Transition-Metal-Catalyzed Addition of Catecholborane to α-Substituted Vinylarenes: Hydroboration vs Dehydrogenative Borylation

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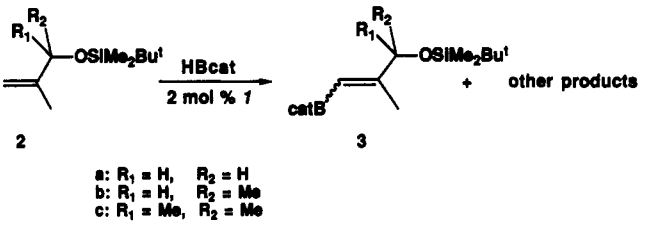
Summary: Addition of catecholborane to vinylarenes in the presence of Wilkinson's catalyst, [RhCl(PPh$_3$)$_3$], gives Markovnikov hydroboration products exclusively, whereas the corresponding reaction with α-substituted vinylarenes gives good yields of vinylboronate esters resulting from dehydrogenative borylation.

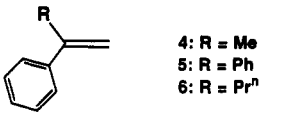
There has been considerable interest in synthetic applications of transition metal-catalyzed hydroboration of alkenes.[1] We reported recently[2] that hydroborations of sterically hindered alkenes using catecholborane, HBcat (cat = 1,2-O$_2$C$_6$H$_4$), carried out in the presence of Wilkinson's catalyst, [RhCl(PPh$_3$)$_3$] (1), are complicated by deleterious side reactions such as alkene isomerization and hydrogenation, as well as hydroboration by BH$_3$ derived from Rh-mediated HBcat degradation.[3a] With allylic silyl ethers 2 significant quantities of vinylboronate esters 3 were formed as well (Scheme I).[2]

Formation of vinylboronate esters in these reactions complements an earlier observation by Sneddon et al. who obtained vinylboranes from PdBr$_2$-catalyzed reactions of alkenes with pentaborane[4] and borazine.[5] Brown and Lloyd-Jones reported recently that vinylboronate esters were obtained, along with equal quantities of hydrogenation products, in Rh-catalyzed hydroborations of vinylarenes using phosphine-free rhodium complexes.[6] In contrast, analogous reactions using rhodium phosphine complexes give alkylboronate esters exclusively. As part

Scheme I



of our ongoing investigations[1g,2,3] into metal-catalyzed hydroborations, we report herein that product distributions from addition of HBcat to α-substituted vinylarenes 4–6 can be controlled by judicious choice of catalyst precursor.



Results and Discussion

Reactions of 2-phenylpropene (4) with 1.1 equiv of HBcat in THF-d_8 in the presence of a wide variety of Rh and Ir catalyst precursors were monitored by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy (Table I). The products observed in solution (Scheme II) were terminal (7) and internal (8) hydroboration products, (*E*)-vinylboronate ester (VBE, 9), bis(boronate ester) (10) (from hydroboration of 9), and isopropylbenzene (11) (from hydrogenation). Most reactions were complete within 1 h, although some unreacted 4 remained when significant amounts of 10 were formed. Note that 1,1-disubstituted vinylboronate esters such as 9 cannot be prepared by conventional alkyne hydroboration.[7] Compounds 7 and 8 were reported previously,[1g] and 9 and 10 were isolated (see Experimental Section) and characterized by high-resolution MS and multinuclear NMR spectroscopy. The trans relationship between methyl and vinyl CH groups in VBE 9 was assigned on the basis of a ^{1}H NMR NOE study.[8]

† Contribution No. 6290.

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(5) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 6201.

(6) Brown, J. M.; Lloyd-Jones, G. C. *J. Chem. Soc., Chem. Commun.* **1992**, 710.

(7) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.

(8) Irradiation of the methyl group of 2-phenylpropene (4) gave 6% and 4% intensity reductions in the ^{1}H NMR resonances of the phenyl ortho hydrogens and cis vinyl hydrogen, respectively. For VBE 9, the same experiment only affected the phenyl ortho hydrogens (6% intensity reduction). In addition, the four-bond HH coupling constants in 4 are 0.8 (vinyl trans to methyl) and 1.8 Hz (cis), and $^4J_{HH}$ = 0.9 Hz for 9.

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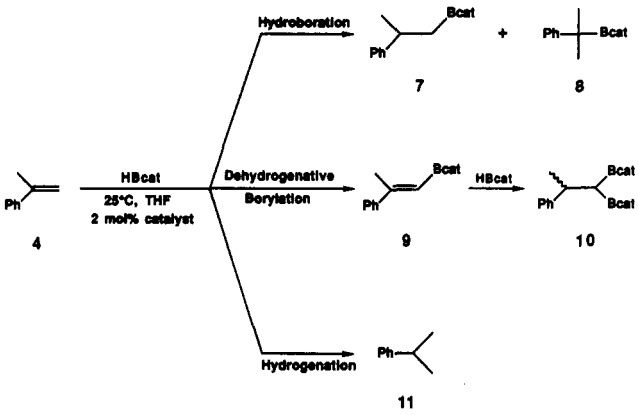
Table I. Hydroboration of 2-Phenylpropene (4)[a]

entry	catalyst	amt, % 7	8	9	10	11
1	$[RhCl(COE)_2]_2/2PPh_3$	98				2
2	$[IrCl(COE)_2]_2/2PPh_3$	98				2
3	$[Ir(acac)(COE)_2]$	95				5
4	$[RhCl(N_2)(PPr^i_3)_2]$	90	1			9
5	$[IrCl(COE)_2]_2/4PPh_3$[b]	89		6		5
6	$[RhCl(DCPE)]_2$	88	6	1		5
7	$[Rh(acac)(COE)_2]$	87	1	4		8
8	$[RhCl(COD)]_2$	86	5	2		7
9	$[RhCl(COE)_2]_2$	75	3	4	4	14
10	$[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$	72		13		15
11	$[Rh(COD)(DPPB)]SbF_6$	65	35			
12	$[IrCl(COE)_2]_2$	56	8	3	6	27
13	$[RhCl\{P(o\text{-}O\text{-}tol)_3\}_3]$	52	3	4	31	10
14	$[RhH(DPPP)_2]$[c]	38	50			12
15	$[Rh(COD)(DPPB)]BF_4$[d]	30	70			
16	$[RhCl(PPh_3)_3]$	14	3	53	27	3
17	[Rh(acac)(DPPB)][e]	5	95			

[a] All reactions were carried out in THF at 25 °C for 1 h with alkene/catecholborane/catalyst = 1.0/1.1/0.02. Product ratios were determined by ^{13}C and ^1H NMR spectroscopy. [b] Significant amounts (ca. 31%) of product arising from addition of BH_3 to 4. Conversion was only 35% after 24 h. [c] 52% products arising from addition of BH_3. [d] Reference 1e. [e] Reference 1g. DCPE = 1,2-bis(dicyclohexylphosphino)ethane; DPPE = 1,2-bis(diphenylphosphino)ethane; DPPP = 1,3-bis(diphenylphosphino)propane; DPPB = 1,4-bis(diphenylphosphino)butane; COD = 1,5-cyclooctadiene; COE = *cis*-cyclooctene; acac = acetylacetonate (2,4-pentanedionate).

Scheme II



Use of multinuclear NMR spectroscopy to investigate the primary products of these catalyzed hydroborations often gives a clearer picture of reaction selectivity than that obtained by analysis of organic derivatives. For instance, while standard oxidative workup (dilute alkaline hydrogen peroxide) converts alkylboronate and vinylboronate esters into the corresponding alcohol and aldehyde, respectively, oxidation of bis(boronate ester) **10** gives both aldehyde and alcohol,[9] thus complicating the assessment of hydroboration selectivity (vs dehydrogenative borylation). In several cases, such as hydroborations using 18e⁻ catalyst precursor $RhH(DPPP)_2$ (entry 14, DPPP = 1,3-bis(diphenylphosphino)propane), significant quantities of BH_3-derived trialkylborane $B(CH_2CHMePh)_3$ were also observed. Oxidation of this trialkylborane would give the terminal alcohol, leading to an *apparent* decrease in the Markovnikov regioselectivity of the catalyzed hydroboration.

Product distributions from hydroborations of **4** were extremely sensitive to the nature and number of phosphine ligands coordinated to the metal center. Results of this study showed the following: (i) Hydroboration products predominated, but phosphine-free catalyst precursors (Table I, entries 7–10, 12), with the exception of Ir(acac)-$(COE)_2$ (entry 3, COE = *cis*-cyclooctene), all gave both hydrogenation and VBE formation. (ii) Addition of 1 equiv of PPh_3 per metal to $[MCl(COE)_2]_2$ (entries 1, 2) shut down VBE formation and afforded terminal hydroboration product **7** with selectivities rivaling that of borane itself. For M = Ir, addition of 2 equiv of PPh_3 per Ir (entry 5) inhibited addition of HBcat to **4** and gave significant amounts of trialkylborane. (iii) Rh(acac)(DPPB) (acac = acetylacetonate, DPPB = 1,4-bis(diphenylphosphino)-butane) gave internal hydroboration product **8** with excellent regiocontrol and no hydrogenation. (iv) $RhCl(PPh_3)_3$ (**1**) and its phosphite analog $RhCl\{P(O\text{-}o\text{-}tol)_3\}_3$ are unusual, giving up to *80% VBE-derived products* (***9***, ***10***) *with minimal hydrogenation.* We therefore investigated in detail catalysis with **1** and closely related complexes (Table II).

Product distributions were tuned easily by minor changes in reaction conditions. Varying the molar ratio of HBcat to 2-phenylpropene from 0.5 to 2.0 increased the amount of bis(boronate ester) at the expense of VBE, while decreasing the amount of hydrogenation product. Use of noncoordinating solvents, such as C_6D_6 or CD_2Cl_2, however, increased hydrogenation significantly. In contrast to hydroborations of allylic silyl ethers **2**,[2] exposure of **1** to air for 24 h prior to use in reactions with 2-phenylpropene slightly increased the amount of VBE-derived products (entry 6). While addition of 10 equiv of PPh_3 to the catalyst solution also maximized production of VBE-derived products,[2,10] minor perturbations in the phosphine ligands coordinated to the metal center had the most profound effect on overall product distribution.[1g,11]

Electronic effects induced by para-substitution of PPh_3 ligands in **1** altered both rates and selectivities of HBcat addition to 2-phenylpropene (Table II, entries 11, 12). For X = F, the rate of disappearance of **4** was retarded without affecting product distribution, whereas, for X = OMe, a significant decrease in VBE-derived products was observed with rates comparable to those using **1**. Reducing steric congestion in **1** by "tying back" two of the phenyl rings (via an ortho C–C bond) increased dramatically formation of internal hydroboration product **8** while decreasing significantly the yield of VBE-derived products (entry 13). Replacing one of the phenyl rings with an alkyl group also decreased formation of **9** and **10**, regardless of the size of the alkyl group (entries 14, 15). The highest yield of **9** was obtained by substituting one phenyl ring for a bulkier aryl ring (entry 16). In preparative experiments, isolation of **9** was facilitated by its propensity to crystallize directly from the reaction mixture in THF.

We examined the reactivity of several other substituted vinylarenes to elucidate the role of substituents on overall product distribution. While β-substituted vinylarenes such as (*E*)-1-phenylpropene and indene both gave hydroboration products exclusively,[1a-g] addition of HBcat to 1,1-diphenylethene (**5**) and 2-phenylpent-1-ene (**6**) catalyzed by **1** gave significant quantities of the corre-

(9) The alcohol arises from initial hydrolysis of bis(boronate ester) **10**, followed by oxidation: Pasto, D. J.; Arora, S. K.; Chow, J. *Tetrahedron* **1969**, *25*, 1571.

(10) Similar effects of added phosphine ligands on product distributions have been observed for rhodium-catalyzed hydrocarbonylation of alkenamides: Ojima, I.; Korda, A.; Shay, W. R. *J. Org. Chem.* **1991**, *56*, 2024.

(11) Matsumoto, Y.; Naito, M.; Hayashi, T. *Organometallics* **1992**, *11*, 2732.

Table II. Hydroboration of 2-Phenylpropene (4) Using [RhCl(PPh$_3$)$_3$] (1) and Related Complexes[a]

entry	catalyst	solvent	amt of HBcat, equiv	amt, % 7	8	9	10	9 + 10	11
1	**1**	THF-d_8	0.5	11	4	57	13	70	15
2	**1**	THF-d_8	1.1	14	3	53	27	80	3
3	**1**	THF-d_8	2.0	15	5	13	67	80	
4	**1**/2PPh$_3$	THF-d_8	1.1	8	4	68	16	84	4
5	**1**/10PPh$_3$	THF-d_8	1.1	10	1	70	18	88	1
6	**1**/air[b]	THF-d_8	1.1	9	4	63	23	86	1
7	**1**	neat	1.1	11	6	41	37	78	5
8	**1**	C_6D_6	1.1	5	2	50	14	64	29
9	**1**	CD_2Cl_2	1.1	4	1	47	12	59	36
10	[RhCl(PPh$_3$)$_2$]$_2$	CD_2Cl_2	1.1	18	1	35	11	46	35
11	RhCl[P(*p*-F-Ph)$_3$]$_3$	THF-d_8	1.1	13	3	55	23	78	6
12	RhCl[P(*p*-OMe-Ph)$_3$]$_3$	THF-d_8	1.1	22	7	34	34	68	3
13	RhCl(5-Ph-BPI)$_3$[c]	THF-d_8	1.1	18	45	15	18	33	4
14	[RhCl(PPh$_2$Hx^n)]$_2$	THF-d_8	1.1	71	8	5	11	16	5
15	[RhCl(PPh$_2$Bu^t)$_2$]$_2$	THF-d_8	1.1	87	5	3		3	5
16	[RhCl{PPh$_2$(*o*-tol)}$_2$]$_2$	THF-d_8	1.1	15		76	8	84	1

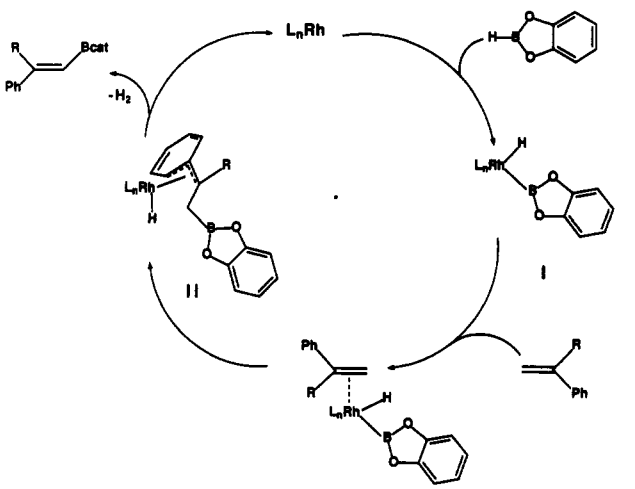
[a] All reactions were carried out at 25 °C for 1 h with alkene/catecholborane/catalyst = 1.0/1.1/0.02. Product ratios were determined by ^{1}H NMR spectroscopy. Some unreacted alkene was observed when significant amounts of **10** were formed. [b] Catalyst was exposed to air for 24 h. [c] BPI = benzo[*b*]phosphindole.

sponding VBE-derived products along with conventional hydroboration products (see Experimental Section). Interestingly, reaction of HBcat with **5** gave bis(boronate ester) as the major VBE-derived product with only trace amounts of vinylboronate ester, implying that hydroboration of Ph$_2$C=CHBcat proceeds at a comparable rate to that of its initial formation.

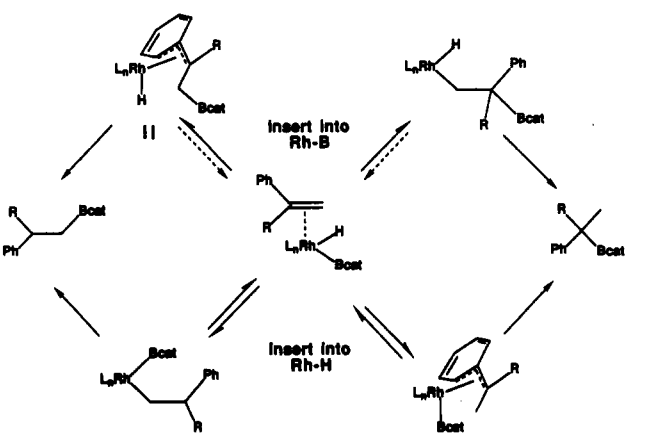
Compared with the results of Brown and Lloyd-Jones,[6] the above findings are distinguished by minimal vinylarene hydrogenation and significant bis(boronate ester) formation. Highly substituted bis(boronate esters) are not prepared easily by conventional hydroborations but may now be obtained in good yields in Rh-catalyzed reactions employing excess HBcat.

Assuming initial rapid oxidative addition of HBcat to Rh(I) to give the [RhH(Bcat)] moiety,[1,2,12] dehydrogenative borylation of **4** then proceeds presumably via initial insertion of alkene into the Rh–B rather than the Rh–H bond (Scheme III). Formation of the hindered tertiary alkylrhodium complex may be facilitated by formation of an η^3-benzyl intermediate **II**. High Markovnikov selectivities observed in hydroboration of vinylarenes catalyzed by rhodium phosphine complexes have been attributed to similar η^3-benzyl intermediates.[1e] β-hydride abstraction from the borylalkyl group and reductive elimination of dihydrogen[14] affords VBE (*E*)-**9**. This reaction proceeds with complete stereocontrol as formation of the (*Z*) isomer was not observed. Rhodium-catalyzed hydroboration of VBE **9** then gives bis(boronate ester) **10**. Finally, hydroboration product **7** could conceivably arise via hydrogenation of VBE,[2] while both **7** and **8** may be formed by C–H reductive elimination from (borylalkyl)rhodium hydrides and/or the "conventional" pathway involving initial insertion of alkene into Rh–H and B–C reductive elimination from alkylrhodium boryl complexes (Scheme IV). Recent model studies using RhCl(Bcat)$_2$(PPh$_3$)$_2$ have

Scheme III



Scheme IV



demonstrated insertion of alkenes into Rh–B bonds,[15] but the reverse reaction, β-boryl elimination, has yet to be observed.

In summary, α-substituted vinylarenes undergo dehydrogenative borylation under conventional catalyzed hydroboration conditions to afford significant amounts of (*E*)-vinylboronate esters and novel bis(boronate esters).

(12) While reactions of RhCl(PPh$_3$)$_3$ and bis(phosphine) complex [RhCl(PPh$_3$)$_2$]$_2$ with HBcat rapidly generate 16e$^-$ RhHCl(Bcat)(PPh$_3$)$_2$,[2,13] such is not the case for RhCl[P(OAr)$_3$]$_3$ (Ar = *o*-tolyl). That the latter is nonetheless an effective catalyst for hydroboration and dehydrogenative borylation of alkenes suggests that substrate binding may precede B–H activation for some catalyst precursors.

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(14) Upon completion of catalysis using **1**, dihydride RhH$_2$Cl(PPh$_3$)$_3$ was the only observable Rh-containing complex in solution (^{1}H, ^{31}P NMR).

(15) Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.*, in press.

Product distributions from these reactions are extremely sensitive to the nature of the catalyst employed, and current work is in progress to elucidate further the role of the metal center.

Experimental Section

General Procedures. NMR spectra were recorded on General Electric QM-300 (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121 MHz) and Nicolet NMC-300 (^{11}B at 96 MHz) spectrometers in THF-d_8 (tetrahydrofuran) unless stated otherwise. ^{1}H NMR chemical shifts are reported in ppm relative to external TMS and were referenced to residual protons in THF-d_8; coupling constants are in hertz. Multiplicities are reported as (s) singlet, (d) doublet, (t) triplet, (q) quartet, (sext) sextet, (m) multiplet, (br) broad, and (ov) overlapping. ^{11}B and ^{31}P chemical shifts are reported in ppm relative to external standards $F_3B{\cdot}OEt_2$ and 85% H_3PO_4, respectively. ^{13}C chemical shifts are reported in ppm relative to external TMS using THF-d_8 (25.3) as an internal standard. Carbon multiplicities were determined from the gated ^{13}C NMR spectra. THF and toluene were freshly distilled from sodium benzophenone ketyl. Catecholborane (Aldrich) was distilled under reduced pressure. Alkenes and phosphine ligands were purchased from commercial suppliers and used as received. Reagent purity was ascertained by ^{1}H NMR spectroscopy. Catalyst precursors $[MCl(COE)_2]_2$ (M = Rh,[16] Ir[17]), $[RhCl(COD)]_2$,[18] M(acac)$(COE)_2$,[19] $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$,[20] RhCl$(N_2)(PPr^i_3)_2$,[21] $[RhCl(DCPE)]_2$,[22] $RhH(DPPP)_2$,[23] $RhCl(PPh_3)_3$,[24] $RhCl[P(p\text{-}F\text{-}Ph)_3]_3$,[25] $RhCl[P(p\text{-}OMe\text{-}Ph)_3]_3$,[26] $RhCl\{P(O\text{-}o\text{-}tol)_3\}_3$,[1g] and [Rh(COD)(DPPB)]A[27] (A = $[BF_4]^-$, $[SbF_6]^-$) were prepared by literature methods. The complexes RhCl(5-Ph-BPI)$_3$, (BPI = benzo[*b*]phosphindole), $[RhCl(PPh_2Bu^t)_2]_2$, $[RhCl(PPh_2Hx^n)_2]_2$, and $[RhCl\{PPh_2(o\text{-}tol)\}_2]_2$ were prepared by addition of the phosphine ligand to $[RhCl(COE)_2]_2$ in THF. Selected NMR data in THF-d_8: RhCl(5-Ph-BPI)$_3$, $^{31}P\{^1H\}$ 42.7 (d tr, J_{PRh} = 175, $^2J_{PP}$ = 42 Hz), 28.1 ppm (br d, J_{PRh} = 134 Hz), ^{1}H δ 6.56 (tr, J = 7 Hz, 2H), 6.80 (ov m, 3H), 7.04 (ov m, 20H), 7.27 (tr, J = 7 Hz, 4H), 7.53 (ov m, 6H), 7.64 (ov m, 4H); $[RhCl(PPh_2Bu^t)_2]_2$, $^{31}P\{^1H\}$ 64.9 ppm (d, J_{PRh} = 210 Hz), ^{1}H δ 1.24 (d, $^3J_{HP}$ = 12 Hz, 18H), 6.95 (m, 8H, meta), 7.12 (tr, J = 7 Hz, 4H, para), 7.87 (m, 8H, ortho); $[RhCl(PPh_2Hx^n)_2]_2$, $^{31}P\{^1H\}$ 42.3 ppm (d, J_{PRh} = 206 Hz), ^{1}H δ 0.79 (tr, 3H, J = 7 Hz), 1.01 (ov m, 4H), 1.13, 1.47, 1.58 (m, 2H), 7.10 (m, 8H, meta), 7.20 (tr, J = 7 Hz, 4H, para), 7.70 (m, 8H, ortho); $[RhCl\{PPh_2(o\text{-}tol)\}_2]_2$, $^{31}P\{^1H\}$ 45.0 ppm (d, J_{PRh} = 195 Hz), ^{1}H δ 2.59 (s, 12H, Me of tol), 6.8–7.6 (ov m, 56H, Ph and tol).

Catalyzed Hydroborations of 2-Phenylpropene (4). All reactions were carried out under an atmosphere of dry nitrogen using a continuous purge Vacuum Atmospheres glovebox. In a typical experiment, a solution of HBcat (132 mg, 1.1 mmol) in 1 mL of THF-d_8 was added dropwise to a mixture of 2-phenylpropene (**4**) (118 mg, 1.0 mmol) and catalyst (0.02 mmol) in 1 mL of THF-d_8. In some experiments, excess phosphine was added to the catalyst/substrate mixture prior to addition of HBcat. Resulting solutions were stirred for 60 min and then analyzed by high-field ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy.

Isolation of Vinylboronate Ester (*E*)-Ph(Me)C=CH-(Bcat) (9). A solution of HBcat (265 mg, 2.2 mmol) in 1 mL of THF was added dropwise to a mixture of 2-phenylpropene (235 mg, 2.0 mmol) and $RhCl[PPh_2(o\text{-}tol)]_2$ (20 mg, 0.04 mmol) in 1 mL of THF in an open 20-mL glass vial with vigorous stirring. The dark red solution became orange with visible gas evolution. After 60 min the vial was capped and let to stand for 48 h. The resulting colorless crystals[28] of **9** (260 mg, 55%) were recrystallized from toluene/hexane at −20 °C, mp 76–78 °C. MS: calcd for $C_{15}H_{13}BO_2$, *m/e* 236.1017; found, 236.1011. NMR (THF-d_8): ^{1}H δ 2.61 (d, J = 1 Hz, 3 H, Me), 6.16 (q, J = 1 Hz, C=CH), 7.03, 7.22 (m, 2H, cat), (ov m, 3H, meta, para), 7.48–7.57 (m, 2H, ortho); $^{13}C\{^1H\}$ 20.7 (CH_3), 112.9, 123.4 (2C, CH of cat), 121.7 (br, =CHB), 126.8, 129.1 (2C, ortho, meta CH of Ph), 129.3 (para CH of Ph), 144.2 (ipso C of Ph), 149.3 (2C, ipso C of cat), 161.8 ppm (=CMePh): $^{11}B\{^1H\}$ 32.5 ppm (br).

Isolation of Bis(boronate ester) Ph(Me)CHCH(Bcat)$_2$ (10). A solution of HBcat (400 mg, 3.3 mmol) in 1 mL of THF was added dropwise to a mixture of 2-phenylpropene (118 mg, 1.0 mmol) and $RhCl(PPh_3)_3$ (20 mg, 0.02 mmol) in 1 mL of THF in an open 20-mL glass vial with vigorous stirring. The dark red solution became orange with visible gas evolution. After 60 min the vial was capped and let to stand for 8 days. The solvent was then removed in vacuo and the residue extracted with 5 mL of 1:2 toluene/pentane. The extract was cooled at −20 °C for 20 h, and the resulting colorless crystals of **10** (215 mg, 60%) were recrystallized from toluene/hexane at −20 °C, mp 101–102 °C. MS: calcd for $C_{21}H_{18}B_2O_4$, *m/e* 356.1391; found, *m/e* 356.1406. NMR (THF-d_8): ^{1}H δ 1.46 (d, J = 7 Hz, 3H, Me), 2.30 (d, J = 10.5 Hz, 1H, BCH), 3.71 (d q, J = 10.5, 7 Hz, 1H, CH), 6.93, 7.24 (m, 2H, cat), 7.06 (ov m, 5H, cat, para H of Ph), 7.17 (m, 2H, meta), 7.33 (m, 2H, ortho); $^{13}C\{^1H\}$ 21.0 (br, B_2CH), 25.4 (CH_3), 39.1 (CH), 112.8, 113.0, 123.2, 123.4 (2C, CH of cat), 127.0 (para CH of Ph), 127.5, 129.3 (2C, ortho, meta CH of Ph), 149.5 (ipso C of Ph), 149.3, 149.6 ppm (2C, ipso C of cat); $^{11}B\{^1H\}$ 34.6 ppm (v br).

Catalyzed Hydroborations of 1,1-Diphenylethene (5) and 2-Phenylpent-1-ene (6). These reactions were performed as described above for **4**. For catalyzed addition of HBcat to **5**, solubility problems prevented quantification of the four products. Selected NMR data (in CD_2Cl_2): ^{1}H δ 1.66 (d, J = 7 Hz, 3H), 4.18 (q, J = 7 Hz) [Ph_2CHCH_3], 2.17 (d, J = 8 Hz, 2H), 4.59 (t, J = 8 Hz) [Ph_2CHCH_2Bcat], 3.05, 5.02 (d, J = 13 Hz) [$Ph_2CHCH(Bcat)_2$], 6.39 (s) [Ph_2C=CHBcat], 7.04–7.48 (ov m, Ph and cat); $^{11}B\{^1H\}$ 22.4 (br, B_2cat_3[3a,29]), 35.6 ppm (br). For substrate **6**, overlapping multiplets from the *n*-propyl residues complicated assignment of the ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR resonances were assigned with the aid of authentic samples of 2-phenylpentane (generated by catalytic hydrogenation of **6** in THF-d_8 using **1**) and Ph(Pr^n)CHCH$_2$Bcat (generated by selective catalytic hydroboration using HBcat and $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ in THF-d_8). Also, the catalyzed reaction of **6** with 3 equiv of HBcat allowed for monitoring conversion of Ph(Pr^n)C=CHBcat to Ph(Pr^n)CHCH(Bcat)$_2$. Selected NMR data (in THF-d_8): ^{1}H δ 1.84 (ov m, 2H, CH$_2$ of Pr^n), 2.39 (d, J = 11 Hz), 3.62 (d d d, J = 5, 9, 11 Hz) [Ph(Pr^n)CHCH(Bcat)$_2$, 25%], 2.65 (d d q, J = 7 Hz) [Ph(Pr^n)CHCH$_3$, 12%], 3.09 (d d d d, J = 7.5 Hz) [Ph(Pr^n)CHCH$_2$Bcat, 13%], 3.12 (tr, J = 7.5 Hz, 2H, CH$_2$ of Pr^n), 6.03 (s) [Ph(Pr^n)C=CHBcat, 50%]; $^{13}C\{^1H\}$ 14.73 (Me), 21.87 (Me–CH_2), 42.47 (CH_2), 44.42 (CHPh), 20.85 (br, BCH) [Ph(Pr^n)CHCH(Bcat)$_2$], 14.51 (Me), 21.75 (CHPhCH_3), 23.02 (Me–CH_2), 41.70 (CH_2), 40.72 (CHPh) [Ph(Pr^n)CHCH$_3$], 14.66 (Me), 21.75 (Me–CH_2), 42.26 (CH_2), 42.10 (CHPh), 20.37 (br, BCH_2) [Ph(Pr^n)CHCH$_2$Bcat], 14.39 (Me), 23.74 (Me–CH_2), 36.50 (CH_2), 167.4 (=CPh(Pr^n)), 114.0 (br, =CHBcat) [Ph(Pr^n)C=CHBcat]; $^{11}B\{^1H\}$ 18.8 (br, B_2cat_3), 33.2 ppm (ov br s).

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