Exploring the mechanism of the hydroboration of alkenes by amine–boranes catalysed by [Rh(xantphos)]+†

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The [Rh(xantphos)]+ fragment acts as an effective catalyst for the hydroboration of the alkene TBE (tert-butyl ethene) using the amine–borane H$_3$B·NMe$_3$ at low (0.5 mol%) catalyst loadings to give the linear product. Investigations into the mechanism using the initial rate method and labelling studies show that reductive elimination of the linear hydroboration product is likely the rate-limiting step at the early stages of catalysis, and that alkene and borane activation (insertion into a Rh–H bond and B–H oxidative addition) are reversible. The resting state of the system has also been probed using electrospray ionization mass spectrometry (ESI-MS) using the pressurised sample infusion (PSI) technique. This system is not as effective for hydroboration of other alkenes such as 1-hexene, or using phosphine borane H$_3$B·PCy$_3$, with decomposition or P–B bond cleavage occurring respectively.

Introduction

Hydroboration, the addition of a B–H bond across an unsaturated C–C bond, is a versatile methodology that affords organoboranes, from which subsequent functionalisation leads to products of use in organic synthesis.$^{1–4}$ Non-metal catalysed hydroboration generally yields the anti-Markovnikov product, whereas transition metal catalysts enable control over the regioselectivity of hydroboration. Such selectivity (i.e. linear versus branched products) has been shown to vary with different catalysts, alkenes and even reaction conditions.$^{5–8}$ Historically metal-catalysed hydroborations have used three-coordinate boron substrates such as catechol (HBCat) or pinacol borane.$^2,3$ By contrast four-coordinate amine–boranes (prototypically H$_3$B·NMe$_3$) have traditionally been used in uncatalysed hydroboration where N–B cleavage is proposed to afford a reactive trivalent BH$_3$ molecule,$^9$ although iodine-induced hydroboration is proposed to operate via an intermediate that retains the B–N bond.$^{10}$ Amine–boranes have, instead, received much recent attention due to their potential as hydrogen storage systems and as precursors to oligomeric or polymeric B–N materials via dehydrocoupling;$^{11}$ and we,$^{11,13}$ alongside others,$^9,11$ have been exploring the role of the metal catalyst in these processes. Recognising that B–H oxidative cleavage from a bound sigma complex to form a metal boryl hydride (Scheme 1a) is closely related to the same mode of activation of a B–H bond at a metal in hydroboration (Scheme 1b), we reported in 2011

![Scheme 1](image-url)

Scheme 1 Rh-catalysed hydroboration using amine–borane (a) and catechol borane (b); hydroboration of TBE using H$_3$B·NMe$_3$, (c).
that the addition of the alkene tert-butylethene (TBE) to the sigma amine–borane complex \([\text{Rh}(\text{P}^3\text{Bu}^1\text{Bu}^2_2[\eta^3-H_2B-N\text{Me}_3])] \) \([\text{BARF}_4] \) resulted in the formation of the linear hydroboration product \([\text{Rh}(\text{P}^3\text{Bu}^1\text{Bu}^2_2[\eta^3-H_2B(CH_2CH_2\text{Bu})-N\text{Me}_3])] \) \([\text{BARF}_4] \). The precursor complex \([\text{Rh}(\text{P}^3\text{Bu}^1\text{Bu}^2_2)] \) \([\text{BARF}_4] \) also slowly (94 h, 5 mol%) catalysed this process to form free \(H_2B(CH_2CH_2\text{Bu})-N\text{Me}_3 \) (I), Scheme 1c.

Kinetic experiments allowed for a mechanism to be proposed in which the hydroborated product inhibited catalytic turnover and reductive elimination of the product was also suggested to be slow.\(^{15}\) Independently, in 2012, a similar methodology using N-heterocyclic carbene–boranes and chiral Rh-based catalysts was reported for intramolecular hydroborations of alkenes.\(^{16}\) Very recently we briefly communicated that by using a \([\text{Rh}(\zeta^2\text{P},\text{O},\text{P-xantphos})] \) based catalyst,\(^{17}\) TBE can be hydroborated to give I. In the absence of this alkene, dehydrogenative homocoupling of the borane occurs (see Scheme 4), a process suggested to occur via the B–H activated intermediate that is no longer intercepted by coordination of alkene.\(^{18}\) We now report in detail on this hydroboration, including kinetic data that support a proposed mechanism, as well as assessing the scope of this catalyst with regard to other alkenes and phosphine–boranes.

**Results and discussion**

**Preliminary stoichiometric and catalytic studies**

Addition of excess TBE to the Rh(III) sigma–borane complex \([\text{Rh}(\zeta^3\text{P},\text{O},\text{P-xantphos})][\text{H}_2][\eta^1-H_2B-N\text{Me}_3])] \) \([\text{BARF}_4] \) 1 resulted in the rapid formation (less than 5 minutes) of the Rh(i) complex \([\text{Rh}(\zeta^2\text{P},\text{P-xantphos})][\eta^1-H_2B(CH_2CH_2\text{Bu})-N\text{Me}_3])] \) \([\text{BARF}_4] \) as the sole metal-containing product (Scheme 2), presumably by initial hydrogenation of one equivalent of alkene to form a Rh(I) species, followed by hydroboration of another equivalent. The solid-state structure and NMR spectroscopic data for the cationic portion of the disordered \(N\text{Me}_3\) and \(\text{SiMe}_3\) groups are shown. Selected bond lengths (Å) and angles (°): Rh1–P1, 2.2398(18); Rh1–P2, 2.2670(17); Rh–Q1, 3.2342(73); Rh–B1, 2.179(7); B1–N1, 1.603(4); P1–Rh–P2, 98.23(6).

![Scheme 2](image)

Scheme 2  Formation of 2 (E = C) and 3 (E = Si). \([\text{BARF}_4] \) anions not shown.

In a similar manner, addition of trimethylvinyl silane to 1 gives the equivalent complex 3, \([\text{Rh}(\zeta^3\text{P},\text{P-xantphos})][\eta^1-H_2B(CH_2CH_2\text{SiMe}_3)-N\text{Me}_3])] \) \([\text{BARF}_4] \), in which \(H_2B(CH_2CH_2\text{SiMe}_3)-N\text{Me}_3 \) (III) is bound to the metal centre.

Complex 3 was characterised by NMR spectroscopy, ESI-MS (electrospray ionisation mass spectrometry) and microanalysis, which together show similar analytical data to 2 and closely related \([\text{Rh}(\text{P}^3\text{Bu}^1\text{Bu}^2_2)[\eta^3-H_2B(CH_2CH_2\text{Bu})-N\text{Me}_3])] \) \([\text{BARF}_4] \).\(^{14}\) The alkyl borane binds to the metal centre through two sigma R–H–B interactions, evidenced by single \(\text{^11B} \) quadrupolar-broadened signal at \(\delta -6.54 \) in the \(\text{^3}H \) NMR spectrum of relative integral 2H, which collapses to an overlapping doublet of doublets (virtual triplet) on decoupling to \(\text{^11B} \) \([\text{Rh}(\text{H})] = 36 \) Hz, \(\text{^11B} \) \([\text{Rh}(\text{H})] = 36 \) Hz. Two, relative integral 2H, multiplets were observed at \(\delta 1.17 \) and \(\delta 0.78 \) for the \(\text{CH}_2 \) groups, indicating that the anti-Markovnikov (i.e. linear) product of hydroboration is bound to the metal centre. A \(\text{^29Si}^1\text{H} \) HMBC NMR experiment showed a correlation between silicon \([\delta(\text{Si}) 2.1] \) and the alkyl protons at \(\delta 1.17 \), assigning these to those \(\alpha \) to \(\text{Si} \). The xantphos methyl groups are observed as two separate environments \(\delta 1.73 \) and \(\delta 1.67 \). In the \(\text{^11B} \) NMR spectrum a broad resonance is observed at \(\delta 37 \), typical for \(\eta^3\)-coordination of an amine–borane to a Rh(I) centre,\(^{19,20}\) which has shifted 45.7 ppm downfield from that in 1 (\(\delta -8.7 \)).\(^{18}\) Similar changes in \(\text{^11B} \) chemical shift have been noted in related systems on moving between Rh(I) and Rh(III) oxidation states.\(^{19,21}\) The \(\text{^31P}^1\text{H} \) NMR spectrum shows a single environment \(\delta 26.7 \) \([\text{d}, \text{~J} = 182 \text{ Hz}] \). The solid-state structure of complex 3 supports the solution data (Fig. 1), in particular a close Rh⋯B distance of 2.179(7) Å, which is the same within error to that found in 2, 2.162(5) Å,\(^{18}\) and the formation of the linear hydroboration product. Complexes such as 2 and 3 are valence isoelectronic analogs of sigma alkane complexes,\(^{22-24}\) while related alkyl sigma amine–borane complexes have previously been prepared.\(^{25}\)

With complexes 2 and 3 in hand the catalytic hydroboration of TBE with \(H_2B-N\text{Me}_3 \) was explored using these as precatalysts (Scheme 3). As previously reported,\(^{18}\) complex 2 (5 mol%) catalyses the complete conversion to \(H_2B(CH_2CH_2\text{Bu})-N\text{Me}_3 \) (I).
from TBE and H$_3$B-NMe$_3$ within 3 hours. The catalysis was conducted with a 2 : 1 ratio of alkene : H$_3$B-NMe$_3$ as the [(Rh(xantphos))$^{11}$] fragment has been reported to promote the slow dehydrogenation homocoupling of H$_2$B-NMe$_3$ to form [Rh(κ$_3$-P$_3$-xantphos)(η$_2$-H$_2$B$_2$-2NMe$_3$)][BARF$_4$] (4) alongside 1 (Scheme 4),$^{18}$ and a two-fold excess of alkene prevents the formation of 4 in detectable quantities (vide infra). During catalysis, complex 2 was the only observed resting state by $^1$H and $^{11}$P{$_1^1$H} NMR spectroscopy.$^{26}$ The $^1$H NMR spectrum of isolated I confirms anti-Markovnikov regioselectivity, with two, integral 2H, multiplets at $\delta$ 1.42 and $\delta$ 0.55 assigned to the methylene groups. The $^{11}$B NMR spectrum shows a triplet at $\delta$ -0.83 [$J$(BH) = 96 Hz].$^{14}$

**Kinetic studies**

Given the promising rate of hydroboration of TBE with catalyst 2 to afford I, the catalyst loading was reduced to 0.5 mol%, relative to H$_2$B-NMe$_3$. Under these conditions ([H$_2$B-NMe$_3$] = 0.19 M, [TBE] = 0.38 M, 1,2-F$_2$C$_6$H$_4$ solvent), consumption of H$_2$B-NMe$_3$ to yield I proceeded to 85% completion after 12 hours as monitored by $^{11}$B NMR spectroscopy, with the balance being made by unreacted H$_2$B-NMe$_3$.

![Scheme 4](image)

**Scheme 4** Formation of complex 4 from addition of excess H$_2$B-NMe$_3$ to 2. [BARF$_4$]$^-$ anions not shown.

**Table 1** Initial rates obtained from variation of concentration of 3, H$_2$B-NMe$_3$ and TBE, 295 K, 1,2-F$_2$C$_6$H$_4$ solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>[3] (10$^{-4}$ M)</th>
<th>[H$_2$B-NMe$_3$] (M)</th>
<th>[TBE] (M)</th>
<th>Initial rate$^a$ (10$^{-3}$ M s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.5</td>
<td>0.19</td>
<td>0.38</td>
<td>6.81 ± 0.12</td>
</tr>
<tr>
<td>2</td>
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<td>0.19</td>
<td>0.19</td>
<td>3.64 ± 0.27</td>
</tr>
<tr>
<td>3</td>
<td>9.5</td>
<td>0.19</td>
<td>0.76</td>
<td>12.98 ± 0.38</td>
</tr>
<tr>
<td>4</td>
<td>19.0</td>
<td>0.19</td>
<td>0.38</td>
<td>13.25 ± 0.56</td>
</tr>
<tr>
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<td>9.5</td>
<td>0.38</td>
<td>0.19</td>
<td>7.41 ± 0.53</td>
</tr>
<tr>
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<td>0.76</td>
<td>0.19</td>
<td>6.33 ± 0.40</td>
</tr>
<tr>
<td>7</td>
<td>9.5</td>
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<td>0.38</td>
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</tr>
<tr>
<td>8</td>
<td>[2] 9.5</td>
<td>0.19</td>
<td>0.38</td>
<td>7.44 ± 0.64</td>
</tr>
<tr>
<td>9</td>
<td>9.5</td>
<td>0.19$^b$</td>
<td>0.38</td>
<td>5.09 ± 0.07</td>
</tr>
</tbody>
</table>

$^a$ Calculated from the pseudo zero-order region of the temporal evolution of I as measured by $^{11}$B NMR spectroscopy over the first 300 s of catalysis. $^b$ With an additional 70 equiv. I at the start of catalysis. $^c$ Using D$_3$B-NMe$_3$ instead of H$_3$B-NMe$_3$.

**Fig. 2** Initial rate experiments: (a) variation of [TBE]; (b) variation of [3]; (c) variation of H$_2$B-NMe$_3$. See Table 1 for more details.
as observed to a lesser degree with the [Rh(P^{i}Bu_{4})Bu_{2}][BARF_{4}] system.\textsuperscript{14} Catalyst 3 and catalyst 2 operated at the same initial rate, within error (entries 1 and 8), suggesting that the identity of the bound primary borane (i.e. I or II) does not influence initial rate of turnover.

Hydroboration of TBE and H_{2}B-NMe_{3} catalysed using 3 enables more information to be gleaned about possible resting states. At 0.5 mol\% loading, the catalyst concentration is too low to be observable by NMR spectroscopy under the conditions used. However, at 5 mol\% loading the rhodium-containing species can be probed by \(^{1}H\) and \(^{31}P\)\(^{(1)}H\) NMR spectroscopy. The diagnostic, broad, hydride signals for 2 and 3 appear at similar chemical shifts in 1,2-F_{2}C_{6}H_{4} solvent [\(\delta -6.85\textsuperscript{18} \) and \(\delta -6.54\textsuperscript{18} \) respectively]. In the early stages of catalysis (~20\% conversion), the \(^{1}H\) NMR spectrum shows a mixture of 2 and 3, evident by broad overlapping hydride peaks. As catalysis progresses, this broad overlapping resonance sharpens and 2 becomes the dominant species demonstrating that I displaces II in the resting state during catalysis. Under the conditions of excess H_{2}B-NMe_{3} (cf. entry 6), using 5 mol\% 3 to enable monitoring by \(^{1}H\) NMR spectroscopy, complex 4 grows in over time, whereas under conditions of excess TBE it is not observed. This is consistent with the kinetic data that suggest removal from the system of active catalyst at high [H_{2}B-NMe_{3}], leading to inhibition.

The change in resting state from 3 to 2 has also been probed using electrospray ionization mass spectrometry (ESI-MS) using the pressurised sample infusion (PSI) technique.\textsuperscript{28-30} The particular advantage of this technique is that it allows for very high data density over a wide dynamic range, and is thus ideal for analysing evolving mixtures during catalysis. Fig. 3 shows the temporal profile of the catalysis using 3. This experiment was run at 15 mol\%, which was determined to be the best conditions for the optimal (low) concentration necessary for PSI-ESI-MS. Immediately at the start of catalysis the resting state moves from 3 to 2, consistent with the NMR experiments. These ESI-MS experiments also reveal the presence, at early stages of the reaction of three other species. The first is identified as [Rh(xantphos)[H_{2}B-NMe_{3}]]\textsuperscript{+}, (\(m/z = 754.24\); calc. 754.20), although we cannot comment on the precise structure: it could be a Rh(i) sigma-bound amine–borane complex, or a Rh(ii) B–H activated hydrido-boryl. Both structural forms have precedent\textsuperscript{19,21} and are likely to be in equilibrium with one another.\textsuperscript{32} Indeed both have been calculated to be accessible, but thermodynamically unfavoured, compared with 2.\textsuperscript{18} [Rh(xantphos)[H_{2}]]\textsuperscript{+} (\(m/z = 683.15\); calc. 683.11) and [1]\textsuperscript{1} are also observed, which we suggest both come from a small amount of [1]\textsuperscript{1} formed parallel with 4 during catalysis (Scheme 4). That we do not observe any of these species by \(^{1}H\) NMR spectroscopy (hydride region) suggests that ESI-MS is particularly sensitive to their observation. These species decay at a very similar rate to [3]\textsuperscript{3}, which suggests that the build-up of I during catalysis pushes any equilibria operating to favour of 2. This observation is also consistent with product inhibition from initial rate experiments.

**Labelling studies**

Complex 3 (and 2) are initially produced under conditions of excess alkene (Scheme 2), suggesting that the alkene does not bind competitively with II (or I), while the dependence of the rate law upon both [TBE] and [H_{2}B-NMe_{3}] indicates that irreversible B–H oxidative addition prior to alkene coordination is not rate-determining. The potential for reversibility of the binding of both H_{2}B-NMe_{3} and TBE to the metal centre was further probed using D_{3}B-NMe_{3} instead of H_{2}B-NMe_{3} during catalysis. Initial rate experiments (Table 1, entry 9) showed a KIE of 1.34 ± 0.04, consistent with irreversible B–H activation not being rate determining. However, due to the H/D exchange observed between the amine–borane and alkene (vide infra) interpretation of the absolute magnitude of this measurement should be treated with a degree of caution.

After 1 hour of catalysis under conditions of excess alkene (28\% conversion, Scheme 5) \(^{3}H\) NMR spectroscopy showed incorporation of deuterium into the internal position of the free, unreacted, alkene (\(\delta 5.89\)), while the corresponding signal in the \(^{1}H\) NMR spectrum decreased by ca. 25\% relative to the other alkene signals at \(\delta 4.99\) and 4.89. This demonstrates that H/D exchange occurs only occurs at the internal alkene proton. H/D exchange in free amine–borane was evidenced by the \(^{1}B\) NMR spectrum that at early stages of catalysis showed a broad peak corresponding to D_{3}B-NMe_{3} and evolved with time to show significant signs of B–H coupling.\textsuperscript{33} The final product d-I showed no H/D exchange.

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**Fig. 3** ESI-MS under PSI conditions\textsuperscript{29} of the reaction of TBE with H_{2}B-NMe_{3} catalysed by 3. Conditions: H_{2}B-NMe_{3} 0.006 M, TBE 0.015 M; [3] 0.001 M, 1,2-F_{2}C_{6}H_{4}. Under these conditions of concentration and experiment catalysis proceeded to 80\% conversion.

**Scheme 5** The products observed after 1 hour of catalysis using D_{3}B-NMe_{3}. Conditions: [D_{3}B-NMe_{3}] = 0.19 M, [TBE] = 0.38 M, 1,2-F_{2}C_{6}H_{4}, 0.5 mol\% 3.
α- to the borane, and ~40% H/D exchange at the β position (i.e. 60% D).

These data suggest that coordination of H$_2$B-NMe$_3$, B–H activation, coordination and insertion of the alkene into the Rh–H bond are all reversible, to ultimately give the linear product. Moreover the lack of H/D exchange in the final product at the α-position, and a similar lack of exchange in the terminal positions of the free alkene, suggests that insertion to form the branched product is not occurring. We also suggest that hydride migration to the alkene, rather than boryl migration to form the branched product is not occurring. We also suggest that hydride migration to the alkene, rather than boryl migration to form an intermediate such as F (Scheme 6), is by far dominant.34 Intermediates such as F have been postulated in dehydrogenative borylation reactions,5,8,15,16 the products of which are not observed here. Although we cannot fully discount that boryl migration from F is reversible but the barrier to reductive elimination from F is high, we consider that this scenario is less likely based upon literature precedent.5–8,15

Bringing these data and observations together leads us to propose the catalytic pathway shown in Scheme 6 for the hydroboration of TBE using H$_2$B-NMe$_3$ and 3. This pathway is similar to that reported for using the [Rh(PiBu$_2$Pr)$_3$]$^+$ catalyst system,14 as well as late transition metal hydroboration systems that use, for example, HBCat$_3$.5,6,8

The elementary steps in this cycle are thus: complex 2 does not react with TBE but undergoes reversible B–H activation with H$_2$B-NMe$_3$, (i) and (ii), as shown by H/D exchange into free D$_2$B-NMe$_3$ during the early phases of catalysis. Monitoring by ESI-MS shows a species consistent with A or B (m/z = 754.24) before 2 becomes the only species observed. TBE binding and insertion into Rh–H is reversible, (iii), as demonstrated by H/D exchange into the free alkene during catalysis. No branched product is observed37 and no H/D exchange at the α-position of the linear product is measured, showing that insertion from C to form D (vi) is neither kinetically competent nor reversible. Insertion from C to give the linear intermediate E is reversible (iv), as there is significant (40%) H/D exchange at the β-position in the final product, as well as into the free alkene when D$_2$B-NMe$_3$ is used, that suggests that β-H-elimination from E occurs. Overall these H/D labelling experiments suggest that reductive elimination (v) is the turnover-limiting step during the early stages of catalysis. As reductive elimination would be expected to have a small (close to unity) KIE, the modest measured value might reflect a system at equilibrium before the turnover limiting step (as postulated), i.e. an equilibrium isotope effect.38

**Scheme 6** Proposed mechanism for the catalytic hydroboration using data from the early phase of catalysis. [Rh] = [Rh(xantphos)]$^+$. 

**Scheme 7** Reversible deuterio-insertion with cyclohexene.
to re-orientation of the sp³ alkyl and boryl groups prior to reductive coupling, which is expected to be greater for locally bulkier substituents. Thus TBE undergoes hydroboration, while cyclohexene does not.

With 1-hexene, catalysis (5 mol% of 3 relative to H₂B·NMe₃) reached 37% conversion after 30 minutes yielding a product consistent with Me(CH₂)₃H₂B·NMe₃, as shown by a triplet [J(HB) = 91 Hz] in the ¹³B NMR spectrum at δ ~ -1.4, although we were not able to isolate this material pure and thus cannot comment on the linear : branched ratio. After 1 week, a maximum conversion of 63% is reached. However, significant decomposition of the catalyst was observed, for which we cannot definitively provide a structure derived from the spectroscopic data. Thus, the hydroboration of alkenes with 3 appears to work best with TBE, with other alkenes only of limited utility.

**Hydroboration with phosphine–boranes**

The addition of H₂ to [Rh(xantphos)(NBD)][BAR⁻] (NBD = norbornadiene) in the presence of the tertiary phosphine–borane H₂B·PCy₃ afforded [Rh(k⁺₂,p,p'-xantphos)(H)₂(η−¹-H₂B·PCy₃)][BAR⁻] (5) in quantitative yield by NMR spectroscopy (Scheme 8). Complex 5 was characterised in situ using NMR spectroscopy, and presents very similar data to the analogous complex 1. It is also related to the sigma phosphine–borane complex [Ru(xantphos)(H)(PPh₂H)(H₃B·PCy₃)][BAR⁻]. The ¹H NMR spectrum shows 3 hydride environments in a 3 : 1 : 1 ratio, consistent with the phosphine–borane bound in an η¹ fashion that is undergoing rapid exchange between B–H–Rh and B–H groups, and two mutually cis hydrides: δ ~ -1.42 [br, BH₃, sharpens on ¹¹B decoupling], δ ~ -14.62 [br dtd, RhH] and δ ~ -19.13 [ddt, RhH]. Two ³¹P environments are observed in the ³¹P[¹H] NMR spectrum at δ ~ 41.8 [d, J(RhP) = 114 Hz] and δ ~ 20.1 [br, PCy₃] in a 2 : 1 ratio respectively. Attempts to crystallise 5 were unsuccessful, resulting in decomposition.

Addition of 2 equivalents of TBE to pale yellow 5 resulted in the formation of a dark green solution of a new compound formulated as [Rh(k⁺₂,p,p'-xantphos)(η−¹-H₂B·PCy₃)][BAR⁻] (6), Scheme 9, in quantitative yield by NMR spectroscopy. Removal of volatiles allowed the isolation of 6 as a dark green solid. The NMR data for 6 are consistent with η² binding of the phosphine–borane; in the ¹H NMR spectrum, a quadrupolar broadened, integral 3H signal is observed at δ ~ -2.38, which sharpens on ¹¹B decoupling, while the ¹³B NMR spectrum shows a broad signal at δ ~ -3.0. The ³¹P[¹H] NMR spectrum is also consistent with a Rh(η²) phosphine–borane complex, with two signals observed at δ 28.9 [dt, J(RhP) = 190 Hz] and δ 17.3 (br, PCy₃). These data are consistent with those reported for other [Rh(chelating phosphine)(H₂B·PR₃)⁺] complexes. Addition of H₂ (4 atm) to a CD₂Cl₂ solution of 6 reforms complex 5 in quantitative yields by NMR spectroscopy. Degassing a CD₂Cl₂ solution of 5 and placing under static vacuum for 4 hours resulted in an approximately 1 : 1 ratio of 5 : 6, suggestive of an equilibrium between the two species. Interestingly, for the [Rh(xantphos)]⁺ fragment we cannot isolate, or observe by NMR spectroscopy, the equivalent Rh[i] H₂B·NMe₃ complex to 6, as 4 forms instead from homocoupling.

The ability of 6 to mediate hydroboration was probed by addition of excess (2.5 equiv.) TBE in 1,2-F₂C₆H₄ solvent, by addition of the alkene to in situ generated 6, Scheme 9. After 45 minutes a new peak is apparent in the ¹H NMR spectrum at δ ~ -5.58 that is assigned to an Rh–HB interaction, consistent with the slow formation of [Rh(k⁺₂,p,p'-xantphos)(η−¹-H₂B(CH₂CH₂CH₂Bu·PCy₃)][BAR⁻] (7), similar to 2 and 3. After 16 hours the ratio of 7 had increased relative to 6 (~5 : 1 : 7:6). However small amounts (ca. 5% by ³¹P[¹H] NMR spectroscopy) of a parallel product resulting from P–B cleavage [Rh(k⁺₂,p,p'-xantphos)[η−¹-H₂B(CH₂CH₂CH₂Bu·PCy₃)][BAR⁻] (8) were also observed by ³¹P[¹H] NMR spectroscopy at δ ~ 61.3 [dt, J(RhP) = 192, J(PP) = 34 Hz] and δ ~ 37.8 [dd, J(RhP) = 155, J(PP) = 34 Hz]. P–B bond cleavage has been noted previously during metal-catalysed dehydrocoupling of phosphine–boranes. After a further 12 hours all of 6 was consumed, but a greater proportion of 8 (ca. 33%) was also present. Recrystallisation of the reaction mixture after several hours afforded a small crop of green crystals of 7 suitable for X-ray diffraction, and although the resulting data quality was poor and only the gross connectivity can thus be discussed, the solid-state structure of 7 suggests anti-Markovnikov hydroboration, as with 2 and 3 (see ESI†). The bulk composition could not be reliably determined by NMR spectroscopy as the alkyl region of the ¹H NMR spectrum is dominated by the cyclohexyl peaks from the mixture of 6 and 8.

From such mixtures, several orange crystals of 8 also grew, confirming its solid-state structure (Fig. 4) as a square planar
hexanes, CH$_2$Cl$_2$ and MeCN were dried using a Grubbs type.
Synthesis of $[\text{Rh}^{\text{κ-p,p,P-xanthophos}}]_2[\text{H}^{\text{1-H-B-P-PCy}_3}]$\text{[BARF]} (5). $[\text{Rh}^{xantphos}][\text{nbd}]$\text{[BARF]} (20 mg, 0.01 mmol) and H$_2$-PCy$_3$ (2.5 mg, 0.01 mmol) were dissolved in 1,2-F$_2$C$_6$H$_4$ in a high pressure NMR tube, the contents immediately frozen in liquid N$_2$, and the argon headspace replaced with H$_2$ (ca. 4 atm), yielding 5 in situ upon warming to room temperature and shaking. 5 could not be isolated due to loss of deuterium upon removal from the H$_2$ atmosphere. Attempts to recrystallise under H$_2$ resulted in impure oil, as measured by NMR spectroscopy. However, the following NMR spectroscopic data were obtained from the hydrogenation of preformed 6. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 8.10–7.27 (m, 26H, xanthophs aryl signals), 7.73 (s, 8H, [BARF]), 7.56 (s, 4H, [BARF]), 2.05–0.81 (39H, 39H, overlapping Cy and xanthophs CH$_3$ signals), −1.63 (br, 3H, BH$_3$), −14.80 (br, 1H, RH$_7$), −19.40 (br, 1H, RH$_7$). $^1$H NMR (500 MHz, CD$_2$Cl$_2$). 200 K, selected data: δ 1.87 (s, 3H, xanthophs CH$_3$ signal), 1.47 (s, 3H, xanthophs CH$_3$ signal), −14.34 (br m, 1H, RH$_7$), −19.40 (br dtd, J(RH$_7$) = 26, J(PH) = 14, J(RH$_7$) = 7 Hz, RH$_7$). $^{31}$P$^1$(H) NMR (202 MHz, CD$_2$Cl$_2$): δ 41.8 [d, J(RP) = 116 Hz], 20.2 [br, PCy$_3$]. $^{11}$B NMR (160 MHz, CD$_2$Cl$_2$): δ −6.6 [s, [BARF]], −43.5 [br, PH$_3$].

Synthesis of $[\text{Rh}^{\text{κ-p,p,P-xanthophos}}]_2$\text{[H}^{\text{1-H-B-P-PCy}}$_3$\text{][BARF]} (6). 5 (55 mg, 0.03 mmol) was formed in situ under H$_2$ (4 atm) in a Young’s crystallisation flask. The flask was degassed (3 freeze–pump–thaw cycles), opened to an argon atmosphere, and TBE (8 μL, 0.06 mmol) was added. The solution turned from pale yellow to dark green. After 5 minutes, the volatiles were removed in vacuo to prevent onward reactivity, and washed twice with pentane (3 mL) with sonication. The resulting oil was solidified in the minimum amount of 1,2-F$_2$C$_6$H$_4$ and layered with pentane, affording green needle-like crystals (not suitable for X-ray diffraction) at −30 °C. Mass 40 mg (73% yield) $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.73 (s, 8H, [BARF]), 7.56 (s, 4H, [BARF]), 7.64–6.40 (m, 26H, xanthophs aryl signals), 1.86–1.08 (m, 39H, PCy$_3$ and xanthophs CH$_3$ signals), −2.38 (br, 3H, BH$_3$). Upon decoupling to $^{11}$B, the signal at −2.38 sharpened. $^{31}$P$^1$(H) NMR (202 MHz, CD$_2$Cl$_2$): δ 28.9 [d, J(RP) = 190 Hz], 17.3 (br, PCy$_3$). $^{11}$B NMR (160 MHz, CD$_2$Cl$_2$): δ −3.0 (br, BH$_3$), −6.6 [s, [BARF]]. ESI-MS (1,2-F$_2$C$_6$H$_4$, 60 °C, 4.5 kV) was attempted but decomposition resulted under these conditions. Elemental microanalysis: calc. RhP$_5$OC$_8$H$_8$B$_2$F$_{24}$ (1839.03 g mol$^{-1}$); C, 58.13; H, 4.38. Found: C, 57.43; H, 4.59.

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Notes and references

9. A. Staubitz, A. P. M. Robertson, M. E. Sloan and I. Manners, Chem. Rev., 2010, 110, 4023–4078.
15. In this report we did not describe H/D labelling studies. Subsequent studies using D,B-NMe₃ showed that alkene coordination and deuteride insertion to form the linear product where all reversible, as found in this current study consistent with reductive elimination being the rate-determining step at the early stages of catalysis. L. J. Sewell, DPhil Thesis, University of Oxford, 2013.
33. Reliable integration to quantify the degree of H/D exchange in the borane was frustrated by the quadrupolar-broadened signals.