

Photochemical oxidative addition of B–H bonds at ruthenium and rhodium†

Philip L. Callaghan,^a Rodrigo Fernández-Pacheco,^a Naser Jasim,^a Sébastien Lachaize,^a Todd B. Marder,^b Robin N. Perutz,^{*a} Eleonora Rivalta^a and Sylviane Sabo-Etienne^c

^a Department of Chemistry, University of York, York, UK YO10 5DD

^b Department of Chemistry, University of Durham, Durham, UK DH1 3LE

^c Laboratoire de Chimie de Coordination, CNRS, 205 Route de Narbonne, 31077 Toulouse, Cedex 04, France

Received (in Cambridge, UK) 2nd October 2003, Accepted 22nd October 2003

First published as an Advance Article on the web 7th November 2003

Metal phosphine hydrides of type RuP₄H₂ and RhP₃H₃ react photochemically with HB(pin) (pin = pinacolate) to form metal boryl hydride complexes *via* 16-electron intermediates generated by H₂ loss; the second order rate constants for reaction of the intermediates with HB(pin) are even larger than those for reaction with Et₃SiH.

The oxidative addition of B–H bonds in boronate esters of type HB(OR)₂ is fundamental to both catalytic hydroboration and dehydrogenative borylation.^{1,2} The recent use of HB(pin) (pin = pinacolate) in catalytic borylation of aromatics probably depends on B–H oxidative addition.^{3,4,5} It is now recognised that such boronate esters can react at transition metal centres to form η²-borane complexes or oxidative addition products.^{6,7,8} In spite of thorough studies of structure and bonding,⁹ we are not aware of any studies of the kinetics of oxidative addition,¹⁰ nor of any explicit reports of photochemical B–H oxidative addition.¹¹ We show here that metal phosphine dihydride complexes undergo photo-induced B–H oxidative addition with HB(pin) and that these reactions may be studied by laser flash photolysis. The resulting rate constants provide the first kinetic information for the elementary step of B–H activation.

The ruthenium(II) hydrides, Ru(dmpe)₂H₂ and Ru(depe)₂H₂ do not react with HB(pin) thermally at room temperature, even when HB(pin) is in excess.‡ However, broad-band UV irradiation converts them to new hydride-containing products. More specifically, irradiation of Ru(depe)₂H₂ in C₆D₆ with 6 eq. of HB(pin) at room temperature leads to two products; the major product exhibits one hydride resonance as a doublet of quartets at δ –10.13 (dq, J_{PH} = 61.0, 20.7 Hz) and four resonances in the ³¹P NMR spectrum belonging to an ABMQ spin system. One of the ³¹P resonances is broadened considerably (w_{1/2} = 90 Hz), probably by the presence of a *trans* ¹¹B nucleus. The presence of a boryl group is indicated by a broad resonance at δ 50 (w_{1/2} = 600 Hz) in the ¹¹B spectrum in the region characteristic of metal-boryl complexes.⁷ The ¹H-¹³C correlation spectrum in C₆D₆ shows a methyl resonance (δ 1.18, 12 H s) correlated with a quaternary carbon at δ 79.2, that may be assigned to the BOC carbon, a significant upfield shift compared to HB(pin) (δ 82.9). The product is therefore assigned as *cis*-Ru(depe)₂(H){B(pin)}, *cis*-**1** (Scheme 1). The minor product

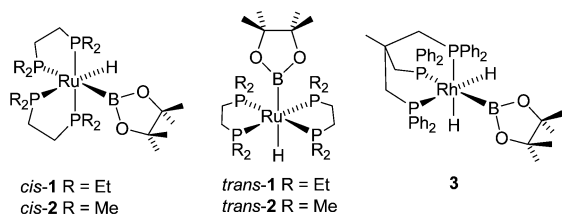
exhibits a hydride resonance as a quintet at δ –9.09 (J_{PH} = 21.3 Hz) and a singlet in the ³¹P NMR spectrum and is assigned as *trans*-**1** (*cis*-**1** : *trans*-**1** ca. 9 : 1).

DB(pin) was synthesised with >99% isotopic purity by reaction of liquid HB(pin) with D₂ in the presence of RuH₂(H₂)₂(PCy₃)₂ as catalyst¹² and was characterised by ²H and ¹¹B NMR spectroscopy and IR spectroscopy (see ESI†). Photolysis of Ru(depe)₂H₂ with DB(pin) in C₆H₆ yielded only Ru(depe)₂(D){B(pin)} and allowed independent assignment of the ³¹P resonance *trans* to H or D.

The reaction of Ru(dmpe)₂H₂ proceeds similarly to yield the two isomers of Ru(dmpe)₂(H){B(pin)}, *cis*-**2** and *trans*-**2**. The sharp hydride resonances with large ³¹P coupling constants observed in all these species are consistent with Ru(II) hydrides, but not with η²-borane complexes. (see Table in ESI).†

We have also investigated the reactivity of Rh(triphos)(H)₃ towards HB(pin).‡ This complex reacts thermally at 323 K to form a single product assigned as Rh(triphos)(H)₂{B(pin)} **3** on the basis of ¹H, ³¹P, ¹¹B and ¹³C NMR data. Complex **3** is fluxional at 300 K but its spectrum sharpens at 245 K to reveal two ³¹P resonances at δ 17.0 (dd) and δ 12.9 (dt) with coupling constants J_{RhP} of 97.8 and 79.5 Hz respectively. The higher field resonance, due to the unique P nucleus is broadened significantly by the boryl group *trans* to it. The RhP coupling constants indicate that the complex **3** has oxidation state III consistent with a metal boryl hydride formulation (compare Rh(triphos)(H)₃ J_{RhP} = 89 Hz) and that the boryl ligand has a greater *trans* influence than hydride. No photochemical studies of Rh(triphos)(H)₃ have been reported previously. Initial evidence for photochemical exchange of H₂ by D₂ was obtained by photolysis of Rh(triphos)(H)₃ in the presence of D₂ in THF-*d*₈, resulting in formation of Rh(triphos)D_xH_{3-x}. Room temperature photolysis of Rh(triphos)(H)₃ with HB(pin) in [²H₈]-THF generates **3** and a further product tentatively assigned as Rh(triphos)(H){B(pin)}₂ **4**. The ³¹P{¹H} spectrum of **4** shows resonances at δ 6.88 (dt J_{RhP} = 92 Hz) and δ 4.52 (broad dd J_{RhP} = 78 Hz). In contrast to the spectrum of **3**, the resonance of **4** with doublet of doublets splitting is broadened and J_{RhP} is reduced, consistent with two phosphorus nuclei lying *trans* to boron (see Table in ESI).†

We have studied the laser flash photolysis of the ruthenium hydride precursors previously and measured the rate constants for the reactions of the resulting 4-coordinate Ru⁰P₄ transients with dihydrogen and triethylsilane.¹³ The laser flash photolysis of Ru(depe)₂H₂ was carried out at a range of concentrations of HB(pin) in cyclohexane.§ The resulting Ru(depe)₂ decayed by pseudo first order kinetics leading to a second-order rate constant for reaction with HB(pin) of (1.28 ± 0.03) × 10⁷ dm³ mol⁻¹ s⁻¹ (Fig. 1). The determination of the rate constant with DB(pin) allowed measurement of a kinetic isotope effect k_H/k_D of 0.87. Fig. 1c shows the confidence limits on the linear fit, demonstrating that k_H/k_D is significantly less than unity at the 95% level. The rate constant for reaction of Ru(dmpe)₂ with HB(pin) was determined similarly (Table 1). Laser flash photolysis of Rh(triphos)(H)₃ in THF (chosen for solubility) under argon generated a transient that decayed leaving considerable residual absorption. Nevertheless, addition of HB(pin) led to an increase in the rate of decay of the



Scheme 1

† Electronic supplementary information (ESI) available: Selected NMR data of **1**–**4**. See <http://www.rsc.org/suppdata/cc/b3/12246h/>

transient with satisfactory kinetics and a decrease in the residual absorption.

The flash photolysis data for the ruthenium complexes show a return to the pre-flash level at the monitoring wavelength after reaction with HB(pin) that is only consistent with formation of a Ru(II) product, *i.e.* oxidative addition is complete. The rate constants for reaction of Ru(dmpe)₂ and Ru(depe)₂ with HB(pin) lie between those for reaction with Et₃SiH and those for reaction with H₂ (see Table 1),¹³ but the Ru(depe)₂ intermediate shows more discrimination between substrates. Inverse kinetic isotope effects (kie) for C–H activation have been the subject of intense study.^{14,15} We have previously shown by flash photolysis that Ru(PP₃) exhibits an inverse kie for oxidative addition of benzene, whereas

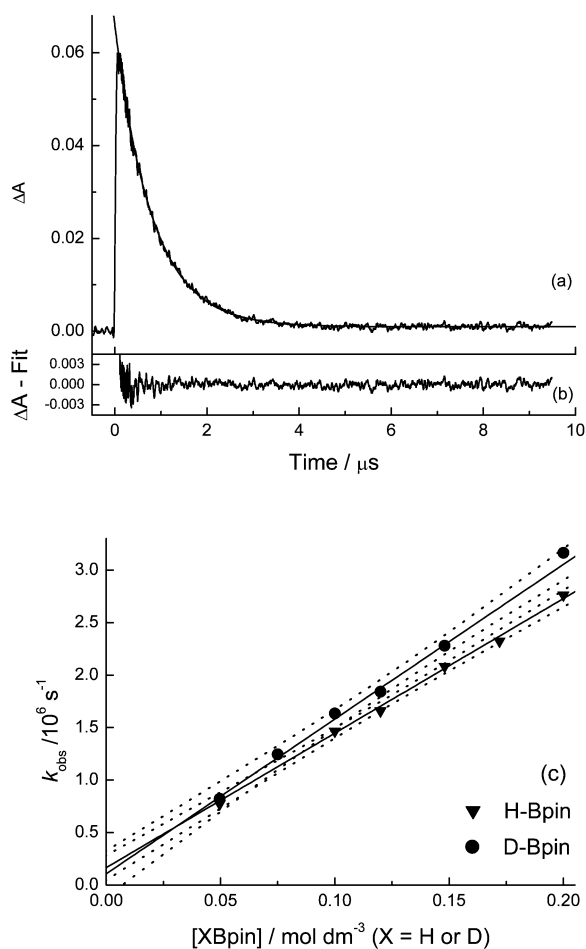


Fig. 1 (a) Transient decay following laser flash photolysis (308 nm) of Ru(depe)₂H₂ in cyclohexane at 297 K. The kinetic fit is superimposed. (b) The difference between the observed and the fitted transient absorption shown on an expanded scale. (c) Plot of the pseudo first order rate constant, k_{obs} , vs. the concentration of HB(pin) (▼) and DB(pin) (●). — lines of best fit, 95% confidence limits.

Table 1 Second order rate constants for reaction of transients with HB(pin)/DB(pin). (Errors as standard deviations on linear fit.)^a

| Complex | Solvent | Substrate | $k_2 / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ |
|--------------------------------------|---------------------------------------|-----------|---|
| Ru(dmpe) ₂ H ₂ | C ₆ H ₁₂ /296 K | HB(pin) | $(1.3 \pm 0.2) \times 10^9$ |
| Ru(depe) ₂ H ₂ | C ₆ H ₁₂ /297 K | HB(pin) | $(1.28 \pm 0.03) \times 10^7$ |
| Ru(depe) ₂ H ₂ | C ₆ H ₁₂ /296 K | DB(pin) | $(1.47 \pm 0.06) \times 10^7$ |
| Rh(triphos)H ₃ | THF/296 K | HB(pin) | $(2.28 \pm 0.07) \times 10^8$ |

^a Comparative rate constants Ru(dmpe)₂/H₂ 6×10^9 , Ru(depe)₂/H₂ 4×10^8 , Ru(dmpe)₂/Et₃SiH 2×10^8 , Ru(depe)₂/Et₃SiH $1 \times 10^5 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Os(PP₃) exhibits a normal kie.¹⁶ The inverse kie is usually associated with the inverse equilibrium isotope effect for the coordination of the substrate prior to oxidative cleavage.

Laser flash photolysis of Rh(triphos)H₃ may be assumed to generate Rh(triphos)H as the transient species. The latter reacts extremely rapidly with HB(pin). The second order rate constant lies between those for Ru(dmpe)₂ and Ru(depe)₂ (see Table 1). There is no sign of inhibition by THF although the solvent is present in large excess compared to the borane, suggesting that the solvent is not coordinated in the intermediate.

We have demonstrated here that UV photolysis of metal phosphine hydrides in the presence of HB(pin) yields metal phosphine boryl hydrides. We have developed NMR criteria for identification of these products in the absence of crystallographic data. The kinetics of reaction of the 16-electron intermediate may be followed by laser flash photolysis demonstrating the extreme rapidity of B–H oxidative addition. The methodology can now be widened to other compounds with B–H bonds.

We acknowledge the support of EPSRC and the European Union for Marie-Curie fellowships.

Notes and references

‡ dmpe = Me₂PCH₂CH₂PMe₂, depe = Et₂PCH₂CH₂PEt₂, PP₃ = P(CH₂CH₂PPh₂)₃, triphos = MeC(CH₂PPh₂)₃. The *cis* : *trans* ratio is *ca.* 3 : 1 for Ru(depe)₂H₂ and *ca.* 30 : 1 for Ru(dmpe)₂H₂. There is no reaction between Ru(depe)₂H₂ and HB(pin) even at 343 K. Photolysis was performed in pyrex NMR tubes ($\lambda > 290 \text{ nm}$) fitted with Young's stopcocks and H₂ was pumped away periodically. Conversions to product of 84% were achieved with **2** after 80 min irradiation.
§ Flash photolysis experiments were carried out with 308 nm excitation (50 ns pulses). The transients were monitored at the following wavelengths: Ru(depe)₂ and Ru(dmpe)₂ 470 nm, Rh(triphos)H 415 nm. Concentration range of HB(pin) for Ru(depe)₂ 0.05–0.2 mol dm⁻³, for Ru(dmpe)₂ 0.001–0.005 mol dm⁻³.

- I. Beletskaya and A. Pelter, *Tetrahedron*, 1997, **53**, 4957; E. Fernandez, K. Maeda, M. W. Hooper and J. M. Brown, *Chem. Eur. J.*, 2000, **6**, 1840.
- M. Murata, K. Kawakita, T. Asana, S. Watanabe and Y. Masuda, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 825.
- J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka and M. R. Smith III, *Science*, 2002, **295**, 305.
- S. Shimada, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Angew. Chem., Int. Ed.*, 2001, **40**, 2168.
- T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 390; T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2003, **680**, 3.
- V. Montiel-Palma, M. Lumbierres, B. Donnadieu, S. Sabo-Etienne and B. Chaudret, *J. Am. Chem. Soc.*, 2002, **124**, 5624.
- G. J. Irvine, G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell and J. Wright, *Chem. Rev.*, 1998, **98**, 2685.
- G. J. Kubas, in *Metal Dihydrogen and σ -Bond Complexes*, Ed. J. P. Fackler, Kluwer Academic/Plenum Publishers, New York, 2001.
- W. H. Lam, S. Shimada, A. S. Batsanov, Z. Lin, T. B. Marder, J. A. Cowan, J. A. K. Howard, S. A. Mason and G. J. McIntyre, *Organometallics*, 2003, **22**, 4557 and refs therein.
- Kinetics of reductive elimination has been studied. B. P. Cleary and R. Eisenberg, *Organometallics*, 1995, **14**, 4524.
- Photo-induced B–H oxidative addition is likely for Mn(CO)₄(Me)(PR₃) + BH₃PMe₃. T. Yasue, Y. Kawano and M. Shimoi, *Angew. Chem., Int. Ed.*, 2003, **42**, 1727.
- A. F. Borowski, B. Donnadieu, J. C. Daran, S. Sabo-Etienne and B. Chaudret, *Chem. Commun.*, 2000, 543.
- C. Hall, W. D. Jones, R. J. Mawby, R. Osman, R. N. Perutz and M. K. Whittlesey, *J. Am. Chem. Soc.*, 1992, **114**, 7425; L. Cronin, M.-C. Nicasio, R. N. Perutz, R. G. Peters, D. M. Roddick and M. K. Whittlesey, *J. Am. Chem. Soc.*, 1995, **117**, 10047.
- W. D. Jones, *Acc. Chem. Res.*, 2003, **36**, 140.
- D. G. Churchill, K. E. Janak, J. S. Wittenberg and G. Parkin, *J. Am. Chem. Soc.*, 2003, **125**, 1403.
- R. Osman, D. I. Pattison, R. N. Perutz, C. Bianchini, J. A. Casares and M. Peruzzini, *J. Am. Chem. Soc.*, 1997, **119**, 8459.