Reaction between rhodium(iii) bisboryls and diborane(4) compounds: evidence for a σ-bond metathesis process

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The rhodium bis(boryl) complex [RhCl(PPh₃)₂{B(cat)}₂] (cat = 1,2-O₂C₆H₄) reacts with the diborane(4) compounds B₂(O₂R)₂ {O₂R = 1,2-O₂C₆H₃Me-4, 1,2-O₂C₆H₂But₂-3,5 and dimethyl-L-tartrate [OCH(CO₂Me)CH(CO₂Me)O]} affording unsymmetrical metal bis(boryls) [RhCl(PPh₃)₂{B(cat)}{B(O₂R)}] and diborane(4) compounds (cat)B–B(O₂R), one possible mechanism for which involves σ-bond metathesis.

The oxidative addition of the B–B bond in certain diborane(4) compounds to low-valent transition-metal centres is now well established and results in metal bis(boryls) of the general formula [L$_n$M{BR₂}₂] some of which are active catalysts for the diboration of alkenes and alkynes.[1] During studies of the reactivity of metal boryls, we recently demonstrated that reversible oxidative addition–reductive elimination of B₂(cat)₂ **1a**[2] (cat = 1,2-O₂C₆H₄) occurs with the rhodium(iii) tris(boryl) complex [Rh(PMe₃)₃{B(cat)}₃],[3] and also that the platinum(ii) bis(boryl) compound cis-[Pt(PPh₃)₂{B(cat)}₂] reacts with the

diborane(4) species B₂(1,2-O₂C₆H₃But-4)₂ **1b** to give the platinum bis(boryl) complex cis-[Pt(PPh₃)₂{B(1,2-O₂C₆H₃-But-4)}₂] presumably via reductive elimination of **1a** followed by oxidative addition of **1b**.[1c] Reductive elimination of **1a** from the rhodium(iii) bis(boryl) complex [RhCl(PPh₃)₂{B(cat)}₂] **2a**[1a] in the presence of isocyanides has also been observed.[1f] In order to gain further insight into the factors which influence the oxidative addition–reductive elimination reaction of B–B bonds with transition-metal centres, we undertook a study of the reaction between complex **2a** and a series of diborane(4) compounds, preliminary results for which are described herein.

The reaction between **2a** {generated in situ from the reaction between equimolar ratios of either [RhCl(PPh₃)₃] **3a** or [{RhCl(PPh₃)₂}₂] **3b** and **1a** in CH₂Cl₂ solution}[1a] and 1 equiv. of the diborane(4) compound B₂(1,2-O₂C₆H₃Me-4) **1c** was followed by ³¹P NMR spectroscopy which revealed the formation, after 2 h, of three products in a ratio of 1:2:1 (Fig. 1). One of these products was unreacted **2a** (δ 31.15, $J_{Rh–P}$ 112.9 Hz)[1a] and a second (δ 31.45, $J_{Rh–P}$ 114.8 Hz) was identified as the symmetrical bis(boryl) compound [RhCl(PPh₃)₂{B(1,2-O₂C₆H₃Me-4)}₂] **2b**, prepared and identified independently from the reaction between **3b** and **1c**. The third, and major, product (δ 31.30, $J_{Rh–P}$ 114.8 Hz) we propose to be the mixed or unsymmetrical bis(boryl) complex [RhCl(PPh₃)₂{B(cat)}{B(1,2-O₂C₆H₃Me-4)}] **2c** on the basis of the ³¹P NMR chemical shift, which is intermediate between those of the two symmetrical bis(boryls) **2a** and **2b**, and the value of $J_{Rh–P}$ which is almost identical to those of **2a** and **2b**. An identical ³¹P NMR spectrum to that shown in Fig. 1 was observed for the reaction between equimolar amounts of **2b** and **1a**.

Whilst the formation of the unsymmetrical bis(boryl) complex **3c** was unexpected, the generality of the reaction was
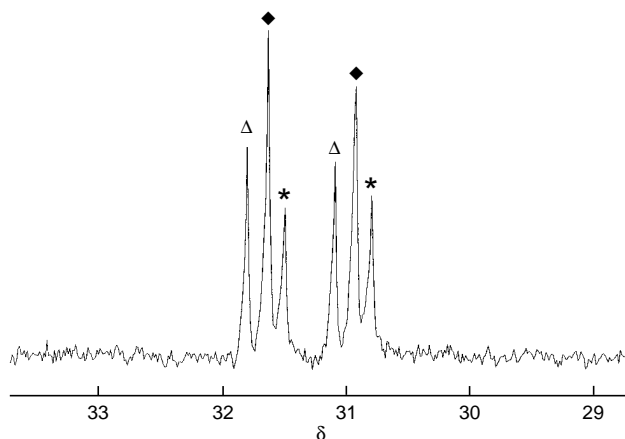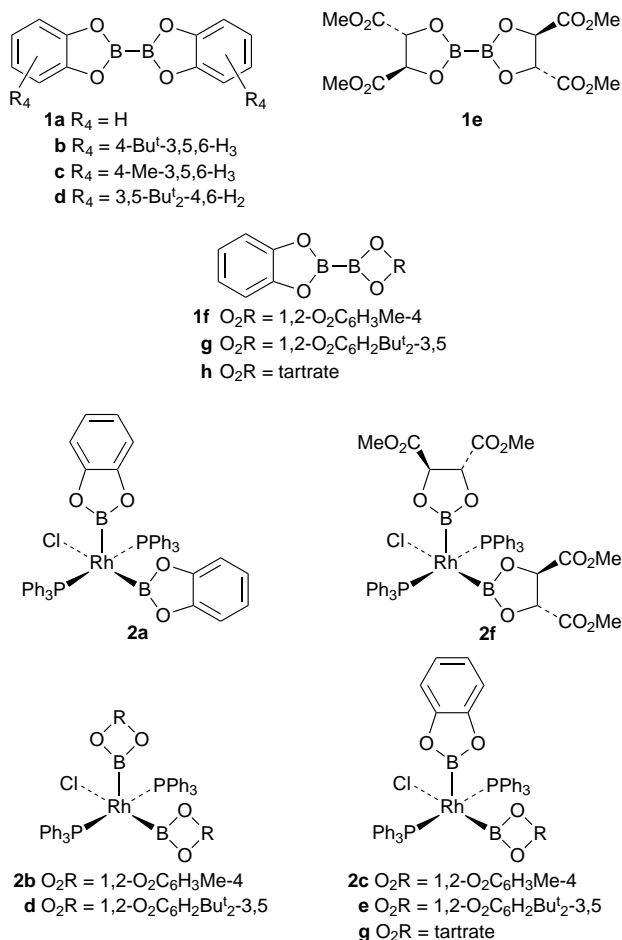

1a R₄ = H
b R₄ = 4-But-3,5,6-H₃
c R₄ = 4-Me-3,5,6-H₃
d R₄ = 3,5-But₂-4,6-H₂

1e

1f O₂R = 1,2-O₂C₆H₃Me-4
g O₂R = 1,2-O₂C₆H₂But₂-3,5
h O₂R = tartrate

2a

2f

2b O₂R = 1,2-O₂C₆H₃Me-4
d O₂R = 1,2-O₂C₆H₂But₂-3,5

2c O₂R = 1,2-O₂C₆H₃Me-4
e O₂R = 1,2-O₂C₆H₂But₂-3,5
g O₂R = tartrate

Fig. 1 A ³¹P{¹H} NMR spectrum of the reaction between **2a** and **1c** in CH₂Cl₂ solution showing the presence of the compounds **2a** (*), **2b** (△) and **2c** (◆). Chemical shift and coupling constant data are given in the text. All spectra were recorded on a JEOL GX 400 spectrometer.

established with further examples. Thus the reaction between **2a** and $B_2(1,2-O_2C_6H_2Bu^t_2-3,5)_2$ **1d** afforded both the symmetrical species $[RhCl(PPh_3)_2\{B(1,2-O_2C_6H_2Bu^t_2-3,5)\}_2]$ **2d** (δ 31.85, J_{Rh-P} 114.9 Hz)[1a] and the unsymmetrical compound $[RhCl(PPh_3)_2\{B(cat)\}\{B(1,2-O_2C_6H_2Bu^t_2-3,5)\}]$ **2e** (δ 31.70, J_{Rh-P} 114.9 Hz) as well as unreacted **2a**, although in this case **2a** was present as the major species, the ratio of **2a**:**2e**:**2d** being *ca.* 7:1:1, and the reaction was observed to be considerably slower, taking about 24 h to reach completion.† Similarly, the reaction between **2a** and $B_2(tart)_2$‡ [tart = dimethyl l -tartrate, $OCH(CO_2Me)CH(CO_2Me)O$] **1e** afforded, in addition to un-reacted **2a**, the symmetrical compound $[RhCl(PPh_3)_2\{B(tart)\}_2]$ **2f** (δ 32.05, J_{Rh-P} 116.8 Hz) (prepared and identified independently from the reaction between **3b** and **1e**) and the unsymmetrical species $[RhCl(PPh_3)_2\{B(cat)\}\{B(tart)\}]$ **2g** (δ 31.55, J_{Rh-P} 114.9 Hz), although the formation of **2f** was very slow and was only observed after about 9 days at which time the ratio of **2a**:**2g**:**2f** was 21:16:1.§ Interestingly, the reaction between **2f** and **1a** showed initial formation of **2a** and the unsymmetrical bis(boryl) **2g** was only observed after 6 days at which time the ratio of **2a**:**2g**:**2f** was 5:1:5.

All of these results imply that a scrambling of the diborane(4) compounds is occurring in solution in the presence of rhodium, further evidence for which was the observation and identification, by high-resolution mass spectrometry,¶ of the un-symmetrical diborane(4) compounds $(cat)B-B(1,2-O_2C_6H_3Me-4)$ **1f**, $(cat)B-B(1,2-O_2C_6H_2Bu^t_2-3,5)$ **1g** and $(cat)B-B(tart)$ **1h** in their respective reaction solutions; no such compounds were observed in the absence of rhodium.

In terms of possible reaction mechanisms, we suspect that an oxidative addition–reductive elimination pathway, analogous to those described in the introductory paragraph, does occur since, in the reaction between **2f** and **1a**, the symmetrical bis(boryl) compound **2a** was observed prior to the appearance of the unsymmetrical species **2g**. The fact that unsymmetrical bis-(boryls) and diborane(4) compounds are observed in all reactions, however, implies that an additional reaction mechanism must also be operating since simple oxidative addition–reductive elimination cannot afford such mixed products. Possible mechanisms which might account for the formation of the observed products include a double diborane(4) oxidative addition to give a rhodium(v) tetraboryl species such as $[RhCl(PPh_3)_n\{B(cat)\}_2\{B(O_2R)\}_2]$ (O_2R = $1,2-O_2C_6H_3Me-4$, $1,2-O_2C_6H_2Bu^t_2-3,5$ and dimethyl-l -tartrate), or reductive elimination of $ClB(cat)$ from a symmetrical bis(boryl) (for example, **2a**) followed by oxidative addition of diborane(4) to give a rhodium tris(boryl) complex $[Rh(PPh_3)_n\{B(cat)\}-\{B(O_2R)\}_2]$, reductive elimination from either of which could afford the observed products. Whilst we cannot rule out either of these two possible mechanisms at this stage (particularly in view of the slowness of reactions involving **1d** and **1e** where the presence of trace amounts of undetected intermediates is a possibility), we note firstly the unlikelihood of the formation of a rhodium(v) complex in the former mechanism {although compounds which are formally rhodium(v) such as $[RhH_2(SiEt_3)_2(\eta-C_5Me_5)]$ have been described by Fernandez and Maitlis},[4] and, secondly, the lack of any evidence for oxidative addition of $ClB(cat)$ to rhodium(i) triphenylphosphine centres (in this and other systems studied) which would subsequently be required in the latter mechanism in order to

give the observed rhodium chloride bis(boryls). At this stage, the mechanism we prefer as the simplest explanation for these observations is one involving σ-bond metathesis, as shown in Scheme 1. Thus, whilst we have no direct evidence for this mechanism, we note that such mechanisms have been proposed by Smith[1d] to account for the reaction between **1a** and the platinum metallacyclopentane complex *cis-*$[Pt(PPh_3)_2\{(CH_2)_4\}]$ which affords *cis-*$[Pt(PPh_3)_2\{B(cat)\}_2]$ and $(cat)B(CH_2)_4B(cat)$, and by Hartwig *et al.* in discussing the reaction between $[RuMe(PMe_3)_2(\eta-C_5H_5)]$ and $HB(cat)$.[5] Furthermore, we note that complexes such as **2a** may be compared to the ruthenium(iv) alkylidene species of the form $[RuCl_2(=CR_2)(PR_3)_2]$ characterised by Grubbs and co-workers[6] which are known to be active alkene metathesis catalysts.

Further studies relating to these observations are in progress, but the preliminary results described herein indicate the potential mechanistic complexity of systems involving metal boryls and diborane(4) compounds which will be an important consideration in any reactions in which metal boryls are employed as catalysts in diboration reactions.

Footnotes

† We attribute the fact that the reaction between **2a** and **1d** is considerably slower than that between **2a** and **1c** to the fact that **1d** is much more sterically demanding than **1c**, consistent with which is the related observation that whilst **3a,b** react in minutes with **1a**, the corresponding reaction between **3a,b** and **1d** takes nearly 1 h to reach completion; steric congestion at the rhodium centre is also likely to favour a preponderance of the bis-B(cat) complex **2a** as observed.

‡ Compound **1e** was prepared from $B_2(NMe_2)_4$ and dimethyl-l -tartaric acid, $HOCH(CO_2Me)CH(CO_2Me)OH$, according to the general preparative routes described in ref. 2 and references therein; full details will be described in a future publication.
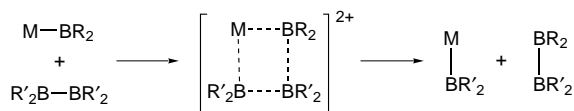
§ The slowness of this reaction is consistent with the observation that the reaction between **3a,b** and **1e** takes several days to go to completion.

¶ $(cat)B-B(1,2-O_2C_6H_3Me-4)$ **1f** $C_{13}H_{10}B_2O_4$, (M^+) calc. *m/z* 252.076. Found *m/z* 252.076; $(cat)B-B(1,2-O_2C_6H_2Bu^t_2-3,5)$ **1g** $C_{20}H_{24}B_2O_4$, $(M^+ - {}^{12}C^1H_3)$ calc. *m/z* 335.163. Found *m/z* 335.163.

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Scheme 1

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