Insertion of Alkenes into Rh–B Bonds†

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While B–H bonds of many organoboranes add readily to alkenes, some hydroboration reagents such as catecholborane (HBcat) react only at elevated temperatures.[1] The discovery that transition-metal complexes catalyze alkene hydroboration using HBcat[2] has led recently to applications in organic synthesis.[3] A proposed catalytic cycle using $RhCl(PPh_3)_3$ (**1**) invokes oxidative addition of the B–H bond of HBcat to the metal center, followed by insertion of alkene into the Rh–H bond and reductive elimination of alkylboronate ester.[2] A viable mechanistic alternative involves insertion of alkene into the Rh–B bond, followed by C–H rather than B–C bond formation. Production of vinylboranes[4] and vinylboronate esters[5–7] in several metal-catalyzed additions of boranes to alkenes suggests a competing "dehydrogenative borylation" pathway involving insertion of alkene into the Rh–B bond and β-H elimination from the resulting borylalkylmetal complex. In another application of transition-metal catalysis to borane chemistry, Corcoran and Sneddon demonstrated the dehydrocoupling of two B–H bonds to give a new B–B bond.[8] We report herein the first discrete examples of alkene insertion into Rh–B bonds and B–B bond reductive elimination and discuss implications for catalyzed diboration of alkenes.

We reported recently that addition of excess HBcat to $RhHCl(Bcat)(PPh_3)_2$ (**2**),[2,9] a purported intermediate in hydroborations using **1**, gave the 16e⁻ bis(boryl) complex $RhCl(Bcat)_2(PPh_3)_2$ (**3**) in high yield.[6] The molecular structure of **3**, determined by X-ray diffraction, is a distorted square-pyramid with trans phosphine ligands (Figure 1).[10] While the Rh1–B1 bond trans to chloride is 0.052 Å longer than the cis Rh1–B2 distance (1.956(8) Å), both are consistent with Rh–B σ-bonds.[11] The BO_2 planes of the two boryl moieties are essentially perpendicular.

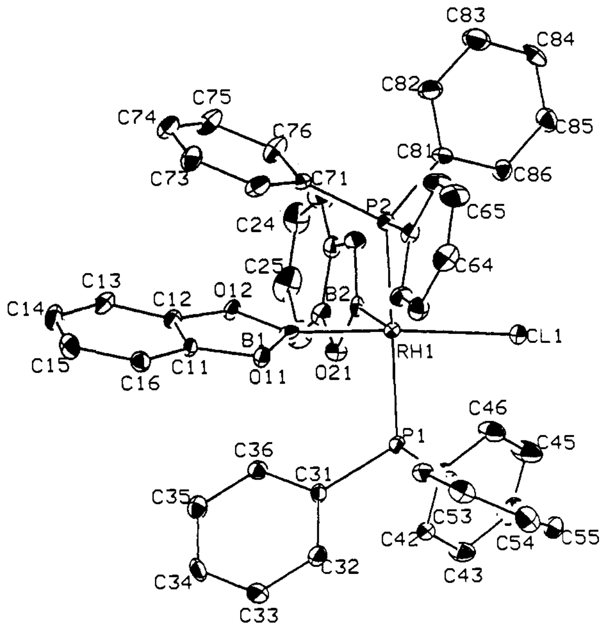

Figure 1. Molecular structure of $RhCl(Bcat)_2(PPh_3)_2$ (**3**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–Cl = 2.428(2), Rh–P1 = 2.342(2), Rh–P2 = 2.342(2), Rh–B1 = 2.008(7), Rh–B2 = 1.956(8), Cl–Rh–P1 = 88.09(6), Cl–Rh–P2 = 91.14(6), Cl–Rh–B1 = 163.4(2), Cl–Rh–B2 = 117.5(2), P1–Rh–P2 = 169.88(7), P1–Rh–B1 = 92.2(2), P1–Rh–B2 = 93.5(2), P2–Rh–B1 = 85.7(2), P2–Rh–B2 = 95.8(2), B1–Rh–B2 = 79.0(3).

Reactions of this novel bis(boryl) complex with unsaturated organic molecules were investigated to examine the feasibility of substrate insertion into Rh–B bonds. Addition of *o*-xylylisocyanide to **3**, however, resulted in rapid reductive elimination of B_2cat_2[12] and formation of monovalent *trans*-$RhCl(CNAr)(PPh_3)_2$ (Ar = 2,6-$Me_2C_6H_3$, **4**) (Scheme I).[13] This B–B reductive elimination is driven presumably by stabilization of the monovalent state by the π-acceptor ligand, as reaction of **3** with excess PEt_3 (a poor π-acid) gave the new bis(boryl) complex $RhCl(Bcat)_2(PEt_3)_2$ (**3′**).[14]

Addition of 2 equiv of 4-vinylanisole $CH_2{=}CHAr'$ (Ar′ = C_6H_4OMe), to a CH_2Cl_2 solution of **3** gave bis(boronate ester) $CH_2(Bcat)CHAr'(Bcat)$ (**6**), vinylboronate ester (*E*)-$CH(Bcat){=}CHAr'$ (**7**), and internal hydroboration product $CH_3CHAr'(Bcat)$ (**8**) in a 3:2:2 ratio along with a trace of terminal hydroboration product $(Bcat)CH_2CH_2Ar'$ (**9**) and an orange precipitate of $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ (**10**) (Scheme II).[15] We propose that initial insertion of alkene into one Rh–B bond affords

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(10) Crystal data for **3**·3[$ClCH_2CH_2Cl$] (from $ClCH_2CH_2Cl$): formula = $C_{54}H_{50}B_2O_4P_2Cl_7Rh$, FW = 1197.64, triclinic, space group $P\bar{1}$ (No. 2), a = 13.360(1) Å, b = 14.032(2) Å, c = 17.927(2) Å, α = 108.78(1)°, β = 99.25(1)°, γ = 113.32(1)°, V = 2756.7 Å^3, Z = 2, ρ(calcd) = 1.443 g cm^{-3}; T = 203 K. Anisotropic refinement of all non-hydrogen atoms (H fixed; 685 variables) using 5442 unique reflections with $I \geq 3\sigma(I)$, from 13 050 data collected, gave R = 0.059 and R_w = 0.047.

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(12) 2,2′-Bis(1,3,2-benzodioxaborole): Welch, C. N.; Shore, S. G. *Inorg. Chem.* **1968**, *7*, 225. MS: *m/e* 238 amu for $M^+ = {}^{12}C_{12}{}^{1}H_8{}^{11}B_2{}^{16}O_4$; intensities of the 236–240-amu mass envelope matched calculated intensities within 1%. NMR data in CD_2Cl_2: ^1H δ 7.18, 7.36 (mult, 4H); $^{13}C\{^1H\}$ δ 148.28 (ipso C), 123.99, 113.51 (CH); $^{11}B\{^1H\}$ δ 30.5 (br, $\Delta\nu_{1/2}$ = 380 Hz).

(13) NMR data for **4** in CD_2Cl_2: ^1H δ 1.67 (s, 6H, CH_3 of Ar), 6.74 (d, 2H, J = 7.5 Hz, meta H of Ar), 6.90 (tr, para H of Ar), 7.31 (ov m, 18H, meta, para H of PPh_3), 7.78 (m, 12H, ortho H of PPh_3); $^{31}P\{^1H\}$ δ 30.0 (d, J_{PRh} = 135 Hz). IR (KBr): ν_{CN} = 2098 (vs).

(14) NMR data for **3′**: ^1H δ 1.06 (mult, 18H, CH_3), 2.09 (mult, 12H, CH_2), 6.88, 7.04 (mult, 4H, catecholate); $^{31}P\{^1H\}$ δ 29.4 (d, J_{PRh} = 106 Hz); $^{11}B\{^1H\}$ δ 35.9 (br).

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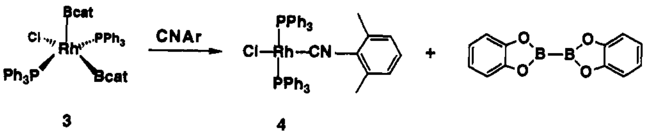
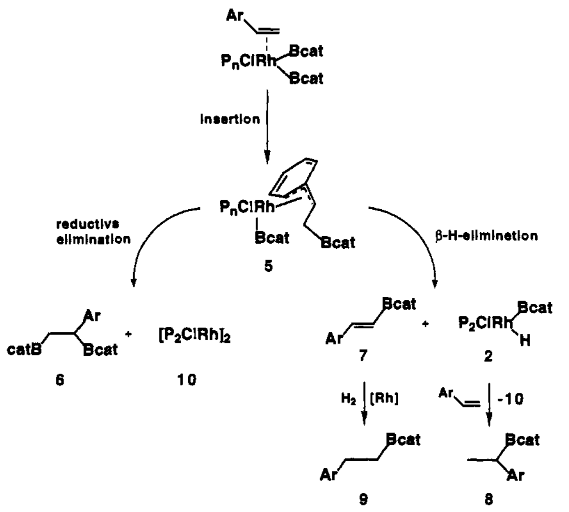
Scheme I



Scheme II



borylalkyl intermediate **5**,[16] which then undergoes reductive elimination to give diborated product **6** or β-H elimination to afford vinylboronate ester **7** and hydridoboryl rhodium complex **2**. In fact, **2** was observed by multinuclear NMR spectroscopy in corresponding reactions of **3** with 2-phenylpropene which gave predominantly (*E*)-CH(Bcat)=C(Me)Ph (**11**). Reaction of 4-vinylanisole with **2** then gives hydroboration product **8**, as reported previously for other alkenes.[2,17]

Formation of vinylboronate esters from alkenes and HBcat using **1** is favored by addition of excess phosphine to the catalyst.[6,7] Indeed, reaction of **3** and 2 equiv of PPh_3 with 4-vinylanisole shut down the reductive elimination pathway and gave only **7**, **8**, **9**, and Rh complex **1**. In the absence of substrate, **3** reacts only slowly with PPh_3 to give a mixture of products, including **1** and B_2cat_3, derived from B-substituent redistribution.[18] Further investigations into stoichiometric reactions of both **2** and **3** with a variety of alkenes are currently underway.

In summary, reaction of bis(boryl) complex **3** with donor ligands gives phosphine substitution or elimination of B_2cat_2, depending on the ligand's π-acidity. We have also provided the first confirmed example of *alkene insertion into Rh–B bonds*.[19] The chemistry of 1,2-bis(boronate esters) has not been investigated in detail;[1,20] we hope now to couple these insertion reactions with oxidative addition of B–B bonds in order to catalyze alkene diboration with B_2cat_2.[21]

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles (12 pages); observed and calculated structure factors for **3** (13 pages). Ordering information is given on any current masthead page.

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(15) 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 alkene (0.4 mmol) in 1 mL of CD_2Cl_2 was added to a suspension of **3** (180 mg, 0.2 mmol) in 1 mL of CD_2Cl_2. The resulting mixture was stirred for 24 h, filtered, and then analyzed by high-field ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy and GC/MS. Authentic samples of **7** were prepared by uncatalyzed addition of HBcat to HC≡CAr′ at 80 °C. Catalyzed hydroboration of **7** using **1** and HBcat gave nearly pure samples of **6** (by ^{1}H NMR and GC/MS). MS: **6**, 372 amu ($M^+ = {}^{12}C_{21}{}^{1}H_{18}{}^{11}B_2{}^{16}O_5$) (intensities of the 370–374-amu mass envelope matched calculated intensities within 1%, and the fragmentation pattern was distinct from that for an authentic sample of 1,1-bis(boronate ester)); **7**, 252 amu (M^+ = for ${}^{12}C_{15}{}^{1}H_{13}{}^{11}B{}^{16}O_3$); NMR data in CD_2Cl_2; **6**, ^{1}H δ 1.96 (dd, J = 16.5, 7 Hz, CH_2Bcat), 2.20 (dd, J = 16.5, 9 Hz, CH_2Bcat), 3.37 (dd, J = 9, 7 Hz, C*H*Ar′Bcat), 3.79 (s, OCH_3), $^{13}C\{^{1}H\}$ (−80 °C) δ 13.3 (br, *C*H_2Bcat), 24.3 (br, *C*HAr′Bcat), 55.35 (O*C*H_3); $^{11}B\{^{1}H\}$ δ ca. 35 (v br); **7**, ^{1}H δ 7.71 (d, J = 18.5 Hz, =C*H*(Bcat)), 7.59, 6.94 (mult, 2H, Ar′), 7.23, 7.06 (mult, 2H, catecholate), 6.34 (d, J = 18.5 Hz, =C*H*Ar′), 3.85 (s, OC*H*)$_3$; $^{13}C\{^{1}H\}$ δ 160.47 (c), 151.29 (=*C*HAr′), 147.98 (C), 129.30 (C), 128.82 (CH), 122.43 (CH), 113.81 (CH), 112.14 (CH), 55.17 (O*C*H_3) (at −80 °C an additional resonance was observed at 109.4 ppm (br, =*C*HBcat)); $^{11}B\{^{1}H\}$ δ 31.5. Multinuclear NMR spectra for boronate esters **8**, **9**,[3g] and **11**[7] have been reported previously.

(16) Intermediate **5** is depicted as an η^3-benzyl complex as these have been proposed[3c] to account for the Markovnikov selectivity observed for catalyzed hydroborations of vinylarenes.

(17) Complex **2** and 4-vinylanisole also give rise to some vinylboronate ester **7** and H_2, which react further (catalyzed by **1**) to give terminal hydroboration product **9**.

(18) This aryloxy boron compound is often formed as an HBcat degradation product in alkene hydroborations catalyzed by **1**.[6] See also: Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.*, in press.

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