Vinylborane Formation in Rhodium-catalysed Hydroborations; Ligand-free Homogeneous Catalysis

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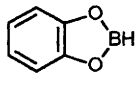
The reaction of vinylarenes with oxazaborolidine **4** catalysed by (bis-alkene) rhodium chloride complexes leads exclusively to coproduction of (*E*)-vinylborane and ethylarene.

Catalysis of alkene hydroboration with catecholborane **1** by rhodium complexes is well established, following the initial observations of Mannig and Noth.[1] Enantioselective and diastereoselective variants have been described.[2] In previous work we have shown that oxazaborolidines **2** and **3** derived from ephedrine or pseudoephedrine are effective for hydroboration–oxidation of styrenes to give the corresponding 1-arylethanol with high regioselectivity and up to 76% enantiomeric excess (e.e.), without the need to deploy a chiral diphosphine.[3] In order to improve this reagent-controlled catalytic asymmetric synthesis,[4] several variants on the struc-



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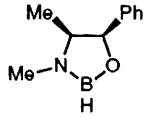

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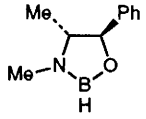

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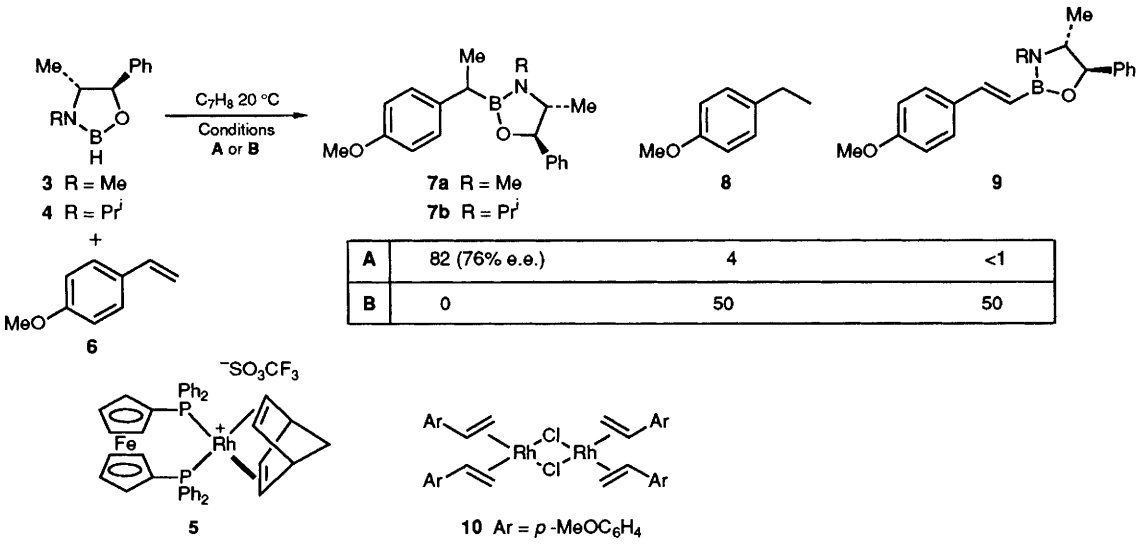
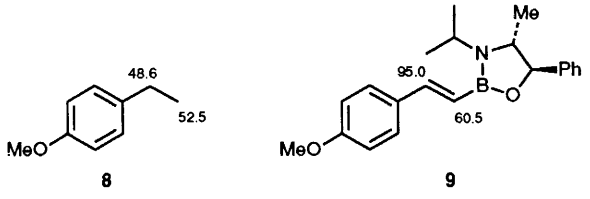


A	82 (76% e.e.)	4	<1
B	0	50	50

Scheme 1 Reaction products; yields quoted as percentages. *Conditions*: **A**: catalyst **5**, borane **3**, remaining 13% as primary regioisomer of **7**; **B**: catalyst **10**, borane **4**.



Scheme 2 Deuterium distribution in products **8** and **9** formed from complete reaction of (*Z*)-1,2-[$^2H_2$]-**6** as determined by ^1H NMR in C_7D_8 at 500 MHz. Distributions are expressed as percentage of ^2H incorporation at the site relative to the analogous reaction performed with unlabelled **6**.

ture of **2** and **3** have been examined with the objective of increasing the specificity and extending the range of utility. In this context a novel alternative catalytic pathway has been discovered, which is the subject of the present communication.

To increase the steric bulk around the B–H bond of the reagent, the *N*-isopropyl analogue **4** was prepared from (1*R*,2*R*)-1-hydroxy-2-aminophenylpropane (nor-pseudoephedrine) {Me_2CO–EtOH, Pt, H_2, 96%; BH_3·Me_2S, 0–120 °C, distil 65 °C, 0.015 mbar; 82%; ^{11}B δ 28.5 (d, 155 Hz), $[\alpha]_D^{20}$ −59.7 (*c* 0.98, $CHCl_3$)} as a colourless mobile oil. In initial experiments, solutions of catalyst **5** (0.5–1 mol%), 4-methoxystyrene **6** and reagent **4** in toluene were found to be stable, although concurrent ^{31}P NMR studies indicated that the Rh catalyst had been cleanly converted into a new species (δ = 37.2 and 30.7, $J_{P\text{-}Rh}$ 274, 185, $J_{P\text{-}P}$ 31 Hz). If catalytic quantities of O_2 (1–5 mol%) were deliberately introduced, then the starting materials were consumed, ^{31}P NMR spectroscopy indicating that the rhodium species partly decomposes under these conditions with formation of the corresponding diphosphine dioxide (δ 21.6). The expected hydroboration product **7b** is totally absent from the reaction product which consists of 4-methoxyethylbenzene **8** and the (*E*)-vinylborane **9** in equal proportions (Scheme 1). This implies a 1 : 2 ratio of reactants **4** and **6**, which was independently verified.

Since removal of the phosphine ligand by oxidation produces an active catalyst, the reaction of **4** with **6** was carried out in the presence of catalytic quantities (0.1–0.2 mol%) of the dimeric tetrakis (η^2-*p*-methoxyphenylethene)di-μ-chlorodirhodium **10**. A rapid reaction occurred, and again the only products were hydrocarbon **8** and vinylborane **9**. With borane reagents **2** or **3**, this reductive disproportionation was the main reaction pathway although detectable amounts (5%) of the conventional hydroboration product were also observed. An extremely rapid reaction ensued between reagent **1** and the alkene **6** catalysed by complex **10** (*ca.* 2000 turnovers min^{-1}, 20 °C) with hydroboration again the minor pathway (24%) and reductive disproportionation predominant.[5] Aromatic (*E*)-vinylboranes have characteristic olefinic ^1H NMR resonances [*e.g.*, **9**, δ (C_7D_8) 6.45 and 7.70] and inspection of the NMR spectra of many crude reaction mixtures from Rh-catalysed hydroborations of vinylarenes shows that traces of the (*E*)-vinylborane are frequently formed under more conventional catalytic conditions. Some (*E*)-pent-1-enylpentaborane was observed in the $PdBr_2$-catalysed hydroboration of pent-1-ene with pentaborane, and similar observations were made in catalytic hydroboration with borazines.[6] Rhodium-catalysed hydrosilylation of styrene gives some vinylsilane accompanied by hydrogenation, particularly at low catalyst concentration.[7]

The mechanism of formation of vinylborane **9** was investigated. 4-Methoxyphenylethyne[8] was converted into the (*Z*)-1,2-[$^2H_2$]-analogue of **6** {D_2, [$(MePh_2P)_2Rh(cod)]^+BF_4^-$ (cod = cyclooctadiene), $MeO(CH_2)_2OH$},[9] and the 1,1,2-[$^2H_3$]-analogue similarly from 1-[^2H]-4-methoxyphenylethyne in $(CD_3)_2CO$. Employing catalyst **10**, the reaction of (*Z*)-1,2-[$^2H_2$]-**6** with borane **4** was followed by ^1H NMR spectroscopy in C_7D_8 at 500 MHz. Under these conditions the final products showed the isotopic distribution shown in Scheme 2. Reaction of the trideuteriated styrene reinforced the conclusion that the hydrogen atom from reagent **4** (R_2B–**H**) is uniquely transferred to the benzylic position of **8**. At moderate reaction times a competing exchange process is observed with the consequence of rapid *E*,*Z*-isomerisation of terminal deuterium in **6**; employing a 1 : 1 mixture of undeuteriated and trideuteriated alkene indicates that the exchange process is intermolecular. The kinetics of reaction were followed with varied initial concentrations, and initial rate analysis indicated first-order dependence on borane **4** and half-order dependence on (dimeric) Rh catalyst **10** (Fig. 1); there is an inverse dependence on alkene concentration. A short induction period (20–60 s) was invariably observed.

Taken together, these results support the mechanism shown in Scheme 3. A dimeric Rh hydride is first formed in a

reductive preactivation step, and connects to the catalytic cycle by dissociation. The monomeric hydride undergoes *cis*-ligand migration (step **A**) giving essentially exclusively the branched alkyl, in competition with reversible alkene association. Reversal of this step and alkene dissociation–reassociation lead to the isotopic scrambling observed in the starting material. The alkyl thus formed reacts with borane **4** in the rate-limiting step **B**, followed by elimination of the alkyl hydride in step **C**. This is followed by boron migration which again gives the branched benzylrhodium complex in step **D**, and a stereospecific β-hydride transfer to rhodium then affords the (*E*)-vinylborane **9** coordinated to rhodium (step **E**). Alkene exchange with the reactant in step **F** regenerates the rhodium hydride, ready to sustain the catalytic cycle. This mechanism differs substantially from the one likely to operate in catalytic hydroboration; the fact that boron is delivered to the benzylic site of styrenes (*i.e.* the regioselectivity is opposite to that seen in step **D**) indicates that H-migration occurs first, followed by alkylborane elimination.

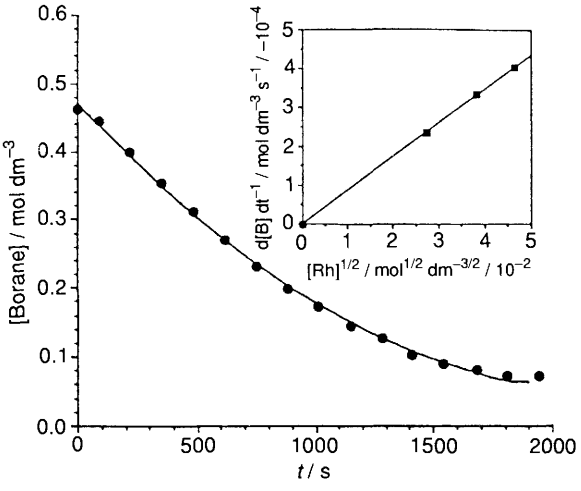
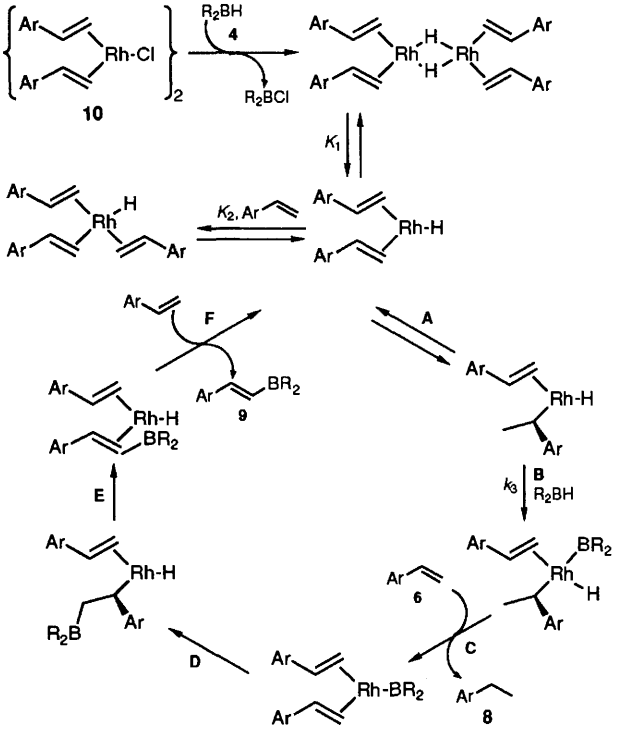


Fig. 1 Consumption of borane measured by 500 MHz ^{1}H NMR with calculated fit (—) according to the parameters K_1 = 7.9 × 10^{-6} mol dm^{-3}, K_2 = 27.7 dm^3 mol^{-1}, k_3 = 16.8 mol dm^{-3} s^{-1}, [Rh-dimer]$_{init}$ = 7.32 × 10^{-4} mol dm^{-3}, [alkene]$_{init}$ = 0.746 mol dm^{-3}, [borane]$_{init}$ = 0.463 mol dm^{-3}. Runs varying all components conform well with this model. *Inset*: Initial rates at varying [Rh]$_{init}$, slope = 8.65 × 10^{-3} mol$^{1/2}$ dm$^{-3/2}$ s^{-1}.



Scheme 3 Mechanistic scheme for catalytic cycle involving reagent **4**, substrate **6** and catalyst precursor **10**

Alkenylboranes enjoy considerable synthetic utility, particularly through their application in the Suzuki modification of catalytic cross-coupling.[10] The present work provides an alternative to their synthesis from alkynes,[11] although at present 50% of the alkene is sacrificed to hydrogenation. We have verified that a range of vinylarenes (*p*-Cl, *p*-H, ferrocenyl) undergo similar behaviour to alkene **6**, and that the product may be isolated at the oxazaborolidine step, or converted into the corresponding vinylboronic acid by hydrolysis. The synthetic scope will be fully discussed in future work.

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