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Nucleophile Promoted Degradation of Catecholborane: Consequences for Transition Metal-Catalyzed Hydroborations†

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Reactions of tertiary phosphines or phosphinorhodium complexes with catecholborane (HB(cat)) give boron-substituent redistribution products. While sterically compact phosphines (PMe_3, PEt_3, PMe_2Ph) react with 1 equiv of HBcat to give $[(PR_3)_2BH_2]^+[B(cat)_2]^-$, bulkier phosphines ($PPh_3$, PPr^i_3, PCy_3) afford phosphine–boranes $H_3B{\cdot}PR_3$ and tris(catecholato)diboron, $B_2(cat)_3$. Reactions of HB(cat) with coordinatively saturated $[RhH(DPPP)_2]$ (DPPP = 1,3-bis(diphenylphosphino)propane) and $[RhH(PMe_3)_4]$ afforded cationic species $[RhH_2(DPPP)_2]^+[B(cat)_2]^-$ and $[RhH_2(PMe_3)_4]^+[B(cat)_2]^-$ respectively, both of which are active catalyst precursors for addition of HB(cat) to 4-vinylanisole. These catalyzed hydroborations, however, gave significant amounts of BH_3-derived products, arising from Rh-mediated HB(cat) degradation. The only catalyst precursors examined which did not lead to degradation of HB(cat) were rhodium(I) chloride complexes containing basic monodentate phosphines. Molecular structures of $B_2(cat)_3$ (**3**), $[(PEt_3)_2BH_2][B(cat)_2]$ (**4b**), and $[RhH_2(PMe_3)_4][B(cat)_2]$ (**9**) were determined by single crystal X-ray diffraction. Colorless crystals of **3** are monoclinic, $P2_1/c$ (No. 14), with four molecules per unit cell of dimensions $a = 12.922(5)$ Å, $b = 12.245(2)$ Å, $c = 10.784(8)$ Å, and $\beta = 109.03°$. Colorless crystals of **4b** are monoclinic, $P2_1/n$ (No. 14), with eight molecules per unit cell of dimensions $a = 17.453(6)$ Å, $b = 11.414(1)$ Å, $c = 26.666(9)$ Å, and $\beta = 95.17(2)°$. Orange crystals of **9** are trigonal, $P3_221$ (No. 154), with three molecules per unit cell of dimensions $a = 13.222(1)$ Å, $b = 13.222(1)$ Å, and $c = 17.294(6)$ Å.

Introduction

Recent reports on rhodium-catalyzed hydroboration of alkenes using catecholborane, HB(cat) (cat = $1,2\text{-}O_2C_6H_4$), demonstrated a variety of promising features, including novel regioselectivity,[1] diastereoselectivity,[1a,2] and asymmetric induction (using chiral catalysts),[3–7] as well as preferential addition to C=C bonds in the presence of more reactive functional groups such as ketones and nitriles.[8] Although much attention has focused on exploiting catalyzed hydroborations for applications in organic synthesis,[9] recent work has also concentrated on the role of the transition metal.[10–13] Männig and Nöth proposed a catalytic cycle[8] resembling one described earlier for rhodium-mediated addition of carborane B—H bonds to the C=C fragment in acrylate esters.[14] Initial oxidative addition of the B–H bond of HB(cat) to the metal center,[15] is followed by insertion of coordinated alkene into Rh–H, and subsequent reductive elimination of an alkyl boronate ester (Scheme I).

We reported recently[13] that catalyzed alkene hydroborations using Wilkinson's catalyst, $[RhCl(PPh_3)_3]$ (**1**), are complicated by alkene isomerization and hydrogenation, vinylboronate ester formation, and by addition of BH_3 (arising from degradation of HB(cat)). Hydroborations of 2-methylbut-2-ene, $CHMe{=}CMe_2$, using HB(cat) in the presence of **1**, for example, gave significant amounts of disiamylborane, $HB(CHMeCHMe_2)_2$ (45%). Formation of this byproduct was reduced substantially, however, by addition of excess PPh_3 which efficiently traps borane as $H_3B{\cdot}PPh_3$. We noted additionally that competing alkene hydrogenation derives from the dihydride $[RhH_2Cl(PPh_3)_3]$, which is formed as a result of HB(cat) degradation by **1**. To investigate factors influencing HB(cat) degradation, we examined reactions of HB(cat) with related phosphinorhodium(I) complexes and with several phosphine ligands and report herein on implications for transition metal-catalyzed hydroboration of alkenes.

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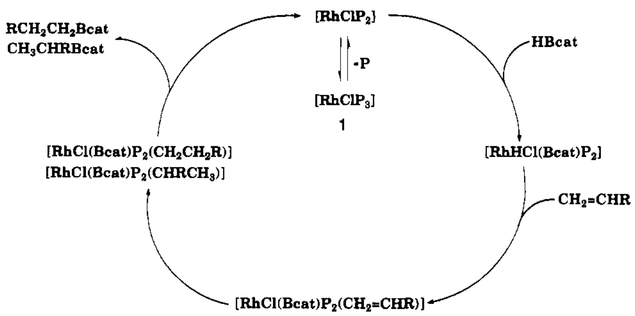
Scheme I



Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen using a continuous purge glovebox (Vacuum Atmospheres). 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), Nicolet NMC-300 (^{11}B at 112 MHz) and Bruker AM250 (^{1}H at 250 MHz, ^{31}P at 101 MHz, ^{11}B at 93 MHz) instruments. ^{1}H chemical shifts are reported in ppm relative to external TMS and referenced to residual protons in THF-d_8 or CD_2Cl_2; coupling constants are in Hz. Multiplicities are reported as (br) broad, (ov) overlapping, (s) singlet, (d) doublet, (t) triplet, (q) quartet, and (m) multiplet. ^{11}B and ^{31}P chemical shifts are reported in ppm relative to the standards $F_3B{\cdot}OEt_2$, and external 85% H_3PO_4 respectively. ^{13}C chemical shifts are reported in ppm relative to external TMS using CD_2Cl_2 (53.8) as an internal standard. Carbon multiplicities are listed as (C) quaternary, (CH) methine, (CH_2) methylene, and (CH_3) methyl. THF and toluene were distilled freshly from sodium benzophenone ketyl. CH_2Cl_2 was distilled freshly from CaH_2. Catecholborane (Aldrich Chemical Co.) was distilled under reduced pressure before use. [RhH(DPPP)$_2$],[16a] [Rh(DPPP)$_2$]Cl,[16a] [RhH(PMe$_3$)$_4$],[17] [RhH(N$_2$)(PPr$^{i}_3$)$_2$],[18] and [RhCl(PMe$_3$)$_3$][19] were prepared by established methods. Reagent purity was ascertained by ^{1}H NMR spectroscopy.

Reactions of Phosphines with HB(cat). A solution of HB(cat) (120 mg, 1.0 mmol) in 1 mL of THF-d_8, was added dropwise to a solution of phosphine (1.0 mmol) in 1 mL of THF-d_8. Reactions were also examined with 3 and 30 equiv of HB(cat) per phosphine. The resulting solutions were stirred for 30 min and then analyzed by high-field ^{1}H, ^{31}P, and ^{11}B NMR spectroscopy.

Selected NMR Data for [(Me$_2$PhP)$_2$BH$_2$]$^+$[B(cat)$_2$]$^-$ (4c) (in CD$_2$Cl$_2$). ^{1}H NMR: δ 1.56 (d, $^{2}J_{\mathrm{HP}}$ = 11 Hz, 12 H, CH$_3$), 6.57 (br, 8H, [B(cat)$_2$]$^-$), 7.44 (ov m, 10H, Ph). ^{11}B NMR: δ −32.8 (t t, J_{BH} = 190, J_{BP} = 95 Hz, [(Et$_3$P)$_2$BH$_2$]$^+$), 15.2 (s, [B(cat)$_2$]$^-$). ^{31}P NMR: −2.05 (q, J_{PB} = 95 Hz).

Reactions of Phosphines with H$_3$B·THF. A solution of H$_3$B·THF (1 M in THF, 1.0 mmol) in 1 mL of THF-d_8 or CD$_2$Cl$_2$ was added dropwise to a solution of phosphine (1.0 mmol) in 1 mL of THF-d_8 or CD$_2$Cl$_2$. The resulting solutions were stirred for 30 min and then analyzed by high-field ^{31}P and ^{11}B NMR spectroscopy.

Isolation of B$_2$(cat)$_3$ (3). A commercially obtained sample of HB(cat) (100 g) was distilled at 60 °C under reduced pressure. The remaining residue was washed with 3 × 5 mL hexane and dried in vacuo to give colorless solid **3** (amounts vary with conditions from ca. 200–600 mg). Selected NMR data are as follows (in CD$_2$Cl$_2$). ^{1}H NMR: δ 6.75 (br, 8H), 6.96 (br, 2H), 7.11 (br, 2H). ^{13}C NMR: δ 113.5 (CH, 2C), 122.9 (CH, 1C), 124.3 (CH, 2C), 126.7 (CH, 1C), 144.4 (C, 1C), 149.0 (C, 1C). ^{11}B{^{1}H} NMR: δ 22.7 (br).

Reaction of [Rh(DPPP)$_2$]Cl (5) with HB(cat). A solution of HB(cat) (36 mg, 0.3 mmol) in 1 mL of CD$_2$Cl$_2$, was added dropwise to a solution of **5** (50 mg, 0.05 mmol) in 1 mL of CD$_2$Cl$_2$. The resulting solution was stirred for 30 min and then analyzed by high-field ^{1}H, ^{31}P, and ^{11}B NMR spectroscopy. Selected NMR data are as follows (in CD$_2$Cl$_2$). ^{31}P{^{1}H}: δ 5.2 (br d t, J_{PRh} = 82 Hz, $^{2}J_{\mathrm{PP}}$ = 30 Hz, **6**), 7.5 (d, J_{PRh} = 131 Hz, **5**), 17.0 (d t, J_{PRh} = 100 Hz, $^{2}J_{\mathrm{PP}}$ = 30 Hz, **6**). ^{11}B NMR: δ −50.5 (br), −39.5 (br), −3.0 (t, J_{BH} = 134 Hz), 3.0 (d, J_{BH} = 158 Hz), 15.2 (s), 22.8 (br), 31.8 (br). ^{1}H NMR: δ −8.15 (complex d m, J_{HPtrans} = 141 Hz).

Reaction of [RhH(DPPP)$_2$] (7) with HB(cat). A solution of HB(cat) (36 mg, 0.3 mmol) in 1 mL of CD$_2$Cl$_2$, was added dropwise to a solution of **7** (48 mg, 0.05 mmol) in 1 mL of CD$_2$Cl$_2$. The resulting solution was stirred for 30 min and then analyzed by high-field ^{1}H, ^{31}P, and ^{11}B NMR spectroscopy. Selected NMR data are as follows (in CD$_2$Cl$_2$). ^{31}P{^{1}H} NMR: δ 5.2 (br d t, J_{PRh} = 82 Hz, $^{2}J_{\mathrm{PP}}$ = 30 Hz, [RhH$_2$(DPPP)$_2$]$^+$, **6**), 17.0 (d t, J_{PRh} = 100 Hz, $^{2}J_{\mathrm{PP}}$ = 30 Hz, **6**). ^{11}B{^{1}H} NMR: δ 14.8 (s), 18.6 (br), 22.7 (br). ^{1}H NMR: δ −8.15 (complex d m, J_{HPtrans} = 141 Hz, **6**).

Reaction of [RhH(PMe$_3$)$_4$] (8) with HB(cat). A solution of HB(cat) (36 mg, 0.3 mmol) in 1 mL of THF-d_8, was added dropwise to a solution of **8** (41 mg, 0.1 mmol) in 1 mL of THF-d_8. The resulting solution was stirred for 30 min and analyzed by high-field ^{1}H, ^{31}P, and ^{11}B NMR spectroscopy. Selected NMR data are as follows (in THF-d_8). ^{31}P{^{1}H} NMR: δ −33.3 (br, minor), −25.5 (ov m, minor), −22.3 (ov m), −22.2 (d t, J_{PRh} = 85 Hz, $^{2}J_{\mathrm{PP}}$ = 27 Hz, **9**), −16.5 (d t, J_{PRh} = 92 Hz, $^{2}J_{\mathrm{PP}}$ = 29 Hz), −13.2 (d t, J_{PRh} = 92 Hz, $^{2}J_{\mathrm{PP}}$ = 29 Hz), −10.6 (d t, J_{PRh} = 96 Hz, $^{2}J_{\mathrm{PP}}$ = 27 Hz, **9**), −6.9 (br q, J_{PB} = 90 Hz), −0.4 (q, J_{PB} = 60 Hz, H$_3$B·PMe$_3$), 0.9 (d, J_{PRh} = 109 Hz). ^{11}B{^{1}H} NMR: δ −37.4 (d, J_{BP} = 59 Hz, H$_3$B·PMe$_3$), −33.0 (t, J_{BP} = 90 Hz, [(Me$_3$P)$_2$BH$_2$]$^+$), 15.1 (s, [B(cat)$_2$]$^-$), 25.3 (s, HB(cat)), 46.9 (br). ^{1}H NMR: δ −10.71 (d m, J_{HPtrans} = 137 Hz, J_{HRh} = J_{HPcis} = 16 Hz, **9**), −9.50 (d q, J_{HPtrans} = 146 Hz, J_{HRh} = J_{HPcis} = 21 Hz).

Reaction of [RhH(N$_2$)(PPr$^{i}_3$)$_2$] (10) with HB(cat). A solution of HB(cat) (36 mg, 0.3 mmol) in 1 mL of THF-d_8, was added dropwise to a solution of **10** (90 mg, 0.2 mmol) in 1 mL of THF-d_8. The resulting solution was stirred for 30 min and analyzed by high-field ^{1}H, ^{31}P, and ^{11}B NMR spectroscopy. Selected NMR data are as follows (in toluene-d_8). ^{31}P{^{1}H} NMR: δ 53.6 (d, J_{PRh} = 132 Hz), 69.2 (d, J_{PRh} = 140 Hz), 76.8 (d, J_{PRh} = 106 Hz). ^{11}B{^{1}H} NMR: δ 22.5 (br, B$_2$(cat)$_3$), 26.9 (br s), 30.9 (br, major). ^{1}H NMR: δ −13.10 (br m, J = 14 Hz), −7.67 (br, major).

Reaction of [RhCl(PMe$_3$)$_3$] (13) with HB(cat). A solution of HB(cat) (36 mg, 0.3 mmol) in 1 mL of THF-d_8, was added dropwise to a solution of **13** (73 mg, 0.2 mmol) in 1 mL of THF-d_8. The resulting solution was stirred for 30 min and analyzed by high-field ^{1}H, ^{31}P, and ^{11}B NMR spectroscopy. Selected NMR data are as follows (in THF-d_8). ^{31}P{^{1}H} NMR: δ −20.6 (br), −4.1 (d d, J_{PRh} = 101 Hz, $^{2}J_{\mathrm{PP}}$ = 28 Hz). ^{11}B{^{1}H} NMR: δ 42.8 (br). ^{1}H NMR: δ −8.93 (d q, J_{HPtrans} = 177 Hz, J_{HRh} = J_{HPcis} = 18 Hz), −4.87 (br d, J_{HPtrans} = 92 Hz).

Catalyzed Hydroborations of 1-Octene with HB(cat). A solution of HB(cat) (264 mg, 2.2 mmol) in 1 mL of THF-d_8 was added dropwise to a solution of 1-octene (224 mg, 2.0 mmol) and 0.04 mmol of catalyst in 1 mL of THF-d_8. Reactions were monitored by high-field ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy.

Catalyzed Hydroborations of 4-Vinylanisole with HB(cat). A solution of HB(cat) (264 mg, 2.2 mmol) in 1 mL of THF-d_8 was added dropwise to a solution of 4-vinylanisole (268 mg, 2.0 mmol) and 0.04 mmol of catalyst in 1 mL of THF-d_8. Reactions were monitored by high-field ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy.

Fate of the Catalyst Precursors During Catalysis. (i) Selected NMR spectroscopic data for catalytic hydroborations of 4-vinylanisole using **5**–**7** are as follows (in THF-d_8). ^{31}P{^{1}H} NMR: δ 6.9 (br d t, J_{PRh} = 82 Hz, $^{2}J_{\mathrm{PP}}$ = 30 Hz, **6**), 19.4 (d t, J_{PRh} = 100 Hz, $^{2}J_{\mathrm{PP}}$ = 30 Hz, **6**). ^{11}B{^{1}H} NMR: δ 15.3 (s, [B(cat)$_2$]$^-$), 22.6 (br, B$_2$(cat)$_3$), 35.1 (br, alkylboronate esters), 83.1 (br, alkylboranes). ^{1}H NMR: δ −8.65 (complex d m, J_{HPtrans} = 141 Hz, **6**). Hydroborations were complicated by formation of BH$_3$ arising from the metal-mediated degradation of HB(cat). (ii) Selected NMR spectroscopic data for catalytic hydroborations of 4-vinylanisole using **8** and **9** are as follows (in THF-d_8). ^{31}P{^{1}H} NMR: δ −22.2 (d t, J_{PRh} = 85 Hz, $^{2}J_{\mathrm{PP}}$ = 27 Hz, **9**), −10.6 (d t, J_{PRh} = 96 Hz, $^{2}J_{\mathrm{PP}}$ = 27 Hz, **9**); ^{11}B{^{1}H} NMR: δ 15.1 (s, [B(cat)$_2$]$^-$), 22.7 (br, minor B$_2$(cat)$_3$), 35.3 (br, alkyl boronate esters), 82.6 (br, alkylboranes). ^{1}H NMR: δ −10.71 (d m, J_{HPtrans} = 137 Hz, J_{HRh} = J_{HPcis} = 16 Hz, **9**). (iii) Selected NMR spectroscopic data for catalytic hydroborations of 4-vinylanisole using **10** are as follows (in THF-d_8). ^{31}P{^{1}H} NMR: δ 52.3 (d, J_{PRh} = 113 Hz), 70.0 (d, J_{PRh} = 140 Hz), 73.4 (d, J_{PRh} = 145 Hz), 76.5 (d, J_{PRh} = 106 Hz). ^{11}B{^{1}H} NMR: δ 83.0 (br, BH$_3$-derived products), 34.5 (br, major, alkyl boronate esters), 22.8 (br, B$_2$(cat)$_3$, minor), 20.7 (br, minor), 14.7 (s, minor, [B(cat)$_2$]$^-$). ^{1}H NMR: δ −25.82 (d t, J = 30, 17 Hz), −13.10 (br m), −7.67 (br). (iv) Selected NMR spectroscopic data for catalytic hydroborations of 4-vinylanisole using **13** are as follows (in THF-d_8). ^{31}P{^{1}H} NMR: δ −20.6 (br), −4.1 (d d, J_{PRh} = 101 Hz, $^{2}J_{\mathrm{PP}}$ = 28 Hz).

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Table I. Summary of X-ray Crystallographic Data

	$B_2(cat)_3$	$[(Et_3P)_2BH_2]^+$-$[B(cat)_2]^-$	$[RhH_2(PMe_3)_4]^+$-$[B(cat)_2]^- \cdot C_6H_6$
chem formula	$C_{18}H_{12}B_2O_6$	$C_{24}H_{40}B_2O_4P_2$	$C_{30}H_{52}BO_4P_4Rh$
a, Å	12.922(5)	17.453(6)	13.222(1)
b, Å	12.245(2)	11.414(1)	13.222(1)
c, Å	10.784(8)	26.666(9)	17.294(6)
β, deg	109.03(1)	95.17(2)	
V, Å^3	1613.1	5290.5	2618.3
Z	4	8	3
fw	345.91	476.15	714.36
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P3_221$ (No. 154)
temp, °C	−70	−70	−70
λ, Å	0.710 69	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	1.424	1.195	1.359
μ, cm^{-1}	0.98	1.85	6.92
transm coeff			0.84–0.90
R^a	0.042	0.056	0.059
$R_w{}^b$	0.041	0.047	0.061

[a] $\sum||F_o| - |F_c||/\sum|F_o|$. [b] $[\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table II. Selected Interatomic Distances (Å) and Angles (deg) for $B_2(cat)_3$ (**3**)

(a) Interatomic Distances

O(1)–C(1)	1.395(3)	C(3)–C(4)	1.380(4)
O(2)–C(2)	1.378(3)	C(4)–C(5)	1.373(4)
O(3)–C(12)	1.388(3)	C(5)–C(6)	1.383(4)
O(4)–C(11)	1.389(3)	C(11)–C(12)	1.374(4)
O(5)–C(21)	1.391(3)	C(11)–C(16)	1.369(4)
O(6)–C(22)	1.385(3)	C(12)–C(13)	1.369(4)
O(1)–B(1)	1.352(4)	C(13)–C(14)	1.391(4)
O(2)–B(2)	1.351(3)	C(14)–C(15)	1.379(4)
O(3)–B(1)	1.382(3)	C(15)–C(16)	1.385(4)
O(4)–B(1)	1.379(4)	C(21)–C(22)	1.377(4)
O(5)–B(2)	1.380(3)	C(21)–C(26)	1.367(4)
O(6)–B(2)	1.385(3)	C(22)–C(23)	1.364(4)
C(1)–C(2)	1.385(4)	C(23)–C(24)	1.390(4)
C(1)–C(6)	1.380(4)	C(24)–C(25)	1.382(4)
C(2)–C(3)	1.379(4)	C(25)–C(26)	1.391(4)

(b) Interatomic Angles

C(1)–O(1)–B(1)	121.3(2)	C(3)–C(4)–C(5)	120.9(3)
C(2)–O(2)–B(2)	126.0(2)	C(4)–C(5)–C(6)	120.0(3)
C(12)–O(3)–B(1)	103.6(2)	C(1)–C(6)–C(5)	119.0(3)
C(11)–O(4)–B(1)	103.9(2)	C(12)–C(11)–C(16)	122.2(3)
C(21)–O(5)–B(2)	104.3(2)	C(11)–C(12)–C(13)	122.1(3)
C(22)–O(6)–B(2)	104.2(2)	C(12)–C(13)–C(14)	116.5(3)
O(1)–C(1)–C(2)	119.5(2)	C(13)–C(14)–C(15)	121.1(3)
O(1)–C(1)–C(6)	119.1(2)	C(14)–C(15)–C(16)	122.0(3)
O(2)–C(2)–C(1)	116.0(2)	C(11)–C(16)–C(15)	116.2(3)
O(2)–C(2)–C(3)	124.8(2)	C(22)–C(21)–C(26)	122.4(3)
O(4)–C(11)–C(12)	109.4(2)	C(21)–C(22)–C(23)	122.4(3)
O(4)–C(11)–C(16)	128.4(3)	C(22)–C(23)–C(24)	116.1(3)
O(3)–C(12)–C(11)	109.7(2)	C(23)–C(24)–C(25)	121.6(3)
O(3)–C(12)–C(13)	128.1(3)	C(24)–C(25)–C(26)	121.6(3)
O(5)–C(21)–C(22)	109.3(2)	C(21)–C(26)–C(25)	115.9(3)
O(5)–C(21)–C(26)	128.3(2)	O(1)–B(1)–O(3)	125.7(3)
O(6)–C(22)–C(21)	109.6(2)	O(1)–B(1)–O(4)	121.0(3)
O(6)–C(22)–C(23)	128.0(3)	O(3)–B(1)–O(4)	113.2(3)
C(2)–C(1)–C(6)	121.2(3)	O(2)–B(2)–O(5)	127.9(3)
C(1)–C(2)–C(3)	119.2(3)	O(2)–B(2)–O(6)	119.5(3)
C(2)–C(3)–C(4)	119.7(3)	O(5)–B(2)–O(6)	112.6(2)

$^{11}B\{^1H\}$ NMR: δ 35.0 (br, alkyl boronate esters), 42.8 (br). ^1H NMR: δ −8.93 (d q, $J_{HPtrans}$ = 177 Hz, J_{HRh} = J_{HPcis} = 18 Hz), −4.87 (br d, $J_{HPtrans}$ = 92 Hz).

Molecular Structure Determinations. Crystals of $B_2(cat)_3$ (**3**) suitable for X-ray diffraction studies were obtained from a refluxing solution of HB(cat) which was allowed to cool slowly to room temperature. Crystals of $[(Et_3P)_2BH_2]^+[B(cat)_2]^-$ (**4b**) were obtained by recrystallization from a cold (−30 °C) THF/Et_2O solution and crystals of $[Rh(H)_2(PMe_3)_4]^+[B(cat)_2]^-$ (**9**) were grown from a solution of THF/benzene. A summary of the crystal data and parameters for data collection is presented in Table I. All sets of data were collected at low temperatures on an Enraf-Nonius CAD4 diffractometer using graphite-filtered Mo Kα radiation (λ = 0.710 69 Å) and ω scan methods. The data were reduced in the usual fashion for Lorentz–polarization, and corrected for 12 (**4b**) and 4% (**9**) decreases in intensity vs the standard reflections. Azimuthal scans showed some variation in intensity and the data set for **9** was corrected for absorption (azimuthal). Solution and refinement of the structures were performed on a VAX/IBM cluster system using a local program set. The structures were solved by direct methods (SHELXS,[20] **4b**, and MULTAN,[21] **3** and **9**). All refinements were performed using full-matrix least-squares methods on *F*, with anisotropic thermal parameters for all non-hydrogen atoms, and included anomalous dispersion terms[22] for Rh and P, as well as idealized hydrogen coordinates as fixed atom contributors. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, *w*, assigned as $[\sigma^2(I)^2 + 0.0009I^2]^{-1/2}$. The atomic scattering factors were taken from the tabulations of Cromer and Waber.[23] For **9**, the coordinates used were those corresponding to the enantiomorph with the lowest *R* value. Selected bond distances and angles are given in Tables II, IV, and VI and final atomic coordinates are given in Tables III, V, and VII. Final positional and thermal parameters for the non-hydrogen atoms, general temperature factors, calculated hydrogen atom positions and structure factor listings are available as Supplementary Material.

Results and Discussion

Reactions of HB(cat) with Phosphines. Catalytic hydroborations are frequently carried out in the presence of (i) neutral arylphosphine-derived rhodium(I) catalyst precursors, or (ii) cationic rhodium(I) catalyst precursors generated in situ by treatment of $[Rh(diene)_2]^+[A]^-$ (diene = 2,5-norbornadiene or 1,5-cyclooctadiene; A^- = noncoordinating anion) with arylphosphines.[9] The ubiquitous use of PPh_3 arises from the ease with which this phosphine dissociates from the metal center in solution.[24] The possibility that free phosphine (Scheme I), or added phosphine,[13] may be present during catalysis prompted us to investigate their reactivity with HB(cat).

While borane and organoboranes react with phosphines to form Lewis acid–base adducts of the form $R_3B \cdot PR'_3$,[25] we found PPh_3 slowly ($t_{1/2}$ = 4 h) induces HB(cat) degradation to $H_3B \cdot PPh_3$ (**2a**) and dinuclear boronate ester $[B(1,2-O_2C_6H_4)]_2[(\mu-1,2-O_2C_6H_4)]$, $B_2(cat)_3$ (**3**). Reactions of HB(cat) with other bulky phosphines afford analogous products (Scheme II). Phosphine–borane adducts were characterized by comparison with products derived from reactions of the corresponding phosphines with $H_3B \cdot THF$. Similar boron-substituent redistribution products have been observed previously in reactions of HB(cat) with $NaBH_4$.[26]

The *o*-phenylene compound $B_2(cat)_3$ (**3**) has been prepared previously by reaction of catechol with B_2O_3[27] or B_2S_3.[28] Consistent with NMR data, both bridging and chelating catecholate groups have been confirmed by a single-crystal X-ray diffraction study of **3**. Although B–O bond lengths are consistent with trigonal planar B–O bond distances found in borates,[29] the two B–O bonds in the bridging catecholate group are somewhat shorter than the chelating catecholate B–O bond distances, averaging 1.352(4) vs 1.382(4) Å, respectively (Figure 1). The

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Table III. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $B_2(cat)_3$ (**3**)

atom	*x*	*y*	*z*	B_{ISO}, Å^2
O(1)	2554(1)	2948(1)	11354(2)	2.7(1)
O(2)	3359(2)	2418(1)	9439(2)	2.8(1)
O(3)	1275(1)	3804(2)	9423(2)	2.8(1)
O(4)	2302(1)	4870(1)	11147(2)	2.9(1)
O(5)	4537(1)	1306(1)	8558(2)	2.6(1)
O(6)	4483(1)	3174(1)	8315(2)	2.7(1)
C(1)	2374(2)	1899(2)	10823(3)	2.4(1)
C(2)	2825(2)	1602(2)	9870(2)	2.4(1)
C(3)	2673(2)	553(2)	9379(3)	2.6(1)
C(4)	2097(2)	−189(2)	9864(3)	3.1(1)
C(5)	1670(2)	103(2)	10827(3)	3.2(1)
C(6)	1809(2)	1155(2)	11320(3)	2.9(1)
C(11)	1587(2)	5528(2)	10200(3)	2.6(1)
C(12)	977(2)	4891(2)	9172(3)	2.7(1)
C(13)	189(2)	5324(2)	8107(3)	3.2(1)
C(14)	38(2)	6448(3)	8111(3)	3.8(1)
C(15)	653(3)	7082(3)	9146(4)	4.1(1)
C(16)	1445(2)	6636(2)	10223(3)	3.7(1)
C(21)	5192(2)	1613(2)	7818(3)	2.5(1)
C(22)	5164(2)	2732(2)	7684(3)	2.6(1)
C(23)	5713(2)	3266(2)	6979(3)	3.3(1)
C(24)	6306(2)	2614(3)	6398(3)	3.6(1)
C(25)	6346(3)	1492(3)	6546(3)	3.8(1)
C(26)	5779(2)	959(2)	7265(3)	3.3(1)
B(1)	2060(3)	3829(3)	10651(3)	2.5(1)
B(2)	4091(3)	2274(3)	8801(3)	2.5(1)
H(3)	2977	336	8704	3.0
H(4)	1986	−919	9503	3.0
H(5)	1281	−431	11170	3.0
H(6)	1514	1373	12002	3.0
H(13)	−231	4881	7380	3.0
H(14)	−503	6797	7375	3.0
H(15)	513	7869	9127	3.0
H(16)	1882	7086	10962	3.0
H(23)	5678	4055	6887	3.0
H(24)	6713	2975	5881	3.0
H(25)	6761	1068	6121	3.0
H(26)	5818	172	7387	3.0

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[(Et_3P)_2BH_2]^+[B(cat)_2]^-$ (**4b**)

(a) Interatomic Distances

P(1)–C(21)	1.842(5)	C(2′)–C(3′)	1.373(7)
P(1)–C(23)	1.789(6)	C(3)–C(4)	1.390(7)
P(1)–C(25)	1.804(5)	C(3′)–C(4′)	1.388(7)
P(1′)–C(21′)	1.807(5)	C(4)–C(5)	1.357(8)
P(1′)–C(23′)	1.801(5)	C(4′)–C(5′)	1.370(7)
P(1′)–C(25′)	1.810(5)	C(5)–C(6)	1.389(7)
P(2)–C(31)	1.798(5)	C(5′)–C(6′)	1.397(7)
P(2)–C(33)	1.819(5)	C(7)–C(8)	1.375(6)
P(2)–C(35)	1.802(5)	C(7)–C(12)	1.371(7)
P(2′)–C(31′)	1.932(16)	C(7′)–C(8′)	1.378(7)
P(2′)–C(31″)	1.791(21)	C(7′)–C(12′)	1.370(7)
P(2′)–C(33′)	1.733(20)	C(8)–C(9)	1.369(6)
P(2′)–C(33″)	1.948(22)	C(8′)–C(9′)	1.369(7)
P(2′)–C(35′)	1.775(6)	C(9)–C(10)	1.398(7)
P(1)–B(2)	1.896(6)	C(9′)–C(10′)	1.383(9)
P(1′)–B(2′)	1.910(6)	C(10)–C(11)	1.352(7)
P(2)–B(2)	1.913(6)	C(10′)–C(11′)	1.341(9)
P(2′)–B(2′)	1.903(6)	C(11)–C(12)	1.401(7)
O(1)–C(1)	1.371(6)	C(11′)–C(12′)	1.399(8)
O(1′)–C(1′)	1.358(5)	C(21)–C(22)	1.462(7)
O(2)–C(2)	1.366(5)	C(21′)–C(22′)	1.520(7)
O(2′)–C(2′)	1.355(6)	C(23)–C(24)	1.518(8)
O(3)–C(7)	1.359(6)	C(23′)–C(24′)	1.510(6)
O(3′)–C(7′)	1.364(6)	C(25)–C(26)	1.501(7)
O(4)–C(8)	1.358(5)	C(25′)–C(26′)	1.509(6)
O(4′)–C(8′)	1.364(6)	C(31)–C(32)	1.508(7)
O(1)–B(1)	1.477(6)	C(31′)–C(31″)	1.050(27)
O(1′)–B(1′)	1.484(7)	C(31′)–C(32′)	1.377(16)
O(2)–B(1)	1.493(7)	C(31″)–C(32′)	1.311(21)
O(2′)–B(1′)	1.490(6)	C(33)–C(34)	1.479(7)
O(3)–B(1)	1.473(7)	C(33′)–C(33″)	1.046(27)
O(3′)–B(1′)	1.473(7)	C(33′)–C(34′)	1.364(27)
O(4)–B(1)	1.473(7)	C(33′)–C(34″)	1.420(23)
O(4′)–B(1′)	1.473(6)	C(33″)–C(34′)	0.751(24)
C(1)–C(2)	1.388(7)	C(33″)–C(34″)	1.676(31)
C(1)–C(6)	1.372(7)	C(34′)–C(34″)	1.347(28)
C(1′)–C(2′)	1.389(6)	C(35)–C(36)	1.529(7)
C(1′)–C(6′)	1.363(7)	C(35′)–C(36′)	1.560(8)
C(2)–C(3)	1.376(7)		

(b) Interatomic Angles

C(21)–P(1)–C(23)	106.4(3)	C(31″)–P(2′)–C(33′)	74(1)
C(21)–P(1)–C(25)	107.2(3)	C(31″)–P(2′)–C(33″)	105(1)
C(23)–P(1)–C(25)	105.1(3)	C(31″)–P(2′)–C(35′)	116.6(9)
C(21′)–P(1′)–C(23′)	105.8(2)	C(33′)–P(2′)–C(33″)	32.4(8)
C(21′)–P(1′)–C(25′)	106.4(2)	C(33′)–P(2′)–C(35′)	116.7(7)
C(23′)–P(1′)–C(25′)	106.7(2)	C(33″)–P(2′)–C(35′)	95.7(7)
C(31)–P(2)–C(33)	108.9(3)	C(21)–P(1)–B(2)	110.9(3)
C(31)–P(2)–C(35)	107.2(2)	C(23)–P(1)–B(2)	117.5(3)
C(33)–P(2)–C(35)	106.7(3)	C(25)–P(1)–B(2)	109.2(2)
C(31′)–P(2′)–C(31″)	32(1)	C(21′)–P(1′)–B(2′)	115.4(2)
C(31′)–P(2′)–C(33′)	104.9(7)	C(23′)–P(1′)–B(2′)	107.7(2)
C(31′)–P(2′)–C(33″)	134.0(9)	C(25′)–P(1′)–B(2′)	114.1(2)
C(31′)–P(2′)–C(35′)	94.7(5)	C(31)–P(2)–B(2)	111.3(2)

two opposing chelating catecholate groups are nearly perpendicular to one another, presumably due to steric contraints imposed by the oxygen lone pairs (Figure 1b). While the chelating catecholate groups are planar, the B–O vectors of the bridge form a dihedral angle of 4.94°.

Although solutions of HB(cat) in THF decomposed after prolonged periods of time (days) to give **3** and $H_3B{\cdot}THF$, addition of phosphines enhanced the rate of degradation. Indeed, addition of HB(cat) to a stoichiometric amount of PMe_3 gave *rapid* formation of $[(Me_3P)_2BH_2]^+[B(cat)_2]^-$ [30] (**4a**) along with minor amounts of $H_3B{\cdot}PMe_3$ and $B_2(cat)_3$. Similar $[(R_3P)_2BH_2]^+[B(cat)_2]^-$ products were obtained, albeit at slower rates, from reactions of HB(cat) with other sterically compact phosphines (Scheme III). The molecular structure of $[(Et_3P)_2BH_2]^+[B(cat)_2]^-$ (**4b**) consists of well-separated anions and cations (Figure 2). The B–P bonds in the cation (1.90–1.91 Å) are shorter than those found in neutral $H_3B{\cdot}PMe_3$ (1.93 Å)[25] and $[BrH_2B{\cdot}(PMe_2)]_2$ (1.97 Å)[31] and in dication $[(PMe_3)_3BH]^{2+}$ (1.93–1.95 Å),[32] but longer than in $H_3B{\cdot}P(NH_2)_3$ (1.89 Å).[33] The pseudotetrahedral $[B(cat)_2]^-$ anion is essentially identical to that determined previously for the $[Et_3NH]^+$ salt.[34]

Assignment of these boron-substituent redistribution products is based on multinuclear NMR spectroscopic data. Particularly diagnostic is the proton coupled ^{11}B NMR spectrum which shows a broad doublet of quartets for $H_3B{\cdot}PR_3$ adducts, a broad resonance at 22.7 ppm for **3**, and a triplet of triplets corresponding to $[(R_3P)_2BH_2]^+$ along with a sharp singlet at 15.2 ppm due to the $[B(cat)_2]^-$ anion.[35]

It is interesting to note that the course of these boron-substituent redistribution reactions is determined by the size of the phosphine ligand. Degradation of HB(cat) proceeds presumably via initial coordination of phosphine, which then increases electron density

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Table V. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $[(Et_3P)_2BH_2]^+[B(cat)_2]^-$ (**4b**)

atom	*x*	*y*	*z*	B_{ISO}, Å^2
P(1)	6743(1)	9574(1)	499	3.1(1)
P(1′)	1678(1)	4948(1)	714	2.6(1)
P(2)	6596(1)	9026(1)	1690	2.6(1)
P(2′)	1703(1)	5329(1)	1942(1)	3.6(1)
O(1)	8133(2)	6332(3)	1027(1)	3.6(1)
O(1′)	4456(2)	8584(3)	1446(1)	3.8(1)
O(2)	9304(2)	5438(3)	1317(1)	3.7(1)
O(2′)	3237(2)	7740(3)	1282(1)	3.7(1)
O(3)	9349(2)	7032(3)	716(1)	3.6(1)
O(3′)	4348(2)	6804(3)	937(1)	3.5(1)
O(4)	9073(2)	7488(3)	1538(1)	3.4(1)
O(4′)	4224(2)	6641(3)	1800(1)	3.8(1)
C(1)	8022(3)	5182(5)	1148(2)	3.1(2)
C(1′)	3908(3)	9426(5)	1368(2)	3.1(2)
C(2)	8713(3)	4650(5)	1315(2)	3.1(2)
C(2′)	3184(3)	8925(5)	1275(2)	3.0(2)
C(3)	8748(3)	3484(5)	1446(2)	4.1(2)
C(3′)	2540(3)	9613(5)	1190(2)	3.6(2)
C(4)	8059(4)	2866(5)	1416(2)	4.8(2)
C(4′)	2647(3)	10818(5)	1196(2)	4.1(2)
C(5)	7380(4)	3388(6)	1261(2)	4.9(2)
C(5′)	3359(4)	11318(5)	1283(2)	4.2(2)
C(6)	7346(3)	4563(5)	1125(2)	4.0(2)
C(6′)	4011(3)	10610(5)	1369(2)	3.8(2)
C(7)	9659(3)	8083(5)	863(2)	2.8(2)
C(7′)	4631(3)	5758(5)	1119(2)	3.2(2)
C(8)	9484(3)	8360(5)	1341(2)	2.8(2)
C(8′)	4550(3)	5652(5)	1626(2)	3.2(2)
C(9)	9725(3)	9392(5)	1565(2)	3.9(2)
C(9′)	4773(3)	4659(6)	1888(2)	4.9(2)
C(10)	10149(3)	10161(5)	1290(3)	4.6(2)
C(10′)	5100(4)	3769(6)	1627(3)	6.4(3)
C(11)	10333(3)	9872(5)	823(2)	4.3(2)
C(11′)	5183(3)	3880(6)	1134(3)	5.9(2)
C(12)	10086(3)	8819(5)	592(2)	3.7(2)
C(12′)	4958(3)	4885(6)	858(2)	4.4(2)
C(21)	7796(3)	9748(6)	567(2)	5.2(2)
C(21′)	722(3)	4348(4)	589(2)	3.2(2)
C(22)	8198(3)	9701(6)	110(2)	5.9(2)
C(22′)	682(3)	3033(5)	674(2)	4.3(2)
C(23)	6556(4)	8141(5)	245(2)	5.1(2)
C(23′)	2258(3)	4232(4)	279(2)	3.2(2)
C(24)	5705(4)	7870(5)	143(3)	6.3(2)
C(24′)	3053(3)	4747(5)	267(2)	4.7(2)
C(25)	6370(3)	10567(5)	10(2)	3.7(2)
C(25′)	1615(3)	6475(4)	530(2)	3.2(2)
C(26)	6538(3)	11842(5)	105(2)	4.7(2)
C(26′)	1401(3)	6685(5)	−24(2)	4.2(2)
C(31)	7600(3)	9189(5)	1897(2)	4.0(2)
C(31′)	773(7)	4499(15)	2062(5)	5.7(5)
C(31″)	1243(15)	4293(21)	2321(9)	8.5(9)
C(32)	7884(3)	8786(5)	2420(2)	4.6(2)
C(32′)	879(6)	3330(8)	2175(3)	9.5(3)
C(33)	6383(3)	7477(4)	1598(2)	4.0(2)
C(33′)	2300(12)	5169(17)	2494(8)	5.9(6)
C(33″)	2575(13)	5922(23)	2376(8)	6.6(8)
C(34)	6386(4)	6721(5)	2049(2)	6.0(2)
C(34′)	2939(15)	5861(26)	2547(6)	10.3(10)
C(34″)	3055(11)	4694(20)	2550(6)	9.4(7)
C(35)	6060(3)	9514(5)	2198(2)	3.4(2)
C(35′)	1242(4)	6706(6)	1843(2)	7.1(3)
C(36)	6203(4)	10798(5)	2340(2)	5.3(2)
C(36′)	904(5)	7220(7)	2318(3)	10.5(3)
B(1)	8960(4)	6582(6)	1145(2)	3.3(2)
B(1′)	4068(4)	7434(6)	1367(2)	3.3(2)
B(2)	6315(3)	9958(5)	1107(2)	2.8(2)
B(2′)	2155(3)	4693(5)	1378(2)	3.1(2)

at boron via σ-donation (Scheme IV). Consequent weakening of the B–O bonds may facilitate addition of a second molecule of HB(cat) to give an incipient borenium-type cation, IIb. This intermediate reacts in turn with either HB(cat) or PR_3 to give $H_3B{\cdot}PR_3/B_2(cat)_3$ or $[(R_3P)_2BH_2][B(cat)_2]$ respectively.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for *cis*-$[RhH_2(PMe_3)_4]^+[B(cat)_2]^-$ (**9**)‡

(a) Interatomic Distances			
Rh(1)–P(1)	2.306(3)	O(2)–B(1)	1.487(12)
Rh(1)–P(2)	2.282(3)	C(2)–C(3)	1.356(13)
P(1)–C(11)	1.834(12)	C(2)–C(7)	1.423(14)
P(1)–C(12)	1.816(12)	C(3)–C(4)	1.407(16)
P(1)–C(13)	1.796(12)	C(4)–C(5)	1.388(16)
P(2)–C(21)	1.804(13)	C(5)–C(6)	1.375(16)
P(2)–C(22)	1.831(12)	C(6)–C(7)	1.377(15)
P(2)–C(23)	1.801(13)	C(31)–C(32)	1.382(18)
O(1)–C(2)	1.350(11)	C(31)–C(33)	1.356(17)
O(2)–C(7)	1.337(12)	C(32)–C(33)[c]	1.356(17)
O(1)–B(1)	1.473(11)		
(b) Interatomic Angles			
P(1)–Rh(1)–P(1)[a]	93.0(1)	O(1)–C(2)–C(3)	130(1)
P(1)–Rh(1)–P(2)[a]	93.0(1)	O(1)–C(2)–C(7)	109.1(8)
P(1)–Rh(1)–P(2)	153.2(1)	O(2)–C(7)–C(2)	111(1)
P(2)–Rh(1)–P(2)[a]	93.3(2)	O(2)–C(7)–C(6)	130(1)
Rh(1)–P(1)–C(11)	125.1(4)	C(3)–C(2)–C(7)	121(1)
Rh(1)–P(1)–C(12)	113.2(4)	C(2)–C(3)–C(4)	118(1)
Rh(1)–P(1)–C(13)	114.1(4)	C(3)–C(4)–C(5)	120(1)
Rh(1)–P(2)–C(21)	114.7(4)	C(4)–C(5)–C(6)	121(1)
Rh(1)–P(2)–C(22)	113.0(4)	C(5)–C(6)–C(7)	120(1)
Rh(1)–P(2)–C(23)	123.5(5)	C(2)–C(7)–C(6)	119(1)
C(11)–P(1)–C(12)	101.4(6)	C(32)–C(31)–C(33)	120(1)
C(11)–P(1)–C(13)	100.3(6)	C(31)–C(32)–C(33)[c]	120(1)
C(12)–P(1)–C(13)	99.0(5)	C(31)–C(33)–C(32)[c]	120(1)
C(21)–P(2)–C(22)	98.5(6)	O(1)–B(1)–O(1)[b]	115(1)
C(21)–P(2)–C(23)	100.9(7)	O(1)–B(1)–O(2)	104.8(4)
C(22)–P(2)–C(23)	102.8(6)	O(1)–B(1)–O(2)[b]	110.1(4)
C(2)–O(1)–B(1)	107.9(7)	O(1)[b]–B(1)–O(2)	110.1(4)
C(7)–O(2)–B(1)	107.0(7)	O(1)[b]–B(1)–O(2)[b]	104.8(4)
		O(2)–B(1)–O(2)[b]	112(1)

‡ Symmetry operator symbols: (a) $y, x, 1 - z$; (b) $-x, y - x, {}^{2}/_{3} - z$; (c) $x - y, -y, {}^{1}/_{3} - z$.

Reaction of HB(cat) with Phosphinorhodium(I) Complexes. We reported recently that reactions of HB(cat) with hydroboration catalyst precursors $[Rh(diene)(P_2)]^+[A]^-$ (P_2 = chelating bis(phosphine)) gave numerous Rh-containing products derived from HB(cat) degradation.[36] In contrast, addition of excess HB(cat) to $[Rh(DPPP)_2]Cl$ (**5**)[16] (DPPP = 1,3-bis(diphenylphosphino)propane) gave dihydride $[RhH_2(DPPP)_2]^+[B(cat)_2]^-$ (**6**) as the only phosphinorhodium complex in solution; extensive degradation of HB(cat), however, was observed by ^{11}B NMR spectroscopy. This reaction was exceedingly slow with only 70% conversion after 12 h. Saturated rhodium hydride $[RhH(DPPP)_2]$ (**7**) is a possible intermediate in this transformation and indeed, treatment of isolated **7** with HB(cat) also afforded **6** in high yield (Scheme V) along with significant amounts of $B_2(cat)_3$ (**3**). That dihydrides are formed in these reactions parallels the observation that HB(cat) degradation by **1** gave $[RhH_2Cl(PPh_3)_3]$ and **3**.[10b,13]

Reactions of HB(cat) with rhodium(I) hydrides are of particular interest due to their relevance in catalyzed alkene hydroborations.[4] Interestingly, degradation of HB(cat) by these complexes gave similar boron substituent redistribution products to those obtained from reactions with the corresponding phosphines. For instance, addition of HB(cat) to $[RhH(PMe_3)_4]$ (**8**) gave $H_3B{\cdot}PMe_3$, $[(Me_3P)_2BH_2][B(cat)_2]$, and a complex mixture of phosphinorhodium species including dihydride *cis*-$[RhH_2(PMe_3)_4]^+[B(cat)_2]^-$ (**9**) (Scheme V) and several complexes containing two or three phosphines/rhodium. The molecular structure of **9**, determined by X-ray diffraction, consists of well-separated cations and anions (Figure 3). Although location of the cation on a special position precluded location of the hydrides, distortion from planarity of the RhP_4 unit (P–Rh–P = 93.1, 153.2°) is typical of *cis*-disubstituted pseudooctahedral geometry.[37]

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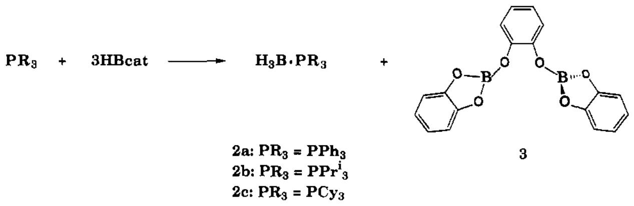
(36) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863.

(37) For leading references see: Hartwig, J. F.; Anderson, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875.

Table VII. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for *cis*-$[RhH_2(PMe_3)_4]^+[B(cat)_2]^-$ (**9**)

atom	x	y	z	B_{ISO}, Å^2
Rh(1)	4190(1)	4190	5000	1.7(1)
P(1)	6024(2)	4759(2)	4516(2)	2.1(1)
P(2)	2287(3)	3724(3)	4879(2)	2.8(1)
O(1)	-364(7)	5235(6)	4012(4)	2.8(2)
O(2)	989(6)	7137(6)	3614(4)	2.8(2)
C(2)	278(8)	5864(8)	4623(5)	2.2(3)
C(3)	210(10)	5551(11)	5376(6)	2.9(4)
C(4)	1036(11)	6357(12)	5898(6)	3.3(4)
C(5)	1894(11)	7449(11)	5645(7)	3.7(5)
C(6)	1932(10)	7772(10)	4885(7)	3.3(4)
C(7)	1118(9)	7004(9)	4368(6)	2.4(4)
C(11)	7275(11)	4961(12)	5093(7)	4.0(5)
C(12)	6657(10)	6127(11)	3986(7)	3.4(4)
C(13)	6038(11)	3832(11)	3762(7)	3.9(5)
C(21)	1445(10)	2565(11)	4202(8)	4.5(5)
C(22)	2121(11)	4880(12)	4419(7)	3.7(5)
C(23)	1287(12)	3295(12)	5681(8)	4.8(5)
C(31)	992(12)	188(12)	2442(7)	4.4(5)
C(32)	1459(12)	1123(10)	1936(8)	4.2(5)
C(33)	444(12)	-923(10)	2170(8)	4.2(5)
B(1)	0	6014(13)	3333	2.8(5)
H(3)	-381	4807	5555	3.5
H(4)	1008	6150	6425	3.5
H(5)	2466	7972	5999	3.5
H(6)	2516	8526	4718	3.5
H(11)	7933	5199	4772	3.5
H(11′)	7088	4252	5346	3.5
H(11″)	7449	5551	5476	3.5
H(12)	7405	6319	3804	3.5
H(12′)	6723	6729	4325	3.5
H(12″)	6164	6052	3565	3.5
H(13)	6820	4124	3592	3.5
H(13′)	5577	3836	3340	3.5
H(13″)	5732	3065	3953	3.5
H(21)	667	2418	4194	3.5
H(21′)	1439	1870	4375	3.5
H(21″)	1783	2773	3710	3.5
H(22)	1318	4645	4388	3.5
H(22′)	2455	5031	3920	3.5
H(22″)	2513	5572	4727	3.5
H(23)	539	3131	5504	3.5
H(23′)	1568	3893	6056	3.5
H(23″)	1210	2597	5911	3.5
H(31)	1047	328	3000	3.5
H(32)	1868	1913	2139	3.5
H(33)	131	-1576	2529	3.5

Scheme II



2a: $PR_3 = PPh_3$
2b: $PR_3 = PPr^i_3$
2c: $PR_3 = PCy_3$

To avoid complicated product distributions arising from loss of phosphine, reactions of HB(cat) with *coordinatively unsaturated* rhodium hydrides were also examined. Initial work focused on $[RhH(DiPPE)]_2$, which afforded the novel zwitterionic species $[Rh(\eta^6\text{-}(cat)B(cat))(DiPPE)]$ in which the $[B(cat)_2]^-$ anion is bound to Rh via one of its arene rings.[10b] Addition of HB(cat) to monodentate analog $[RhH(N_2)(PPr^i_3)_2]$ (**10**),[18] however, resulted in several new phosphinorhodium complexes, one of which is assigned tentatively as oxidative addition product $[RhH_2(B(cat))(PPr^i_3)_2]$. Degradation of HB(cat) was minimal in this reaction, with only minor amounts of **3** observed. Further work is in progress to characterize more completely the other products formed in this reaction.

In the absence of a Rh–H bond, oxidative addition of HB(cat) to a basic metal center can be the sole reaction pathway. We reported recently that reaction of HB(cat) with $[RhCl(N_2)(PPr^i_3)_2]$ (**11**) gave exclusive formation of unsaturated rhodium–boryl complex $[RhHCl(B(cat))(PPr^i_3)_2]$ (**12**).[10b] Likewise, addition of 1.5 equiv of HB(cat) to a THF solution of $[RhCl(PMe_3)_3]$ (**13**) gave saturated $[RhHCl(B(cat))(PMe_3)_3]$ (**14**) quantitively (Scheme VI). The molecular structure of **14** is similar to that reported previously for the iridium analog[11] and confirms

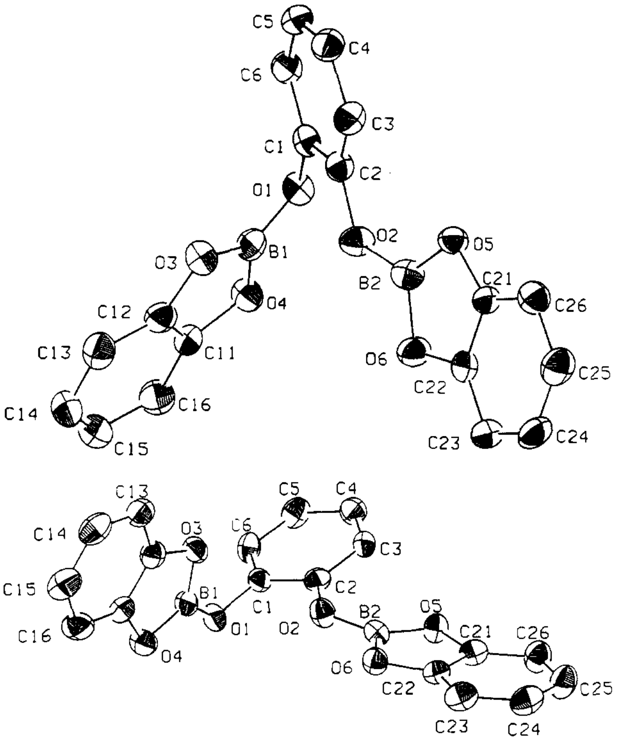


Figure 1. Top: (a) Molecular structure of $B_2(cat)_3$ (**3**) with hydrogens omitted for clarity. Bottom: (b) Side on view of $B_2(cat)_3$ (**3**) with hydrogens omitted for clarity.

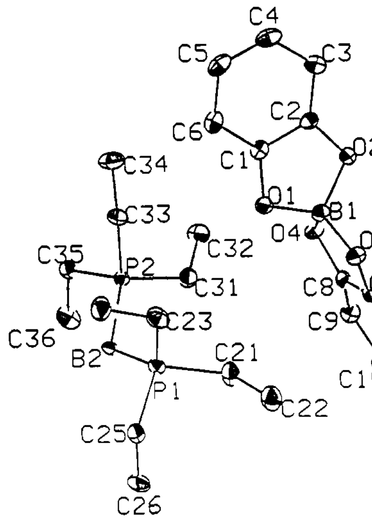
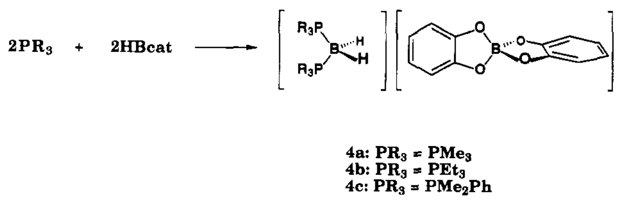


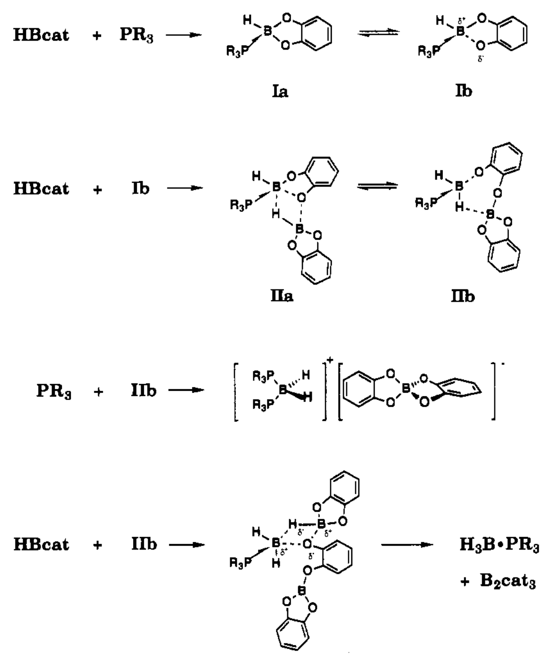
Figure 2. Molecular structure of $[(Et_3P)_2BH_2]^+[B(cat)_2]^-$ (**4b**) with hydrogens omitted for clarity.

Scheme III

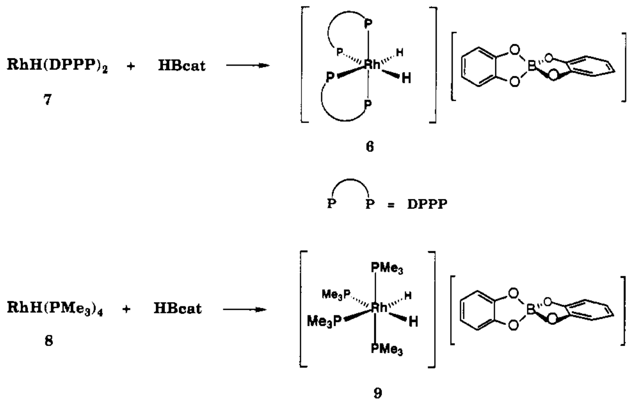


4a: $PR_3 = PMe_3$
4b: $PR_3 = PEt_3$
4c: $PR_3 = PMe_2Ph$

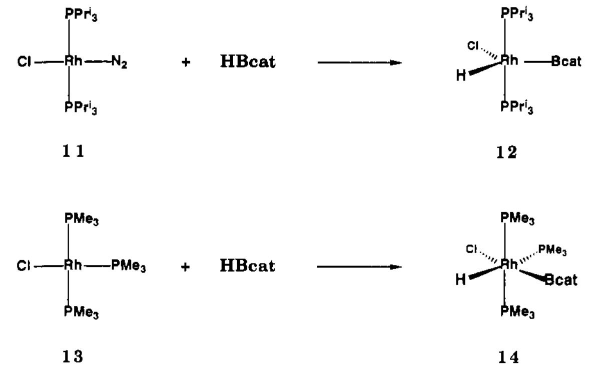
Scheme IV



Scheme V



Scheme VI



the meridional arrangement of phosphine ligands.[38] In contrast, no new phosphinorhodium complexes were observed when chelating bis(phosphine) rhodium chlorides $[Rh(\mu\text{-}Cl)\{(R_2PCH_2)_2\}]_2$ (R = cyclohexyl, isopropyl) were treated with excess HB(cat). In summary, HB(cat) degradation is negligible only for chlororhodium complexes containing basic monodentate phosphines.

Catalysis. Detailed investigations of the efficency of hydroborations using $[Rh(diene)(P_2)]^+[A]^-$ have appeared elsewhere.[9]

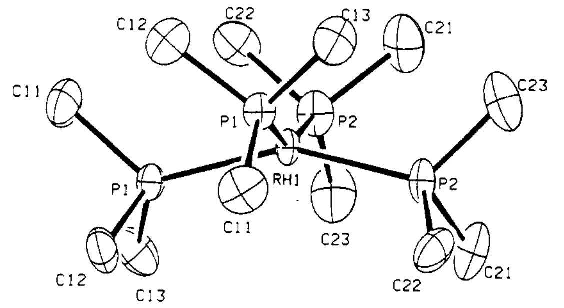


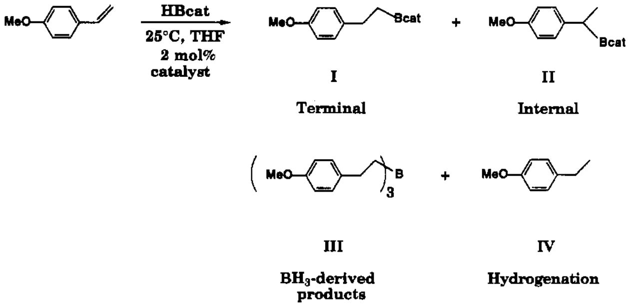
Figure 3. Molecular structure of the cation of $[RhH_2(PMe_3)_4]^+[B(cat)_2]^-$ (**9**) with hydrogens omitted for clarity.

Table VIII. Catalytic Hydroboration of 4-Vinylanisole[a]

catalyst	% I	% II	% III	% IV	time (h)
$[Rh(DPPP)_2]Cl$ (**5**)	18	78	4		0.5
$[RhH_2(DPPP)_2][B(cat)_2]$ (**6**)	37	40	21	2	0.5
$[RhH(DPPP)_2]$ (**7**)	40	35	20	5	0.5
$[RhH(PMe_3)_4]$ (**8**)	46	38	13	4	1
$[RhH_2(PMe_3)_4][B(cat)_2]$ (**9**)	44	23	30	3	1
$[RhH(N_2)(PPr^i_3)_2]$ (**10**)	45	45	5	5	0.5
$[RhCl(N_2)(PPr^i_3)_2]$ (**11**)	95	5			1
$[RhCl(PMe_3)_3]$ (**13**)	55	45			1
$[RhHCl(B(cat))(PMe_3)_3]$ (**14**)	50	50			1

[a] All reactions were carried out in THF at 25 °C in the presence of 2 mol % of catalyst. Alkene/catecholborane/catalyst = 1.0/1.2/0.02. Product distributions determined by ^{13}C and ^{1}H NMR.

Scheme VII



Hydroboration of 4-vinylanisole using $[Rh(DPPP)_2]Cl$ (**5**) gave predominant formation of the corresponding internal boronate ester. An η^3-benzylrhodium intermediate has been invoked to explain the unusually high Markownikoff selectivities observed in rhodium-catalyzed hydroborations of vinylarenes.[5b] The vacant coordination site required for an η^3-benzyl intermediate arises presumably from the ease with which chelating arylphosphines dissociate fully in solution or behave in a monodentate fashion.[16a] Hydroboration with **5**, however, also gave small amounts of BH_3-derived products. It is important to note that the highly reactive hydroborating reagent BH_3 adds rapidly to *3* equiv of substrate. As addition of borane to 4-vinylanisole favors terminal over internal borane by a ratio of 93:7,[39] alcohol ratios (after oxidative workup) would be affected greatly by degradation of HB(cat).

Upon completion of catalysis, ca. 30% of **5** had been converted into its degradation product $[RhH_2(DPPP)_2][B(cat)_2]$ (**6**). The presence of **6** in solution is presumably responsible for *alkylborane* formation. Indeed, hydroborations using isolated **6** gave significantly more BH_3-derived product while reducing dramatically the amount of internal boronate ester. Ironically, while product distributions were more complex in hydroborations using saturated rhodium hydrides $[RhH(DPPP)_2]$ (**7**) or $[RhH(PMe_3)_4]$ (**8**), reactions were clean with respect to catalyst precursor. Complexes **6** and $[RhH_2(PMe_3)_4][B(cat)_2]$ (**9**) were the only phosphinorhodium complexes present at detectable levels, respectively, upon completion of catalysis. In contrast, catalysis with the unsaturated

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(38) Nöth, H. Personal communication to R.T.B.

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

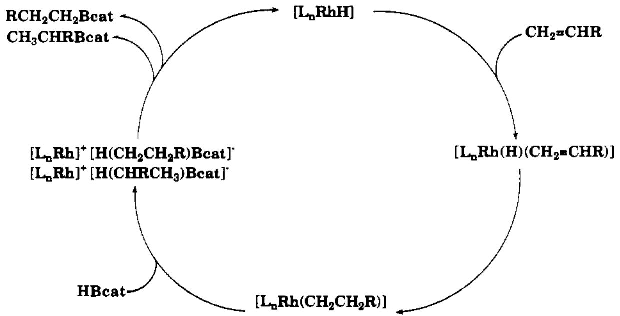
hydride [RhH(N$_2$)(PPr$^i_3$)$_2$] (**10**) gave poor selectivities, BH$_3$-derived products, *and* several phosphinorhodium complexes upon completion of catalysis. Indeed, eventual catalyst degradation resulted in formation of Rh metal.

Interestingly, while more basic analogues of **1**, [RhCl(N$_2$)(PPr$^i_3$)$_2$] (**11**) and [RhCl(PMe$_3$)$_3$] (**13**) catalyzed alkene hydroborations with no observable degradation products, activities were much lower than those using **1**. In situ monitoring of reactions by ^{31}P NMR spectroscopy showed that [RhHCl(B(cat))(PPr$^i_3$)$_2$] (**12**) and *mer*-[RhHCl(B(cat))(PMe$_3$)$_3$] (**14**), respectively, were the only phosphinorhodium complexes present, at detectable levels, in solution at any time during or after completion of catalysis. This is in contrast to reactions using **1** wherein several species were observed.[13] While hydroborations of 4-vinylanisole using **12** favored the corresponding terminal boronate ester,[36] similar reactions carried out in the presence of either **13** or **14** proceeded with little regiocontrol to give both terminal and internal hydroboration products in comparable yields. With **12** and **14**, however, increased steric congestion around the metal center, due to less labile PPr$^i_3$ and PMe$_3$ ligands (cf. PPh$_3$ in **1**), could inhibit formation of the η^3-benzylrhodium intermediate to varying extents. Consequently, significant amounts of terminal product would be produced via the competing conventional hydroboration pathway (Scheme I).

Hydroborations using isolated samples of **12** and **14** gave activities and regioselectivities comparable to those of **11** and **13**; over 600 turnovers were obtained for hydroborations of 1-octene under unoptimized conditions with no sign of catalyst degradation.

Alternative mechanisms for catalyzed hydroborations are also conceivable.[13,36] A plausible mechanism involving reactions employing monohydride rhodium catalysts (cf. complex **7**) invokes initial insertion of alkene into the Rh–H bond to give a rhodium alkyl intermediate which reacts subsequently with HB(cat) via transmetalation to afford the desired hydroboration product (Scheme VIII). We reported recently that addition of organoboranes to [RhMe(DMPE)$_2$] {DMPE = 1,2-dimethylphosphino(ethane)} affords [Rh(DMPE)$_2$]$^+$[MeBHRR′]$^-$, which in turn transfers hydride to give [RhH(DMPE)$_2$] and MeBRR′.[10b] Similar reactions involving zirconium alkyl[40] and alkenyl[41–43] complexes have also been reported.

Scheme VIII



Conclusions

Reactions of HB(cat) with phosphines give different boron-substituent redistribution products depending upon the steric component of the phosphine. Bulky phosphines form phosphine-borane adducts H$_3$B·PR$_3$ along with dinuclear boronate ester B$_2$(cat)$_3$, whereas two sterically compact phosphines coordinate to boron to give [(R$_3$P)$_2$BH$_2$]$^+$[B(cat)$_2$]$^-$. As phosphine-induced degradation of HB(cat) is generally slow, with the exception of PMe$_3$, this competing reaction is only significant for hydroborations of hindered (slow reacting) alkenes.

Phosphinorhodium(I) hydrides also gave boron-substituent redistribution products. While the resulting dihydrides are active catalyst precursors for hydroboration of 4-vinylanisole, significant amounts of alkylboranes, derived from BH$_3$ addition, were also observed. With unsaturated rhodium(I) chlorides containing basic monodentate phosphines, however, only the desired alkylboronate esters were formed.

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Supplementary Material Available: Tables of crystallographic data, positional parameters, thermal parameters, additional bond lengths and angles, and hydrogen atom parameters and figures depicting the structure and numbering of the compounds (25 pages). Ordering information is given on any current masthead page.

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