is significant in compound **7**. Bond lengths and angles within the BzBpin group are similar to those reported for a related ferrocene derivative.[10]

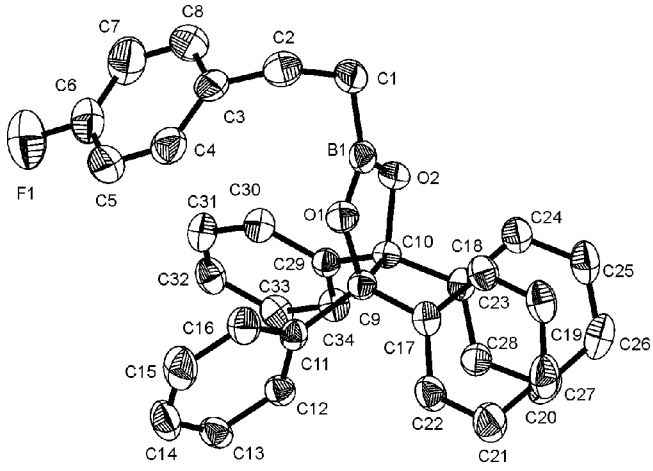
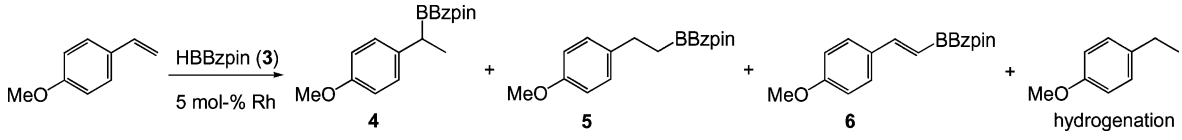


Figure 1. Perspective view of a molecule of **7** with atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B(1)–O(1) 1.361(3), B(1)–O(2) 1.371(3), B(1)–C(1) 1.557(3), C(1)–C(2) 1.543(3), C(6)–F(1) 1.370(3); O(1)–B(1)–O(2) 112.72(18), O(1)–B(1)–C(1) 122.57(19), O(2)–B(1)–C(1) 124.71(19), C(2)–C(1)–B(1) 112.47(19).

We have also investigated the hydroboration of a representative number of other substrates in the presence of $[Cp^*IrCl_2]_2$, and the reactions proceeded selectively at room temperature to give the corresponding terminal products (Figure 2). The new organoboronate ester products **4**–**10** are air- and chromatography-stable and could easily be transformed into the corresponding alcohols upon oxidative workup. Reactions of 1-octene and norbornylene with **3** could be catalysed by both Rh(acac)(dppb) and $[Cp^*IrCl_2]_2$ to give the linear product exclusively, although those using the iridium catalyst were complete within hours, while reac-



Scheme 3. Catalysed hydroboration of 4-vinylanisole with **3**.

tions with the rhodium catalyst took considerably longer (days in the case of norbornylene). Interestingly, the iridium complex also catalysed the selective hydroboration of 5-hexen-2-one to give the organoboronate ester compound **10**. The sluggish nature of **3** towards uncatalysed reactions, even in the presence of the ketone functionality in 5-hexen-2-one, allowed for a selective catalysed addition at the alkene group. Similar selectivities have been reported in an elegant study by Kabalka et al. for reactions using $HBCy_2$.[11]

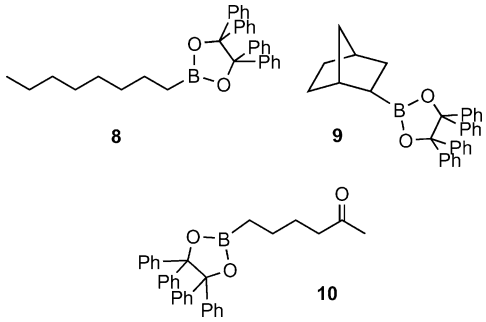


Figure 2. Novel organoboronates generated from the catalysed hydroboration of alkenes with **3**.

Reactions with Metal Complexes

In order to gain further insight into the reactivity of **3**, we investigated the stoichiometric addition of HBBzpin to the metal complexes used in the catalytic runs. Although no reaction was observed with Rh(acac)(dppb) at room temperature in THF, addition of **3** to $[Cp^*IrCl_2]_2$ resulted in a complex mixture of products, as several hydride peaks were observed in the ^1H NMR spectra. Similar product distributions have been reported previously for reactions with this iridium complex and HBcat.[7a] Reaction of **3** with $RhCl(PPh_3)_3$, however, gave the boryl(hydrido) complex $Rh(H)Cl(BzBpin)(PPh_3)_2$ (**11**) as the sole rhodium-containing product. Interestingly, reactions of $RhCl(PPh_3)_3$, with HBcat and HBpin are known to give several (phosphane)-rhodium complexes, including the corresponding boryl-rhodium species.[2,14] The synthesis and reactivity of boryl transition metal complexes has been the subject of intense investigations.[12,13]

Spectroscopic and analytical data for **11** are consistent with its formulation. For instance, a doublet at δ = 40.4 ppm with J_{P-Rh} = 124 Hz in the $^{31}P\{^1H\}$ NMR spectrum and a broad singlet at δ = 32 ppm in the ^{11}B NMR spectrum are similar to those observed in other borylrhodium species.[14] The ^1H NMR spectrum shows a doublet of triplets at δ = –14.34 ppm ($^1J_{H-Rh}$ = 28.8 Hz, $^2J_{H-P}$ = 14.8 Hz) which suggests that the phosphane ligands are magnetically equivalent. The structure of complex **11** has been confirmed by a single-crystal X-ray diffraction study, the results of which are shown in Figure 3. The molecular structure of **11** consists of a 16-electron distorted square-

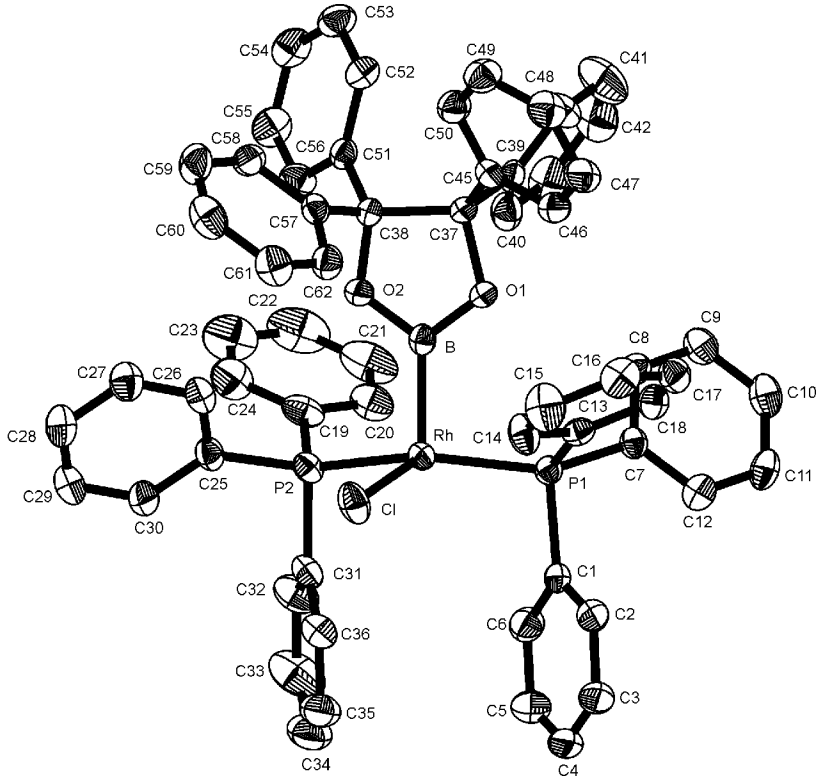


Figure 3. Perspective view of a molecule of **11** with atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms and a molecule of THF omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh–B 1.963(4), Rh–P(2) 2.3227(13), Rh–P(1) 2.3236(13), Rh–Cl 2.4228(14), B–O(1) 1.385(4), B–O(2) 1.390(4); B–Rh–P(2) 95.74(12), B–Rh–P(1) 95.25(12), P(2)–Rh–P(1) 163.49(3), B–Rh–Cl 108.66(10), P(2)–Rh–Cl 92.52(4), P(1)–Rh–Cl 95.60(4), O(1)–B–O(2) 111.3(3), O(1)–B–Rh 124.0(3), O(2)–B–Rh 124.4(3).

pyramidal[15] Rh^{III} centre with *trans*-phosphane ligands and the BzBpin group occupying the apical site. The relatively small P(2)–Rh–P(1) angle of 163.49(3)° presumably arises from steric crowding of the bulky BzBpin group. The Rh–B distance of 1.963(4) Å is well within the range observed for analogous Rh(Bcat) and -(Bpin) complexes.[14] Although the hydrido ligand was not located in the X-ray study, its presence is clearly indicated by the B–Rh–Cl angle of 108.66(10)°, and from solution NMR spectroscopic data.

Conclusions

4,4,5,5-Tetraphenyl-1,3,2-dioxaborolane (HBBzpin, **3**) has been prepared in high yield by the addition of $H_3B{\cdot}SMe_2$ to benzopinacol. HBBzpin is a relatively stable solid that reacts with a variety of alkenes under catalytic conditions to give the corresponding organoboronate esters. The resulting products are stable to air and chromatography and can be readily converted into the alcohols upon oxidative workup. Addition of HBBzpin to $RhCl(PPh_3)_3$ gave $Rh(H)Cl(BzBpin)(PPh_3)_2$ as the only new rhodium-containing product. We are in the process of examining the reactivity of this novel borylrhodium species as well as expanding the scope of hydroborations using HBBzpin and will report our findings in due course.

Experimental Section

General: Reagents and solvents were purchased from Aldrich Chemicals and used as received. NMR spectra were recorded with a JEOL JNM-GSX270 FT NMR (^{1}H 270 MHz; ^{11}B 87 MHz; ^{13}C 68 MHz; ^{19}F 254 MHz; ^{31}P 109 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^{1}H and ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B), CF_3CO_2H (^{19}F), and H_3PO_4 (^{31}P)] and coupling constants (J) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), broad (br.), and overlapping (ov.). Infrared spectra were obtained using a Mattson Genesis II FT-IR spectrometer. GC-MS analyses were conducted using a Varian Saturn 2000 MS, coupled to a CP-3800 GC. The GC was equipped with the 1177 injection port with a CP-8410 liquid autoinjector connected to an SPB-1 (Supelco) fused-silica column (30 m × 0.25 mm i.d. × 0.25 μm) attached to a 50 cm transfer line. Melting points were determined using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, ON). Reactions were performed under dinitrogen.

4,4,5,5-Tetraphenyl-1,3,2-dioxaborolane (HBBzpin) (3): Benzopinacol (4.00 g, 10.91 mmol) was added as a solid to a stirred solution of $BH_3{\cdot}SMe_2$ (6.0 mL of a 2.0 M toluene solution) over a period of 30 min. The mixture was heated to reflux for 12 h at which point the solvent was removed under vacuum. Upon washing with hexane (3 × 5 mL), HBBzpin was collected as a white solid by suction filtration. Yield: 3.50 g (85%); m.p. 132–135 °C. ^{1}H NMR (C_6D_6): δ = 7.33–7.29 (m, 8 H, Ar), 6.89–6.80 (ov. m, 12 H, Ar), 4.95 (br. s, 1 H, *H*B) ppm. ^{11}B NMR (C_6D_6): δ = 27 (br.) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 142.5, 128.8, 127.4, 127.1, 96.4 ppm. IR (N_2, nujol): $\tilde{\nu}$ = 3059, 2960, 2899, 2870, 2602, 1493, 1446, 1379, 1344, 1215, 1190, 1176, 953, 881, 746, 696, 627 cm^{-1}. $C_{26}H_{21}BO_2$ (376.28): calcd. C 82.99, H 5.64; found C 82.62, H 6.00.

General Procedure for the Hydroboration of 4-Vinylanisole in the Presence of Rh(acac)(dppb) as a Catalyst: In a typical reaction, HBBzpin (50 mg, 0.13 mmol) in C_6D_6 (0.5 mL) was added to a C_6D_6 solution (0.5 mL) of 4-vinylanisole (18 mg, 0.13 mmol) and Rh(acac)(dppb) (1 mg, 0.0015 mmol). The reaction was allowed to proceed for 18 h, at which point NMR spectroscopic data were collected. Selected NMR spectroscopic data for 4-Me-$OC_6H_4CH(BBzpin)CH_3$ (**4**): ^{1}H NMR: δ = 2.95 [q, J = 7.4 Hz, 1 H, C*H*(BBzpin)], 1.67 (d, J = 7.4 Hz, 3 H, CH_3); 4-Me-$OC_6H_4CH{=}CH(BBzpin)$ (**6**): ^{1}H NMR: δ = 8.02 (d, J = 18.5 Hz, 1 H, C*H*=CH), 6.61 (d, J = 18.5 Hz, 1 H, CH=C*H*) ppm.

4-$MeOC_6H_4CH_2CH_2$(BBzpin) (5): A toluene solution (5 mL) of HBBzpin (500 mg, 1.30 mmol) was added to a stirred toluene solution (1 mL) of 4-vinylanisole (187 mg, 1.40 mmol) and $[Cp^*IrCl_2]_2$ (11 mg, 0.014 mmol). The reaction was allowed to proceed for 18 h at which point the solvent was removed under vacuum to afford an orange oil. The oil was dissolved in hot hexane (10 mL) and passed through a small plug of silica. The volume of the solution was decreased to 5 mL under vacuum, and the solution was then stored at –30 °C to afford an off-white precipitate after several days. The solid was collected by suction filtration. Yield: 480 mg (72%); m.p. 131–133 °C. ^{1}H NMR (in C_6D_6): δ = 7.31 (d, J = 8.2 Hz, 8 H, Ar), 7.16 (d, J = 8.4 Hz, 2 H, Ar), 6.94–6.85 (ov. m, 12 H, Ar), 6.79 (d, J = 8.4 Hz, 2 H, Ar), 3.35 (s, 3 H, OCH_3), 3.00 (t, J = 7.7 Hz, 2 H, CH_2), 1.66 (t, J = 7.7 Hz, 2 H, CH_2) ppm. ^{11}B NMR (in C_6D_6): δ = 35 (br.) ppm. ^{13}C{^{1}H} NMR (in C_6D_6): δ = 158.2, 143.1, 136.0, 129.3, 128.9, 127.3, 127.0, 113.9, 96.2, 54.6, 29.2, 13.4 (br., *C*B) ppm. IR (nujol): $\tilde{\nu}$ = 2953, 2918, 2856, 1608, 1510, 1446, 1377, 1344, 1306, 1242, 1176, 1034, 1011, 966, 881, 835, 808, 764, 750, 698, 658 cm^{-1}. $C_{35}H_{31}BO_3$ (510.47): calcd. C 82.35, H 6.13; found C 82.30, H 5.77. CI-MS: m/z (%) = 510 (5) [M], 377 (12).

4-F-$C_6H_4CH_2CH_2$(BBzpin) (7): A toluene solution (5 mL) of HBBzpin (500 mg, 1.30 mmol) was added to a stirred toluene solution (1 mL) of 4-fluorostyrene (171 mg, 1.40 mmol) and $[Cp^*IrCl_2]_2$ (11 mg, 0.014 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum to afford an orange oil. The oil was dissolved in hot hexane (10 mL) and passed through a small plug of silica. The volume of the solution was decreased to 5 mL under vacuum, and the solution was then stored at –30 °C to afford a white precipitate after several days. The solid was collected by suction filtration. Yield: 510 mg (79%); m.p. 124–125 °C. ^{1}H NMR (in C_6D_6): δ = 7.30 (d, J = 8.2 Hz, 8 H, Ar), 6.97–6.76 (ov. m, 16 H, Ar), 2.86 (t, J = 7.7 Hz, 2 H, CH_2), 1.54 (t, J = 7.7 Hz, 2 H, CH_2) ppm. ^{11}B NMR (in C_6D_6): δ = 35 (br.) ppm. ^{13}C{^{1}H} NMR (in C_6D_6): δ = 161.7 (d, J_{CF} = 247 Hz, *C*-F), 143.0, 139.5 (d, J_{CF} = 2 Hz), 129.8 (d, J_{CF} = 8 Hz), 128.8, 127.3, 127.1, 115.0 (d, J_{CF} = 21 Hz), 96.2, 29.1, 13.2 (br., *C*B) ppm. ^{19}F{^{1}H} NMR (in C_6D_6): δ = –118.2 ppm. IR (nujol): $\tilde{\nu}$ = 2931, 2856, 1597, 1446, 1377, 1340, 1242, 1219, 1176, 1088, 1012, 964, 883, 841, 816, 750, 696, 660, 615, 542, 480 cm^{-1}. $C_{34}H_{28}BFO_2$ (498.43): calcd. C 81.93, H 5.67; found C 81.96, H 5.55. CI-MS: m/z (%) = 500 (3) [M]$^+$, 422 (19).

1-OctylBBzpin (8): A toluene (5 mL) solution of HBBzpin (500 mg, 1.30 mmol) was added to a stirred toluene solution (1 mL) of 1-octene (156 mg, 1.40 mmol) and $[Cp^*IrCl_2]_2$ (11 mg, 0.014 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum to afford an orange oil. The oil was dissolved in hexane (5 mL) and passed through a small plug of silica. The solvent was then removed under vacuum to afford an orange oil. Yield: 460 mg (72%). ^{1}H NMR (in C_6D_6): δ = 7.41 (d, J = 8.2 Hz, 8 H, Ar), 6.99–6.86 (ov. m, 12 H, Ar), 1.80 (quint, J = 7.9 Hz, 2 H, CH_2), 1.47–1.26 (ov. m, 12 H), 0.89 (t, J = 6.9 Hz, 3

H, CH_3) ppm. ^{11}B NMR (in C_6D_6): δ = 34 (br.) ppm. ^{13}C{^{1}H} NMR (in C_6D_6): δ = 143.3, 128.9, 127.4, 127.0, 96.0, 32.7, 32.0, 29.6, 29.5, 24.3, 22.8, 14.1, 11.5 (br., *C*B) ppm. IR (nujol): $\tilde{\nu}$ = 3059, 3027, 2927, 2856, 1601, 1493, 1446, 1379, 1327, 1225, 1176, 1080, 1036, 1003, 978, 887, 752, 700, 629 cm^{-1}. $C_{34}H_{37}BO_2$ (488.52): calcd. C 83.59, H 7.65; found C 83.25, H 7.94. CI-MS: *m*/*z* (%) = 489 (14) [M]$^+$, 412 (87).

NorbornylBBzpin (9): A toluene solution (5 mL) of HBBzpin (1.20 g, 3.19 mmol) was added to a stirred toluene solution (1 mL) of norbornylene (300 mg, 3.19 mmol) and [Cp*IrCl$_2$]$_2$ (25 mg, 0.031 mmol). The reaction was allowed to proceed for 18 h at which point the solvent was removed under vacuum to afford an orange oil. The oil was dissolved in hexane (10 mL) and passed through a small plug of silica. The volume of the solution was decreased to 5 mL under vacuum, and the solution was then stored at –30 °C to afford a white precipitate after several days. The solid was collected by suction filtration. Yield: 1.15 g (77%); m.p. 116–117 °C. ^{1}H NMR (in C_6D_6): δ = 7.39 (d, *J* = 8.2 Hz, 8 H, Ar), 6.95–6.85 (ov. m, 12 H, Ar), 2.78 (br. s, 1 H), 2.31 (br. s, 1 H), 2.13 (m, 1 H), 1.71–1.20 (ov. m, 8 H) ppm. ^{11}B NMR (in C_6D_6): δ = 34 (br.) ppm. ^{13}C{^{1}H} NMR (in C_6D_6): δ = 143.3, 128.8, 127.4, 127.0, 96.1, 39.2, 38.6, 37.0, 32.7, 32.6, 29.4, 25.8 (br., *C*B) ppm. IR (nujol): $\tilde{\nu}$ = 2964, 2908, 2861, 1599, 1493, 1460, 1446, 1410, 1375, 1311, 1227, 1173, 1016, 976, 885, 843, 748, 700, 658, 633, 607 cm^{-1}. $C_{33}H_{31}BO_2$ (470.45): calcd. C 84.25, H 6.66; found C 83.97, H 6.82. CI-MS: *m*/*z* (%) = 470 (10) [M], 393 (72).

CH$_3$C(O)(CH$_2$)$_4$BBzpin (10): A toluene solution (5 mL) of HBBzpin (760 mg, 2.04 mmol) was added to a stirred toluene solution (1 mL) of 5-hexen-2-one (200 mg, 2.04 mmol) and [Cp*IrCl$_2$]$_2$ (16 mg, 0.020 mmol). The reaction was allowed to proceed for 18 h at which point the reaction mixture was passed through a small plug of silica. Removal of the solvent under vacuum afforded a colourless oil which was triturated with MeOH (3 × 2 mL), and the resulting white solid was collected by suction filtration. Yield: 0.75 g (77%); m.p. 118–120 °C. ^{1}H NMR (in C_6D_6): δ = 7.41–7.37 (m, 8 H, Ar), 6.96–6.83 (ov. m, 12 H, Ar), 1.94 (t, *J* = 7.2 Hz, 2 H, CH_2), 1.66–1.61 (ov. m, 4 H, CH_2), 1.61 (s, 3 H, CH_3), 1.26 (t, *J* = 7.2 Hz, 2 H, CH_2) ppm. ^{11}B NMR (in C_6D_6): δ = 33 (br.) ppm. ^{13}C{^{1}H} NMR (in C_6D_6): δ = 206.0 [*C*(O)], 143.2, 128.8, 127.4, 127.1, 96.1, 43.0, 29.0, 26.5, 23.8, 11.3 (br., *C*B) ppm. IR (nujol): $\tilde{\nu}$ = 3057, 2943, 2877, 1716 (C–O), 1597, 1493, 1446, 1381, 1321, 1263, 1173, 1034, 980, 885, 756, 700, 660, 633 cm^{-1}. $C_{32}H_{31}BO_3$ (474.44): calcd. C 81.00, H 6.60; found C 80.69, H 6.92. CI-MS: *m*/*z* (%) = 474 (12) [M].

Rh(H)Cl(PPh$_3$)$_2$(BBzpin) (11): A THF solution (2 mL) of HBBzpin (162 mg, 0.43 mmol) was added to a stirred THF suspension (5 mL) of RhCl(PPh$_3$)$_3$ (400 mg, 0.43 mmol). The reaction was allowed to proceed for 18 h at which point a white precipitate was collected by suction filtration. Yield: 225 mg (50%); m.p. 144–146 °C (dec.). ^{1}H NMR (in $CDCl_3$): δ = 7.64 (m, 12 H, Ar), 7.31 (t, *J* = 7.4 Hz, 8 H, Ar), 7.18 (t, *J* = 7.4 Hz, 12 H, Ar), 6.97 (t, *J* = 7.4 Hz, 4 H, Ar), 6.86 (t, *J* = 7.4 Hz, 8 H, Ar), 6.73 (d, *J* = 7.4 Hz, 6 H, Ar), –14.34 (dt, $^1J_{HRh}$ = 28.8, $^2J_{HP}$ = 14.8 Hz, 1 H, Rh*H*) ppm. ^{11}B NMR (in $CDCl_3$): δ = 32 (br.) ppm. ^{13}C{^{1}H} NMR (in $CDCl_3$): δ = 143.0, 134.7 (t, J_{CP} = 6 Hz), 132.7 (t, J_{CP} = 23 Hz), 129.9, 129.0, 128.1 (t, J_{CP} = 5 Hz), 126.9, 126.3, 96.2 ppm. ^{31}P{^{1}H} NMR (in $CDCl_3$): δ = 40.4 (d, J_{PRh} = 124 Hz) ppm. IR (N_2, nujol): $\tilde{\nu}$ = 3037, 2897, 2854, 1599, 1479, 1464, 1433, 1379, 1215, 1149, 1095, 1026, 999, 958, 908, 883, 789, 748, 692, 634 cm^{-1}. $C_{62}H_{51}BClO_2P_2Rh$ (1039.34): calcd. C 71.64, H 4.96; found C 71.58, H 5.03.

X-ray Crystallography: Crystals of **7** and **11** (Table 1) were grown from saturated THF solutions at 5 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold stream of the goniometer. A hemisphere of data was collected with a Bruker AXS P4/SMART 1000 diffractometer using ω- and θ-scans with a scan width of 0.3° and exposure times of 10 (**7**) and 40 s (**11**). The detector distances were 5 cm. The data were reduced[16a] and corrected for absorption.[16b] The structures were solved by direct methods (**7**) or Patterson methods (**11**) and refined by full-matrix least squares on F^2.[16c] The THF molecule in **11** was disordered over two positions, and the site occupancies were determined as 0.56 [O(63)–C(67)] and 0.44 [O(63′)-C(67′)] and fixed in subsequent refinement cycles. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were found in Fourier difference maps and refined using isotropic displacement parameters. THF hydrogen atoms were included in calculated positions and refined using a riding model. CCDC-659156 and -659157 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data collection parameters for **7** and **11**.

	7	**11**·THF
Empirical formula	$C_{34}H_{28}BFO_2$	$C_{66}H_{59}BClO_3P_2Rh$
Formula mass	498.37	1111.24
Crystal dimensions [mm]	0.40 × 0.20 × 0.15	0.23 × 0.15 × 0.05
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Z	4	2
a [Å]	11.714(3)	10.483(6)
b [Å]	19.266(5)	12.899(7)
c [Å]	12.181(3)	22.037(12)
α [°]	90	105.452(8)
β [°]	105.319(3)	91.188(8)
γ [°]	90	103.838(7)
Volume [Å^3]	2651.4(11)	2777(3)
$D_{calcd.}$ [mg m^{-3}]	1.249	1.329
T [K]	173(1)	173(1)
Radiation	Mo-K_α (λ = 0.71073 Å)	
μ [mm^{-1}]	0.080	0.460
Total reflections collected	18167	18981
Total unique reflections	5905	11967
No. of variables	455	916
θ [°]	2.03–27.50	0.96–27.50
GoF on F^2	1.062	1.040
R_1[a] [$I > 2\sigma(I)$]	0.0439	0.0429
wR_2[b] (all data)	0.1164	0.1165
Largest diff peak/hole [e Å^{-3}]	0.185/–0.241	0.821/–0.528

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[F_o^4]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0307{\cdot}P)^2 + (0.7756{\cdot}P)]$ (**7**), $w = 1/[\sigma^2(F_o^2) + (0.0515{\cdot}P)^2 + (0.7756{\cdot}P)]$ (**11**), where $P = [\max(F_o^2,0) + 2{\cdot}F_c^2]/3$.

Supporting Information (see footnote on the first page of this article): Crystal data for complexes **7** and **11** and selected NMR spectroscopic data for complexes **3**–**11**.

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