Experimental Section

Compound **1** was synthesized by using mixture of DMF and water as the solvent, and TREN as a structure-directing agent. A reaction mixture containing GeO_2 (0.413 g, 3.95 mmol), TREN (2.35 g, 16.1 mmol), water (5.01 g, 278 mmol), DMF (8.01 g, 110 mmol) was stirred at room temperature over night. The mixture was heated at 180 °C in a Teflon-lined steel autoclave for seven days. Colorless needlelike crystals were obtained in approximately 70% yield (based on GeO_2).

X-ray structure analysis: Needlelike single crystals of FDU-4 ($0.20 \times 0.03 \times 0.04$ mm) were analyzed at room temperature. Crystallographic data for FDU-4: hexagonal, space group $P6_3cm$ (No. 185), $a = 23.941(3)$, $b = 23.941(3)$, $c = 9.798(2)$ Å, $V = 4863.2(14)$ Å^3; $Z = 6$; $\rho_{calcd} = 2.399\ g\,cm^{-3}$, $F(000) = 3360$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å. A full hemisphere of diffracted intensities was measured with graphite-monochromated $Mo_{k\alpha}$ radiation on a Bruker/Siemens Smart1000-CCD. Of 22955 reflections collected, 4681 were independent ($R_{int} = 0.1347$). Cell constants were obtained from least-squares refinement in the range $0.98 < \theta < 23.34°$. The Siemens/Bruker program SHELXTL-PC software package was used to solve the structure by direct methods. Refinement was by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. The final residuals were $R_1(F) = 0.0606$ with $I > 2\sigma$ and $wR_2(F^2) = 0.1551$ with $GOF(F) = 1.050$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151489. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] M. E. Davis, C. Saldarriaga, C. Montes, J. M. Garces, C. Crowder, *Nature* **1988**, *331*, 698.
[2] a) R. M. Dessau, J. G. Schlenker, J. B. Higgins, *Zeolites* **1990**, *10*, 522; b) E. T. L. Vogt, J. N. Richardson, *J. Solid State Chem.* **1990**, *87*, 469.
[3] M. Esterman, L. B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, *Nature* **1991**, *352*, 320.
[4] Q. Hu, R. Xu, S. Li, Z. Ma, J. M. Thomas, R. H. Jones, A. M. Chippindale, *J. Chem. Soc. Chem. Commun.* **1992**, 875.
[5] C. C. Freyhardt, M. Tsapatsis, R. F. Lobo, K. J. Balkus, Jr., M. E. Davis, *Nature* **1996**, *381*, 295.
[6] P. Wagner, M. Yoshikawa, M. Lovallo, K. Tsuji, M. Tsapatsis, M. E. Davis, *Chem. Commun.* **1997**, 2179.
[7] G. Y. Yang, S. C. Sevov, *J. Am. Chem. Soc.* **1999**, *121*, 8389.
[8] J. Zhu, X. Bu, P. Feng, G. D. Stucky, *J. Am. Chem. Soc.* **2000**, *122*, 11563.
[9] a) M. E. Davis, *Chem. Mater.* **1997**, *3*, 1745; b) T. E. Gier, G. D. Stucky, *Nature* **1991**, *349*, 508.
[10] H. Li, A. Laine, M. O'Keeffe, O. M. Yaghi, *Science* **1999**, *283*, 1145.
[11] R. H. Jones, J. Chen, J. M. Thomas, A. George, M. B. Hursthouse, R. Xu, S. Li, Y. Lu, G. Yang, *Chem. Mater.* **1992**, *4*, 808.
[12] a) H. Li, M. Eddoudi, D. A. Richardson, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 8567; b) H. Li, M. Eddaoudi, O. M. Yaghi, *Angew. Chem.* **1999**, *111*, 682; *Angew. Chem. Int. Ed.* **1999**, *38*, 653.
[13] X. Bu, P. Feng, G. D. Stucky, *Science* **1997**, *278*, 2080.
[14] P. Feng, X. Bu, G. D. Stucky, *Nature* **1997**, *388*, 735;
[15] X. Bu, P. Feng, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 11204.
[16] G. O. Brunner, W. M. Meier, *Nature* **1989**, *337*, 146.
[17] G. S. Smith, P. B. Isaacs, *Acta Crystallogr.* **1964**, *17*, 842.
[18] a) C. Cascales, E. Gutierrez-Puebla, M. A. Monge, C. Ruiz-Valero, *Angew. Chem.* **1998**, *110*, 135; *Angew. Chem. Int. Ed.* **1998**, *37*, 129; b) C. Cascales, E. Gutierrez-Puebla, M. Iglesias, M. A. Monge, C. Ruiz-Valero, *Angew. Chem.* **1999**, *111*, 2592; Angew. *Chem. Int. Ed.* **1999**, *38*, 2436; c) M. S. Dadachov, K. Sun, T. Conradsson, X. Zou, *Angew. Chem.* **2000**, *112*, 3820; *Angew. Chem. Int. Ed.* **2000**, *39*, 3674;
[19] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710; b) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548.

Formation of Aryl- and Benzylboronate Esters by Rhodium-Catalyzed C–H Bond Functionalization with Pinacolborane**

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The catalytic functionalization of unreactive C–H bonds remains one of the major challenges in chemistry.[1] Metal–boryl systems have been shown to promote stoichiometric[2] and photocatalytic[3] conversion of alkane and arene C–H bonds into $C-B(OR)_2$ groups by using B_2pin_2 (pin = $OCMe_2CMe_2O$). A [Cp*Ir] complex catalyzes[4] the borylation of benzene with pinacolborane (HBpin), with about three turnovers obtained at 150 °C, and a related complex [Cp*Rh(η^6-C_6Me_6)] is an excellent catalyst[5] for aliphatic and aromatic C–H bond borylation at 150 °C, with B_2pin_2 being more effective than HBpin. As part of our studies of the reactivity of B–H bonds with Rh and Ir complexes,[6] we report herein that $[RhCl(PiPr_3)_2(N_2)]$ (**1**)[7] is an efficient catalyst precursor for the borylation of aromatic and benzylic C–H bonds with HBpin, and that high selectivity for benzylic C–H functionalization was observed for the first time with toluene, *p*-xylene, and mesitylene. The boronate ester products represent an important class of synthetic intermediates.[8]

The reaction of 0.2 M HBpin[9] with benzene in the presence of 1.0 mol% of **1** at 140 °C gave PhBpin in 62% yield (62 turnovers) after 14 h and in 86% yield after 58 h (Scheme 1). When 0.3 mol% of **1** was used, 67% (222 turnovers) of PhBpin was obtained after 104 h. The yield improved at lower HBpin concentrations. Thus, with 1.0 M HBpin in benzene, PhBpin was obtained in 20% yield after 58 h, whereas dilution with hexane (fourfold) improved the yield to 35% in the same time. This effect can be attributed to degradation of HBpin, which is strongly concentration dependent.[10] In addition to PhBpin, the dehydrodimerization product B_2pin_2 was formed, especially with higher concentrations of HBpin (ca. 7% for 1.0 M HBpin in benzene).

Toluene was less active than benzene, indicating that the methyl group deactivates the arene C–H bonds (Table 1, entry 1). Interestingly, the main product, $PhCH_2Bpin$, was not

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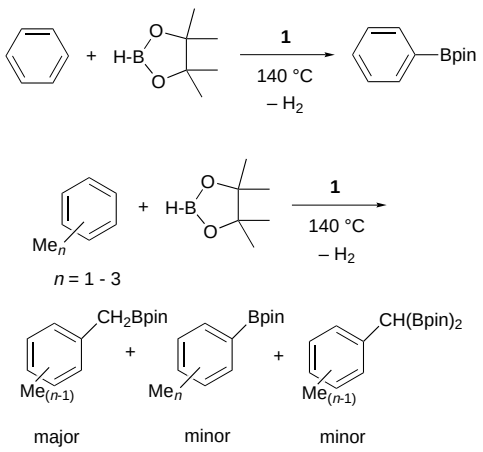

Scheme 1. Reaction of HBpin with benzene and methylarenes catalyzed by **1**.

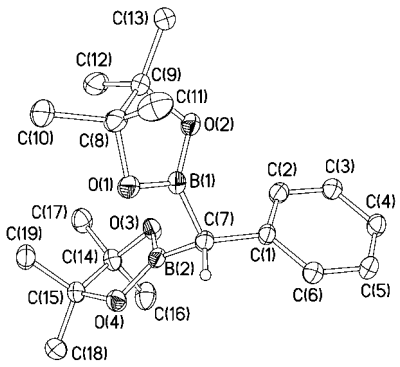

Figure 1. Molecular structure of $PhCH(Bpin)_2$ with hydrogen atoms, other than the benzylic one on C(7), omitted for clarity. Selected bond lengths [Å]: C(7)-B(1) 1.577(2), C(7)-B(2) 1.592(2), B-O (av) 1.370(6), C-O (av) 1.472(3).

derived from aromatic C–H activation but from benzylic C–H activation. In addition, one diborylated compound was formed which was confirmed to be $PhCH(BPin)_2$ by X-ray diffraction (Figure 1).[11] Its yield of up to 7% is much higher than would be expeected from the toluene/HBpin molar ratio of 47/1, indicating that the Bpin substituent activates the remaining benzylic C–H bonds.

We examined $[\{Cp^*RhCl_2\}_2]$ as a precursor for the "Cp*Rh" system[5] and found that it shows completely different selectivity from **1** for toluene borylation. After 36 h at 140 °C, using 0.2 M HBpin in toluene, 0.5 mol% of $[\{Cp^*RhCl_2\}_2]$ gave a 62% yield of monoborylated toluenes. The *m*-isomer, $3\text{-}MeC_6H_4Bpin$, was the main product ($o:m:p = 5:65:30$). Only a trace ($\leq 0.5\%$) of $PhCH_2Bpin$ was formed along with about 0.1% (based on GC-MS integration) of two isomeric disubstituted products, which have different GC retention times from that of $PhCH(Bpin)_2$.

As with toluene, *p*-xylene and mesitylene also reacted with HBpin in the presence of **1** to give benzylic substitution products (Table 1, entries 6 and 7). In contrast to "Cp*Rh",[5] **1** did not catalyze the borylation of benzene with B_2pin_2, nor the reaction of simple alkanes with HBpin under our conditions.

As in some cases the formation of a black deposit was observed, we investigated whether the catalysis proceeds homogeneously or heterogeneously. Inhibition by dibenzo[*a*,*e*]cyclooctatetraene (DCT), a useful check for homogeneity of catalysis,[12] proved unsuitable for the present reaction as the double bonds can be hydroborated by a noncatalytic reaction (Table 1, entry 2). Addition of Hg[12, 13] did not alter selectivity (Table 1, entry 3); the decrease in yield is not nearly as significant as would be expected for a heterogeneous process, and can be attributed to an Hg-enhanced rate of HBpin degradation. This supports the homogeneity of the catalytic borylation. The strong preference for benzylic functionalization could indicate a radical mechanism; however, addition of the radical inhibitor $2,6\text{-}tBu_2\text{-}4\text{-}Me\text{-}C_6H_2OH$ (BHT) did not affect significantly either activity or selectivity (Table 1, entry 4).

The oxidative addition of HBpin to **1** yielding *trans*-$[Rh(Cl)(H)(BPin)(PiPr_3)_2]$ (**2**) is very slow at room temper-

Table 1. Reaction of methylarenes with HBpin catalyzed by **1**.[a]

Entry	Arene	Time [h]	Additive (amount)	Total yield of borylated toluenes [%][b]	Product ratio $PhCH_2Bpin$:2-MeC_6H_4Bpin:3-MeC_6H_4Bpin:4-MeC_6H_4Bpin
1	toluene	14		40(3)	85:3:9:3
		58		64(5)	82:3:11:4
		80		69(7)	81:3:12:4
2	toluene	14	DCT[c] (2.4%)	36(2)	84:3:10:3
3	toluene	14	Hg (0.1 mL)	21(2)	87:3:7:3
4	toluene	14	BHT[d] (50%)	34(2)	86:2:9:3
5[e]	toluene	14		48(4)	83:3:10:4
6	*p*-xylene	80		41[f]	98:2[g]
7	mesitylene	80		17[h]	

[a] In an N_2 filled glove box, a 15-mL tube with a Young's tap was charged with **1** (2.0 mg, 0.0041 mmol, 1.0 mol%), HBpin (58 μL, 0.40 mmol), *n*-dodecane (standard for GC analysis, 0.065 mmol), and methylarene (2.0 mL). The mixture was heated at 140 °C. Small samples were removed periodically for GC (FID) and GC-MS analysis. Yields and product ratios were determined by GC and are based on HBpin. The product can be isolated by bulb-to-bulb distillation or silica gel chromatography. [b] Includes $PhCH(Bpin)_2$ for which the yield is also shown separately in parenthesis. [c] Dibenzo[*a*,*e*]cyclooctatetraene (DCT), 2.4 mol% based on HBpin; see text. [d] $2,6\text{-}tBu_2\text{-}4\text{-}Me\text{-}C_6H_2OH$, 50 mol% based on HBpin; see text. [e] 1.0 mol% of **2** was used instead of **1**. [f] Yield of $4\text{-}MeC_6H_4CH_2Bpin$. [g] Ratio of monoborylated products. The minor isomer (probably $2,5\text{-}Me_2C_6H_3Bpin$) was only characterized by GC-MS. Two bisborylated compounds (4:1 by GC) were also observed. The GC ratio of mono:bisborylated compounds = 95:5. [h] Yield of $3,5\text{-}Me_2C_6H_3CH_2Bpin$. No other isomer was detected. In addition, two bisborylated compounds and one trisborylated compound were detected by GC-MS. The ratio of borylated products = 85:6:8:1 in the order of their GC retention times.

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ature, but almost instantaneous at 140 °C. The structure of **2** was determined by X-ray diffraction (Figure 2).[11] The coordination of the Rh atom in **2** is intermediate between trigonal-bipyramidal (with the phosphane ligands in axial positions) and square-pyramidal with the apical site occupied

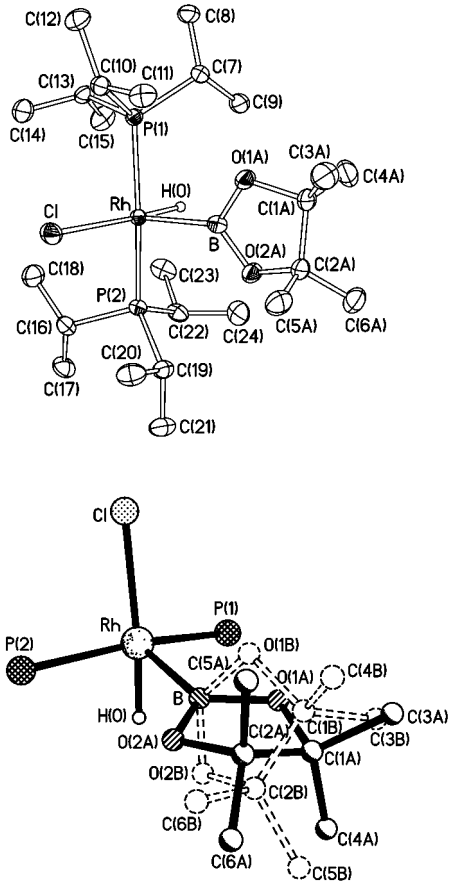
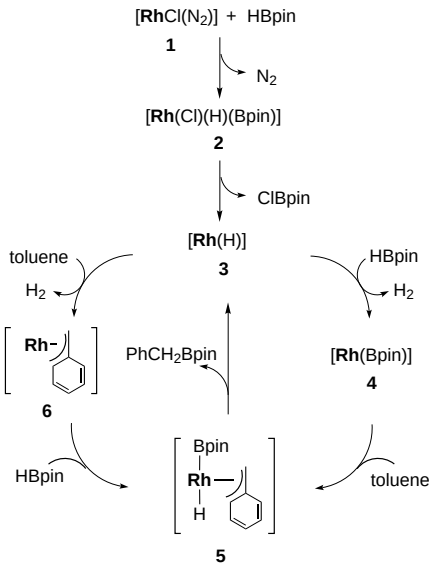


Figure 2. Top: Molecular structure of **2** with hydrogen atoms, other than the rhodium hydride H(0), omitted for clarity. Bottom: The boryl ligand is disordered between two positions with occupancies 85.3(2) % (solid) and 14.7(3) % (dashed). Selected bond lengths [Å] and angles [°]: Rh-P(1) 2.3476(4), Rh-P(2) 2.3442(4), Rh-Cl 2.4392(4), Rh-B 1.9812(15), Rh-H(1) 1.47(2), B-O(1) 1.391(2), B-O(2) 1.379(2); P(1)-Rh-P(2) 163.87(1), P(1)-Rh-Cl 93.25(1), P(2)-Rh-Cl 94.35(1), P(1)-Rh-B 94.32(4), P(2)-Rh-B 94.70(4), Cl-Rh-B 117.73(4), H(1)-Rh-P(1) 85.6(8), H(1)-Rh-P(2) 84.9(8), H(1)-Rh-Cl 172.2(8), H(1)-Rh-B 70.0(8).

by the boryl ligand which is disordered between two orientations by a 114° rotation around the Rh–B bond (Figure 2, bottom). The acute H-Rh-B angle of 70.0(8)° results in a short H···B distance of 2.02(3) Å, suggesting a small degree of residual H···B bonding.[14] The boron atom has a trigonal-planar geometry. The observed Rh–H bond length of 1.47(2) Å is in agreement with neutron diffraction determinations[15] of 1.54–1.58 Å, foreshortened as expected in the X-ray structure.

The isolated complex **2** also catalyzed the reaction of HBpin with toluene to give borylated products with the same ratio and slightly better yield than when using **1** (Table 1, entry 5). NMR analysis of a solution of HBpin in toluene containing 10 mol % of **1** which had been kept at 140 °C for 14 h, showed **2** to be the main Rh species present. However, the reaction of isolated **2** with benzene or toluene in the absence of HBpin at 140 °C for 14 h gave only about 5 % of PhBpin or $PhCH_2Bpin$, respectively. In a separate experiment, reaction of **2** with benzene, monitored by NMR spectroscopy, yielded a large amount of Cl-Bpin (^{11}B NMR: $\delta = 28.1$), an unidentified boron species (^{11}B NMR: $\delta = 34.4$), free $PiPr_3$, and $[Rh(Cl)(H)_2(PiPr_3)_2]$[16] ($^{31}P\{^1H\}$ NMR: $\delta = 63.5$, d, $J_{Rh,P} = 114$ Hz; ^1H NMR: $\delta = -22.8$, dt, 1H, $J_{Rh,H} = 26$, $^2J_{P,H} = 14$ Hz). The same reaction in the presence of one equivalent (to **2**) of HBpin gave a large amount (ca. 30 % by ^{11}B NMR) of PhBpin along with ClBpin, the unidentified boron species, and a small amount of B_2pin_3.

The reaction mechanism outlined in Scheme 2 is consistent with the above observations. Reductive elimination of ClBpin from **2** forms 14-electron $[RhH(PiPr_3)_2]$ (**3**).[17] Oxidative



Scheme 2. A possible reaction mechanism for the formation of $PhCH_2Bpin$. **Rh** = $Rh(PiPr_3)_2$.

addition of HBpin to **3** and reductive elimination of H_2 gives boryl complex **4**, which inserts into the benzylic C–H bond of toluene to form η^3-benzyl complex **5**.[18] Reductive elimination of $PhCH_2Bpin$ from **5** regenerates **3**. Alternatively, **3** may react with toluene to form η^3-benzyl complex **6**,[18] which then reacts with HBpin to form **5**. The formation of B_2pin_2 as a by-product, especially at high HBpin concentrations, can be explained by the oxidative addition of HBpin to **4** to form $[RhH(Bpin)_2(PiPr_3)_2]$, from which reductive elimination of B_2pin_2 regenerates **3**. The catalytic dehydrodimerization of HBpin to $B_2pin_2 + H_2$ represents a potentially useful new route to diboron(4) compounds.

In conclusion, **1** is an efficient homogeneous catalyst precursor for direct borylation of C–H bonds in benzene and methylarenes to form phenyl- and benzylboronate esters. The high degree of benzyl selectivity with toluene, *p*-xylene, and mesitylene is attributed to the formation of η^3-benzyl intermediates which are well known in $[Rh(PiPr_3)_2]$ and related systems. An examination of the scope and mechanism of the reaction, the potential for catalytic asymmetric borylations, and further studies regarding HBpin degredation are in progress.

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Experimental Section

HBpin was prepared by the procedure of Knochel et al. from $BH_3 \cdot SMe_2$ and pinacol.[9] After distillation, the product, which contained a small amount of unreacted $BH_3 \cdot SMe_2$, was treated with additional pinacol and redistilled to give pure HBpin. A commercial sample of HBpin (Aldrich) was also found to contain a small amount of $BH_3 \cdot SMe_2$. For a typical catalytic procedure, see Table 1.

2: A solution of **1** (230 mg, 0.47 mmol) and HBpin (132 mg, 1.0 mmol) in benzene (6 mL) was heated at 120 °C for 18 min under N_2. After the solution had been cooled, the volatiles were removed in vacuo. The solid residue was dissolved in hexane (1.5 mL) and filtered through a membrane filter (0.20 μm), and the filter was washed with hexane (2×0.8 mL). The combined hexane solution was cooled at -40 °C to give light brownish yellow crystals. The liquid portion was quickly removed by syringe, and the crystals were washed with cold hexane (ca. -40 °C, 2×1 mL) and dried in vacuo to give **2** (218 mg; 79 % yield). ^{1}H NMR (299.9 MHz, $CDCl_3$): $\delta = -16.81$ (dt, $J_{Rh,H} = 28$, $^2J_{P,H} = 14$ Hz, 1H), 1.14 (s, 12H), 1.28 (quasi quint, $J = 7$ Hz, 36H), 2.47 – 2.65 (m, 6H); ^{11}B{^{1}H} NMR (96.22 MHz, $CDCl_3$): $\delta = 31.8$; ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): $\delta = 52.3$ ($J_{Rh,P} = 116$ Hz); elemental analysis (%) calcd for $C_{24}H_{55}BClO_2P_2Rh$: C 49.12, H 9.45; found: C 49.30, H 9.57.

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[1] See, for example: W. D. Jones, *Science* **2000**, *287*, 1942 – 1943, and references therein.

[2] a) K. Waltz, X. He, C. Muhoro, J. F. Hartwig, *J. Am. Chem. Soc.* **1995**, *117*, 11357 – 11358; b) K. M. Waltz, J. F. Hartwig, *Science* **1997**, *277*, 211 – 213; c) K. M. Waltz, C. N. Muhoro, J. F. Hartwig, *Organometallics* **1999**, *18*, 3383 – 3393; d) K. M. Waltz, J. F. Hartwig, *J. Am. Chem. Soc.* **2000**, *122*, 11358 – 11369.

[3] H. Chen, J. F. Hartwig, *Angew. Chem.* **1999**, *111*, 3597 – 3599; *Angew. Chem. Int. Ed.* **1999**, *38*, 3391 – 3393.

[4] C. N. Iverson, M. R. Smith III, *J. Am. Chem. Soc.* **1999**, *121*, 7696 – 7697.

[5] a) H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, *Science* **2000**, *287*, 1995 – 1997; b) a related study was published after the submission of our manuscript: J.-Y. Cho, C. N. Iverson, M. R. Smith III, *J. Am. Chem. Soc.* **2000**, *122*, 12868 – 12869.

[6] a) R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams, T. B. Marder, *J. Am. Chem. Soc.* **1990**, *112*, 9399 – 9400; b) S. A. Westcott, N. J. Taylor, T. B. Marder, R. T. Baker, N. J. Jones, J. C. Calabrese, *J. Chem. Soc. Chem. Commun.* **1991**, 304 – 305; c) K. Burgess, W. A. van der Donk, S. A. Westcott, T. B. Marder, R. T. Baker, J. C. Calabrese, *J. Am. Chem. Soc.* **1992**, *114*, 9350 – 9359; d) S. A. Westcott, T. B. Marder, R. T. Baker, J. C. Calabrese, *Can. J. Chem.* **1993**, *71*, 930 – 936; e) P. Nguyen, H. P. Blom, S. A. Westcott, N. J. Taylor, T. B. Marder, *J. Am. Chem. Soc.* **1993**, *115*, 9329 – 9330; f) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685 – 2722.

[7] a) C. Busetto, A. D'Alfonso, F. Maspero, G. Perego, A. Zazzetta, *J. Chem. Soc. Dalton Trans.* **1977**, 1828 – 1834; b) D. L. Thorn, T. H. Tulip, J. A. Ibers, *J. Chem. Soc. Dalton Trans.* **1979**, 2022 – 2025; c) H. Werner, J. Wolf, A. Höhn, *J. Organomet. Chem.* **1985**, *287*, 395 – 407; d) P. Binger, J. Haas, G. Glaser, R. Goddard, C. Krüger, *Chem. Ber.* **1994**, *127*, 1927 – 1929.

[8] a) A. Pelter, K. Smith, H. C. Brown, *Borane Reagents*, Academic Press, London, **1988**; b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457 – 2483; c) A. Suzuki in *Metal-catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, pp. 49 – 97.

[9] C. E. Tucker, J. Davidson, P. Knochel, *J. Org. Chem.* **1992**, *57*, 3482 – 3485.

[10] Heating HBpin at 140 °C in benzene gave several new compounds including B_2pin_3 (see: W. Clegg, A. J. Scott, C. Dai, G. Lesley, T. B. Marder, N. C. Norman, L. Farrugia, *Acta Crystallogr. Sect. C* **1996**, *52*, 2545 – 2547), and a trace (ca. 0.5 %) of PhBpin. HBpin degradation was completely suppressed by addition of about 2 mol % of P*i*Pr$_3$, P*t*Bu$_3$, or pyridine which bind BH_3. It seems likely that BH_3 can promote further degradation of both HBpin and catalyst. For a study of HBcat (cat = 1,2-$O_2C_6H_4$) degradation, see: S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker, J. C. Calabrese, *Inorg. Chem.* **1993**, *32*, 2175 – 2182.

[11] X-ray diffraction experiments were performed with a SMART 1K CCD area detector ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $2\theta \leqslant 58°$). Crystal data for PhCH(Bpin)$_2$: $C_{19}H_{30}B_2O_4$, $M_r = 344.05$, monoclinic space group $P2_1/n$ (no. 14), $a = 11.810(1)$, $b = 11.503(1)$, $c = 15.721(1)$ Å, $\beta = 111.96(1)°$, $V = 1980.7(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.154$ g cm^{-3}, $\mu = 0.08$ cm^{-1}, $T = 100$ K, 23721 reflections (5258 unique), 242 refined parameters, $R = 0.059$ (3853 data with $I > 2\sigma(I)$), $wR(F^2) = 0.165$, residual electron density -0.28 to 0.45 e Å^{-3}. Crystal data for **2**: $C_{24}H_{55}BClO_2P_2Rh$, $M_r = 586.79$, monoclinic space group $P2_1/n$ (no. 14), $a = 10.691(1)$, $b = 14.990(1)$, $c = 19.129(1)$ Å, $\beta = 91.12(1)°$, $V = 3065.0(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.272$ g cm^{-3}, $\mu = 0.77$ cm^{-1}, $T = 120$ K, 40809 reflections (8120 unique), absorption correction by numerical integration (transmission 0.677 to 0.913), reducing R_{int} from 0.064 to 0.027, 359 refined parameters, $R = 0.022$ (7531 data with $I > 2\sigma(I)$), $wR(F^2) = 0.052$, residual electron density -0.32 to 0.46 e Å^{-3}. The hydride H atom was revealed in the difference Fourier map and refined isotropically. The experiment was repeated with a different crystal, giving the same geometry (including the disorder and the location of the hydride ligand) within experimental error. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151581 (**1**) and CCDC-151582 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] D. R. Anton, R. H. Crabtree, *Organometallics* **1983**, *2*, 855 – 859. Classical hydroboration of one of the C=C bonds of the diene removes its ability to inhibit catalysis through strong bidentate binding to the Rh center.

[13] a) Y. Lin, R. G. Finke, *Inorg. Chem.* **1994**, *33*, 4891 – 4910; b) R. J. Young, Jr., V. V. Grushin, *Organometallics* **1999**, *18*, 294 – 296.

[14] a) C. Widauer, H. Grützmacher, T. Ziegler, *Organometallics* **2000**, *19*, 2097 – 2107; b) for σ-borane complexes of Mn and Re involving HBpin see: S. Sabine, J. F. Hartwig, *J. Am. Chem. Soc.* **2000**, *122*, 9435 – 9443.

[15] a) M.-J. Fernandez, P. M. Bailey, P. O. Bentz, J. S. Ricci, T. F. Koetzle, P. M. Maitlis, *J. Am. Chem. Soc.* **1984**, *106*, 5458 – 5463; b) D. Hanke, K. Wieghardt, B. Nuber, R.-S. Lu, R. K. McMullan, T. F. Koetzle, R. Bau, *Inorg. Chem.* **1993**, *32*, 4300 – 4305.

[16] R. L. Harlow, D. L. Thorn, R. T. Baker, N. L. Jones, *Inorg. Chem.* **1992**, *31*, 993 – 997.

[17] T. Yoshida, T. Okano, D. L. Thorn, T. H. Tulip, S. Otsuka, J. A. Ibers, *J. Organomet. Chem.* **1979**, *181*, 183 – 201.

[18] a) The formation of an η^3-benzyl complex from *p*-xylene and [Cp*Ir(PMe$_3$)(Me)(OSO$_2$CF$_3$)] has been reported: P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 10462 – 10463; b) for [(η^3-benzyl)Rh(P*i*Pr$_3$)$_2$] (**6**) see: H. Werner, M. Schäfer, O. Nürnberg, J. Wolf, *Chem. Ber.* **1994**, *127*, 27 – 38.