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Selective B–B bond activation in an unsymmetrical diborane(4) by $[(Me_3P)_4Rh–X]$ (X = Me, O*t*Bu): a switch of mechanism?†

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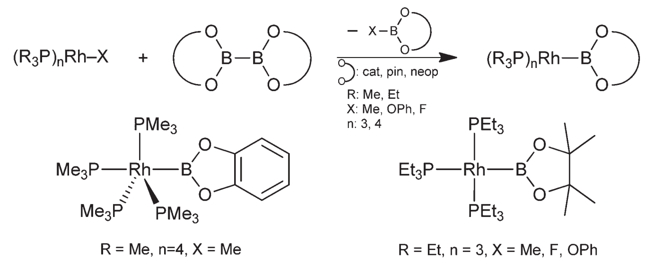
The unsymmetrical diborane(4) pinB–B((RN)$_2$(C$_6$H$_4$)) (R = Me, Bn) reacts with [(Me$_3$P)$_4$Rh–X] (X = Me, O*t*Bu) giving predominantly either [(Me$_3$P)$_4$Rh–Bpin] or [(Me$_3$P)$_3$Rh–B((RN)$_2$(C$_6$H$_4$))] depending on X. At low temperatures in the presence of excess PMe$_3$ the unprecedented equatorial boryl complex [(Me$_3$P)$_4$Rh–B((MeN)$_2$(C$_6$H$_4$))] is formed.

Rhodium boryl complexes have been studied extensively as crucial intermediates in various catalytic transformations such as C–H functionalization, hydroboration and diboration. More fundamentally rhodium boryl complexes have also been studied regarding their coordination chemistry, the oxidative addition chemistry of Rh^{I} boryl complexes to form Rh^{III} trisboryl complexes or, more recently, their use as subunits in boryl pincer complexes.[1–4] In particular, rhodium boryl complexes of the type $[(R_3P)_nRh–B(OR')_2]$ (R = Me, Et; n = 3, 4; $(OR')_2$ = OCMe$_2$CMe$_2$O (pin), 1,2-O$_2$C$_6$H$_4$ (cat), OCH$_2$CMe$_2$CH$_2$O (neop)) have been explored (Scheme 1).[2,3] These complexes are accessible by the reaction of a precursor complex $[(Me_3P)_nRh–X]$ and a symmetrical diborane(4) derivative (B$_2$(OR)$_2$) (Scheme 1).[2]

Marder and co-workers have studied in some detail the chemistry of $[(Me_3P)_4Rh–B(OR)_2]$ complexes and especially their formation from $[(Me_3P)_4Rh–Me]$ (**1a**) and B$_2$(OR)$_2$, presumably proceeding *via* an oxidative addition/reductive elimination pathway.[2a–c,3a] More recently Braun and co-workers demonstrated that also the rhodium phenolato (X = OPh) and fluorido (X = F) complexes $[(Et_3P)_3Rh–X]$ are effective in such B–B bond activation reactions (Scheme 1) and have studied their reactivity to some extent.[2d,e,3b–d] The unsymmetrical diborane(4) derivatives pinB–Bdan (dan = 1,8-(NH)$_2$C$_{10}$H$_6$) have recently gained considerable attention as reagents in transition metal as well as Lewis base catalysed diboration reactions.[5] Moreover, we have recently reported a class of well accessible unsymmetrical diborane(4) derivatives of the type pinB–B((NR)$_2$C$_6$H$_4$) (R = Me (**2a**), Bn (**2b**), TMS) and demonstrated their utility as precursors for diaminoboryl complexes of Cu^{I} and Pt^{II}.[6] Herein we extend our study to Rh^{I} boryl complexes, in particular addressing the influence of the ligand X on the B–B bond activation process with complexes $[(Me_3P)_4Rh–X]$ (X = Me (**1a**), O*t*Bu (**1b**)). Whilst **1a** is an established reagent in related reactions, **1b** has not been described earlier. However, related tris-phosphine complexes have been used in B–B bond activation reactions (*vide supra*).[2d] Complex **1b** is formed virtually quantitatively from equimolar amounts of $[(Me_3P)_4Rh]Cl$ and KO*t*Bu but appears to be only stable in solution and all experiments were conducted with *in situ* prepared **1b**. Several attempts to isolate **1b** led to the isolation of the dimer $[(Me_3P)_2Rh–CH_2–PMe_2]_2$.[7,8] Nevertheless, in solution **1b** was found to be sufficiently stable (no significant decomposition was observed within 30 h).[8] Complex **1b** was characterised by *in situ* NMR spectroscopy. Most characteristically the ^{31}P NMR spectrum at low temperatures shows a doublet of quartets and a doublet of doublets as the AM$_3$ part of an AM$_3$X spin system indicative of a five-coordinate, approximately trigonal-bipyramidal rhodium complex with the alkoxido ligand occupying an apical position.[8]



Scheme 1 General synthesis and two examples of $[(R_3P)_nRh–B(OR)_2]$ complexes.[2]

To study the B–B bond activation of **2a** by **1a** and **1b** the respective reactions were monitored by *in situ* ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectroscopy (Fig. 1). For both reactions, two

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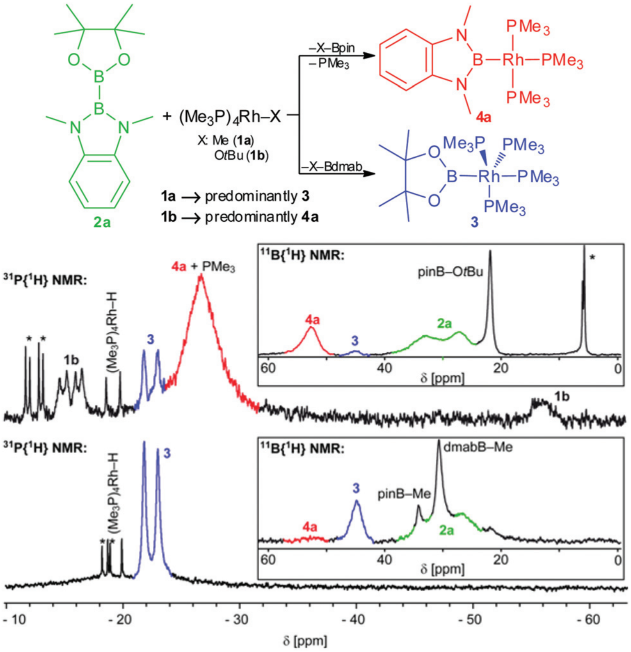

Fig. 1 Reaction pathways and *in situ* $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of the reaction of **2a** with **1a** (bottom, in C_6D_6 after 20 h at rt) and **1b** (top, in THF-d_8 after 20 h at rt) (rt, 122 MHz/96 MHz, *unidentified impurities).[10,11]

^{11}B NMR signals with shift >40 ppm (45 and 52 ppm), characteristic of boryl complexes, were observed. This suggests the formation of the same two boryl complexes in both reactions, albeit in different relative amounts. Furthermore, the ^{11}B NMR data give evidence for the complementary formation of pinB–Me, dmabB–Me and pinB–O*t*Bu, respectively (δ_{11B}: 34, 31 and 22 ppm; these compounds, as well as dmabB–O*t*Bu, were also detected by GC/MS analysis).[8,9] In addition, unreacted **2a**, and for the reaction of **1b**, so far unidentified tetracoordinated boron species are observed.[10] The corresponding $^{31}P\{^1H\}$ NMR spectra indicate overall the formation of two different major rhodium phosphine complexes. For the reaction of **1a** with **2a**, the only major signal observed was a doublet at −22 ppm that is assigned to the complex $[(Me_3P)_4Rh–Bpin]$ (**3**) by comparison with an authentic sample.[2b,8] For the reaction of **1b** with **2a**, this compound is only present in minor amounts and the major very broad signal at −27 ppm was eventually assigned to the novel tris-trimethylphosphine rhodium diaminoboryl complex $[(Me_3P)_3Rh–Bdmab]$ (**4a**) in rapid exchange with free PMe_3 (*vide infra*).[8] In addition, for both reactions, small amounts of by-products/impurities (especially $[(Me_3P)_4Rh–H]$) and, in the case of **1b**, unreacted starting material were detected.[8,11] The selectivity of the B–B bond activation of **2a** with **1a**/**b** (hence the [**3**] : [**4a**] ratio) is cautiously estimated using combined NMR and GC/MS data to be in the order of 10 : 1 for **1a** and 1 : 10 for **1b**, respectively.[8,12]

In order to elucidate further the reaction of **1b** with **2a** a reaction altering the order of addition (first **2a** + KO*t*Bu then addition of $[(Me_3P)_4Rh]Cl$) as well as the reaction of an isolated alkoxide adduct of **2a**, [(18-C-6)K][dmabB–B(O*t*Bu)pin], with $[(Me_3P)_4Rh]Cl$ were studied by *in situ* NMR spectroscopy.[6,8] In both cases, corroborating the above results, the predominant formation of **4a** is observed.

It may be considered that the formation of **4a** from **1b** proceeds *via* its decomposition product $[(Me_3P)_2Rh–CH_2–PMe_2]_2$. Indeed, the latter complex reacts with **2a** giving both **3** and **4a**, however, this reaction is appreciably slower than the B–B activation with *in situ* formed **1b**, furthermore, no indications were found that the decomposition product is present to a substantial amount under the reaction conditions.[8] Moreover, the detection of pinB–O*t*Bu and dmabB–O*t*Bu as concomitantly formed by-products is also suggestive for a reaction pathway *via* the alkoxido complex **1b**.

It may be proposed that an oxidative addition/reductive elimination pathway appears likely in the case of **1a**, in agreement with the literature,[2a] whereas a different (predominant) reaction pathway may be operative in the reaction of **1b**, *e.g.* σ-bond metathesis or abstraction of O*t*Bu$^-$ to form the anionic sp^2–sp^3 diboron species of the type [dmabB–B(O*t*Bu)pin]$^-$. Furthermore, it should be emphasised that the loss of a phosphine ligand concomitant with a B–B bond activation of a diborane(4) derivative is unprecedented amongst the related dialkoxy-/aryloxyboryl systems. This may be rationalised by the increased steric demand of the NR groups compared to an oxygen atom.[2a,b] Nevertheless, tris-phosphine rhodium boryl complexes are readily obtained from tris-phosphine precursors $[(R_3P)_3Rh–X]$ (Scheme 1).[2c–e]

On a preparative scale, complex **4a** was isolated from reactions of **1b** and **2a** in 43% yield.[8] Analogous reactions of **1b** with **2b** and with B_2pin_2, respectively, gave $[(Me_3P)_3Rh–Bdbab]$ (**4b**) and **3** in 15% and 24% isolated yield, respectively.[2b]

The ^{31}P NMR data (in THF-d_8) of **4a** suggest a square-planar solution structure: at lower temperatures, a doublet of triplets for the phosphine ligands *trans* and a doublet of doublets for the phosphine ligand *cis* to the boryl ligand are observed (−80 °C; −23.6 ppm, 1 P, dt, $^1J_{Rh–P}$ = 107 Hz, $^2J_{P–P}$ = 33 Hz, $\Delta w_{1/2}$ = 11 Hz; −12.8 ppm, 2 P, dd, $^1J_{Rh–P}$ = 148 Hz, $^2J_{P–P}$ = 33 Hz, $\Delta w_{1/2}$ = 3 Hz). Towards ambient temperature both signals broaden, the latter ($\Delta w_{1/2}$ = 7 Hz) much less than the first one which loses any fine-structure ($\Delta w_{1/2}$ = 194 Hz). The more pronounced broadening of the signal of the *trans*-phosphine ligand may suggest dynamic processes specific to that ligand (*e.g.* exchange with solvent) in accordance with it being *trans* to the strongly *trans*-influencing boryl ligand. Noteworthily, in the less coordinating solvent C_6D_6 comparable differences in linewidth are observed.[8]

The analogous benzyl-substituted complex **4b** exhibits similar NMR spectroscopic data.[8]

For the complexes **4a,b**, single crystals were obtained and tris-phosphine Rh^I boryl complexes were thus structurally characterised for the first time (Fig. 2). Complex **4a** crystallises in the space group $P2/n$ and is situated on the two-fold axis exhibiting $C2$ symmetry and consequently disorder of the *trans*-boryl PMe_3 ligand.[8] Complex **4b**, in contrast, exhibits no molecular symmetry and crystallises in the space group $P\bar{1}$ as a

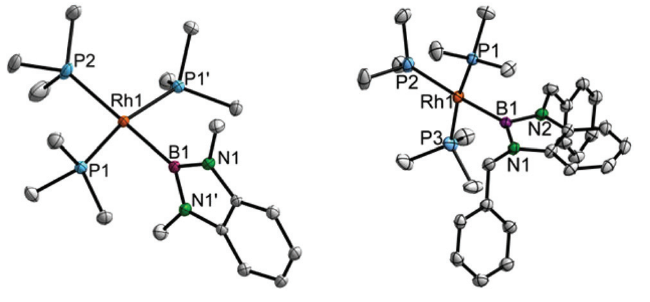

Fig. 2 Molecular structures of **4a** (left) and **4b** (right) at 100 K. Selected bond lengths and angles for **4a**: B1–Rh1 2.074(3) Å, P1–Rh1 2.2697(5) Å, P2–Rh1 2.3194(7) Å, B1–Rh1–P2 180°, B1–Rh1–P1 83.73(1)°, P1–Rh1–P1′ 167.46(2)°, P1–Rh1–P2 96.27(1)° (symmetry equivalent atom denoted by a prime (2-fold axis)); for **4b**, B1–Rh1 2.090(2) Å, P1–Rh1 2.2659(6) Å, P2–Rh1 2.3455(6) Å, P3–Rh1 2.2651(7) Å, B1–Rh1–P2 174.95(7)°, B1–Rh1–P1 83.58(6)°, B1–Rh1–P3 85.37(6)°, P1–Rh1–P3 167.10(2)°, P1–Rh1–P2 96.73(2)°, P2–Rh1–P3 94.87(2)°. Hydrogen atoms and disorder (at P2 in **4a**) are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.[8]

PhMe/*n*-pentane solvate.[8] Both complexes adopt distorted square-planar structures (sum of angles at Rh = 360° and 360.6°, respectively). The Rh–P distances *trans* to the boryl ligand in **4a**,**b** are significantly longer (0.05 and 0.08 Å, respectively) than the respective distances *cis* to the boryl ligand indicating the very strong *trans* influence of the boryl ligand.[2a,6,13] These P–Rh distances may be compared to the respective distances in [$(Me_3P)_4Rh$–Bcat]; despite the trigonal-bipyramidal structure of this complex a similar trend is observed (B–Rh 2.047(2) Å, P_{eq}–Rh 2.29–2.31 Å, P_{trans}–Rh 2.3404(6) Å).[2a] As an effect of the steric crowding in the coordination sphere of these complexes the boryl ligand plane (defined by the $BN_2C_6H_4$ moiety) and the coordination plane (defined by the RhP_3B subunit) are virtually perpendicular to one another with angles of 84.41(3)° (**4a**) and 89.47(4)° (**4b**), respectively.

The ability of the tris-triethylphosphine boryl complex [$(Et_3P)_3Rh$–Bpin] to activate C–H bonds of aromatics to give a rhodium hydrido complex and an aryl boronate has been studied in some detail and employed in catalytic reactions.[2d,3c] Hence, it is not surprising that the related diaminoboryl complex **4a** reacts with benzene under C–H activation. An initial *in situ* study of this reaction suggests – according to NMR and GC/MS analysis – the formation of the hydrido complex [$(Me_3P)_4Rh$–H] as well as dmabB–Ph along with B_2dmab$_2$ and further unidentified species.[8] It can be stated that the C–H bond activation of C_6H_6 (and C_6D_6) by **4a** is a comparably slow process and that NMR measurements of **4a** may be conducted in C_6D_6 within a few hours.[8]

To gain insight into the fundamental coordination chemistry of **4a** its reaction with PMe_3 was investigated. Upon addition of PMe_3 to a solution of **4a** the colour changes from red-orange to yellow and the resulting ^{31}P NMR spectrum exhibits only one broad signal (Fig. 3, bottom).[8] The chemical shift of this signal changes with the relative amount of PMe_3 added and is well described by the weighted average of the ^{31}P NMR chemical shifts of **4a** and PMe_3, whilst the ^{11}B NMR shift does not change noticeably.[8] This indicates that, at ambient temperature, the PMe_3 ligands in **4a** are in rapid exchange with free PMe_3, whilst other species, in particular [$(Me_3P)_4Rh$–Bdmab] **5** (*vide infra*), are only present in minor amounts (<10 mol%).[8] However, at lower temperatures a more complicated behaviour is observed (Fig. 3). The single broad signal (−52 ppm) observed at ambient temperature splits, upon cooling, into a relatively sharp signal indicative of free PMe_3 (−61 ppm) and a very broad signal at −22 ppm (−22 °C). Upon further cooling, the latter first sharpens and then broadens again (−22 to −54 °C), indicating the presence of more than one dynamic process. Finally, at even lower temperatures, this signal splits into two signals of equal intensity (−95 °C: −5.9 ppm, $\Delta w_{1/2}$ = 400 Hz, and −38.4 ppm, $\Delta w_{1/2}$ = 430 Hz; though not fully resolved, the peak shape suggests a pair of broad doublets). These data are consistent with rapid intermolecular exchange of free PMe_3 with coordinated PMe_3 in **4a** at and slightly below ambient temperature. At lower temperatures, however, a single new rhodium species becomes predominant exhibiting intramolecular P_{ax}–P_{eq} exchange, but slower intermolecular exchange with free PMe_3.

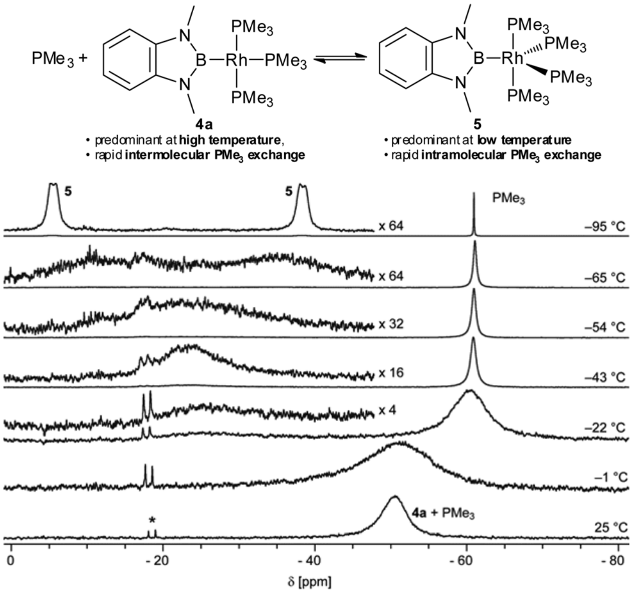

Fig. 3 Selected $^{31}P\{^1H\}$ VT-NMR spectra of **4a** in the presence of 10.2 eq. of PMe_3 (THF-d_8, 162 MHz, *denotes an impurity of [$(Me_3P)_4Rh$–H]).[8,11]

A likely candidate for the novel species observed at low temperature is the tetrakis-trimethylphosphine complex [$(Me_3P)_4Rh$–Bdmab] **5**, though, the intensity of the ^{31}P NMR signals imply a trigonal-bipyramidal structure with an equatorial boryl ligand that is unprecedented amongst related complexes such as [$(Me_3P)_4Rh$–Bcat] or **3**.[2a,3a,8] Attempts to crystallise **5** from solutions of **4a** in THF and/or *n*-pentane in the presence of excess PMe_3 at low temperatures lead repeatedly to a yellow crystalline material. However, these crystals decompose upon removal from the mother liquor and the

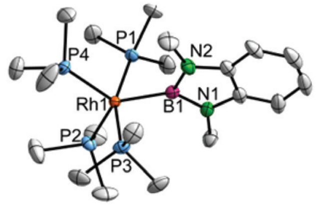

Fig. 4 Molecular structures of **5** at 175 K. Selected bond lengths and angles B1–Rh1 2.109(3) Å, P1–Rh1 2.2765(7) Å, P2–Rh1 2.3396(7) Å, P3–Rh1 2.2660(7) Å, P4–Rh1 2.3616(7) Å, B1–Rh1–P1 79.20(8)°, B1–Rh1–P2 130.45(8)°, B1–Rh1–P3 80.02(8)°, B1–Rh1–P4 121.15(8)°, P1–Rh1–P2 96.04(3)°, P1–Rh1–P3 158.92(3)°, P1–Rh1–P4 96.08(3)°, P2–Rh1–P3 94.69(3)°, P2–Rh1–P4 108.40(3)°, P3–Rh1–P4 97.67(3)°. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.[8]

residue was identified by NMR analysis as **4a**. Eventually, single crystals of **5** suitable for X-ray structure determination were obtained by *in situ* crystallisation from a saturated solution in neat PMe_3 on the diffractometer.[8]

Complex **5** indeed adopts a trigonal-bipyramidal structure with an equatorial boryl ligand (Fig. 4). As this coordination mode is unprecedented amongst related Rh boryl complexes, direct comparison is difficult; however, increased P_{eq}–Rh distances compared to the *cis* boryl P_{ax}–Rh distance are observed.[2a,8] Noteworthy are the small (~80°) P1–Rh1–B1 and P3–Rh1–B1 angles indicating significant steric encumbrance of this complex.

DFT computations were performed to elucidate further the reaction of **4a** with PMe_3 and the formation of **5** (Fig. 5).[8,14] The geometries of **4a** and **5** were optimised starting from the X-ray structures of **4a** and for **5** from a putative isomeric apical boryl complex based on the X-ray structure of **3**. It should be mentioned that the fully optimised structure of **5** represents the equatorial isomer and all attempts to locate a minimum structure for the respective (expected) apical isomer have failed. This is in contrast to the related dialkoxyboryl complexes where the axial boryl complex is preferred for electronic reasons.[3a] The geometrical parameters of the fully optimised structures correspond well with the crystallographically determined data, albeit, in agreement with literature data, the Rh–P bonds are systematically too long.[3a]

In terms of free energy, the dissociation of a PMe_3 ligand from **5** to give **4a** is found to have a marginal or even no barrier at all and, hence, the isolation of **4a**, in agreement with the experimental data, is expected. Moreover, the data are also fundamentally in agreement with a rapid intermolecular exchange of PMe_3 ligands in **4a** with free PMe_3, possibly involving **5** as an intermediate. The 5-coordinate complex **5** is calculated to be higher in energy than **4** at all temperatures examined, but much less so at lower temperatures, consistent with the NMR spectra recorded in the presence of excess PMe_3 at low temperature. As the computed enthalpies/energies were determined in the gas-phase, they cannot be expected to match the experimental findings exactly, which is especially true for the Gibbs free energies which contain entropic contributions, that are expected to be smaller in the condensed phase.

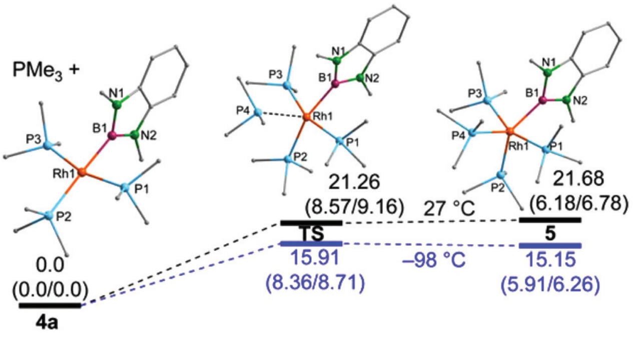

Fig. 5 Calculated structures and relative energies Δ*G*(Δ*H*/Δ*E*) in kcal mol^{-1} for **4a**, **5** and the respective transition states for the two temperatures 27 °C and −98 °C at the B3LYP/6-311G(d,p) level of theory; for further details see ESI.† [8]

Conclusions

The regioselectivity of B–B bond activation of the unsymmetrical diborane(4) derivative pinB–B($(MeN)_2(C_6H_4)$) by $[(Me_3P)_4Rh–X]$ (X = Me, O*t*Bu) (**1a**,**b**) is controlled by the nature of X. Either the dialkoxido boryl complex $[(Me_3P)_4Rh–Bpin]$ (**3**) for X = Me or, accompanied by dissociation of a PMe_3 ligand, the diaminoboryl complex $[(Me_3P)_3Rh–B((MeN)_2(C_6H_4))]$ (**4a**) for X = O*t*Bu is obtained predominantly. This strongly suggests that two fundamentally different mechanisms are operating for B–B activation. The expected penta-coordinated product $[(Me_3P)_4Rh–B((MeN)_2(C_6H_4))]$ (**5**), however, is only stable at low temperatures in the presence of excess PMe_3 and exhibits an unprecedented equatorial boryl ligand. In agreement with DFT computations, this is rationalised considering the steric demand of the NR groups that causes the expected five-coordinate apical boryl complex to be disfavoured over its equatorial isomer **5** and, moreover, favours dissociation of a PMe_3 ligand to give the tris-phosphine complex **4a**. Further studies to elucidate the mechanisms of the B–B bond activation processes with **1a**,**b**, as well as a detailed study on the reactivity of **4a** are in progress.

Acknowledgements

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Notes and references

1 For selected reviews, see: (*a*) J. F. Hartwig, *Acc. Chem. Res.*, 2012, **45**, 864–873; (*b*) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890–931; (*c*) T. Ishiyama and N. Miyaura, *Chem. Rec.*, 2004, **3**, 271–280; (*d*) K. Burgess and M. J. Ohlmeyer, *Chem. Rev.*, 1991, **91**, 1179–1191; (*e*) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685–2722; (*f*) T. B. Marder and N. C. Norman, *Top. Catal.*, 1998, **5**, 63–73; (*g*) D. L. Kays and S. Aldridge, *Struct. Bonding*, 2008, **130**, 29–122.

2 (*a*) C. Dai, G. Stringer, T. B. Marder, A. J. Scott, W. Clegg and N. C. Norman, *Inorg. Chem.*, 1997, **36**, 272–273; (*b*) C. Dai, *Ph. D. Thesis*, University of Waterloo, Canada, 1998; (*c*) T. B. Marder, personal communication; (*d*) M. Teltewskoi, J. A. Panetier, S. A. Macgregor and T. Braun, *Angew. Chem., Int. Ed.*, 2010, **49**, 3947–3951; (*e*) M. Teltewskoi, S. I. Kalläne, T. Braun and R. Herrmann, *Eur. J. Inorg. Chem.*, 2013, 5762–5768.

3 (*a*) K. C. Lam, W. H. Lam, Z. Lin, T. B. Marder and N. C. Norman, *Inorg. Chem.*, 2004, **43**, 2541–2547; (*b*) S. I. Kalläne, T. Braun, B. Braun and S. Mebs, *Dalton Trans.*, 2014, **43**, 6786–6801; (*c*) S. I. Kalläne and T. Braun, *Angew. Chem., Int. Ed.*, 2014, **53**, 9311–9315; (*d*) S. I. Kalläne, M. Teltewskoi, T. Braun and B. Braun, *Organometallics*, 2015, DOI: 10.1021/om500952x.

4 For further examples of Rh boryl complexes see: (*a*) W. Clegg, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, E. G. Robins, A. J. Scott, F. E. S. Souza, G. Stringer and G. R. Whittell, *J. Chem. Soc., Dalton Trans.*, 1998, 301–309; (*b*) P. Nguyen, G. Lesley, N. J. Taylor, T. B. Marder, N. L. Pickett, W. Clegg, M. R. J. Elsegood and N. C. Norman, *Inorg. Chem.*, 1994, **33**, 4623–4624; (*c*) M. Hasegawa, Y. Segawa, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2012, **51**, 6956–6960; (*d*) M. V. Câmpian, J. L. Harris, N. Jasim, R. N. Perutz, T. B. Marder and A. C. Whitwood, *Organometallics*, 2006, **25**, 5093–5104; (*e*) R. J. Lindup, T. B. Marder, R. N. Perutz and A. C. Whitwood, *Chem. Commun.*, 2007, 3664–3666; (*f*) B. Procacci, Y. Jiao, M. E. Evans, W. D. Jones, R. N. Perutz and A. C. Whitwood, *J. Am. Chem. Soc.*, 2015, **137**, 1258–1272.

5 (*a*) N. Iwadate and M. Suginome, *J. Am. Chem. Soc.*, 2010, **132**, 2548–2549; (*b*) J. Cid, J. J. Carbó and E. Fernández, *Chem. – Eur. J.*, 2014, **20**, 3616–3620.

6 C. Borner and C. Kleeberg, *Eur. J. Inorg. Chem.*, 2014, 2486–2489.

7 $[(Me_3P)_2Rh–CH_2–PMe_2]_2$ was previously reported: V. V. Mainz and R. A. Andersen, *Organometallics*, 1984, **3**, 675–678.

8 See ESI† for details.

9 (*a*) R. Goetze, H. Nöth, H. Pommerening, D. Sedlak and B. Wrackmeyer, *Chem. Ber.*, 1981, **114**, 1884–1893; (*b*) H. C. Brown, W. S. Park, J. S. Cha, B. T. Cho and C. A. Brown, *J. Org. Chem.*, 1986, **51**, 337–342; (*c*) B. L. Tran, D. Adhikari, H. Fan, M. Pink and D. J. Mindiola, *Dalton Trans.*, 2010, 358–360; (*d*) C. Kleeberg, L. Dang, Z. Lin and T. B. Marder, *Angew. Chem., Int. Ed.*, 2009, **48**, 5350–5354; (*e*) C. Kleeberg and C. Borner, *Eur. J. Inorg. Chem.*, 2013, 2799–2806.

10 The $^{11}B\{^1H\}$ NMR spectrum of the reaction of **1b** with **2a** exhibits additionally two sharp signals at 6.0 and 5.8 ppm ($\Delta w_{1/2}$ = 3.4, 9.0 Hz) indicating the formation of tetra-coordinated boron species, possibly Lewis acid/base adducts of *t*BuO$^-$ and pinB–O*t*Bu, dmabB–O*t*Bu or **2a**.

11 The formation of small amounts of $[(Me_3P)_4Rh–H]$ in related reactions was reported earlier and may be associated with the presence of adventitious moisture.[2a,e] Alternatively it is formed slowly by C–H activation of aromatics.[2d,3c,d,8] For spectroscopic data see: (*a*) D. Zargarian, P. Chow, N. J. Taylor and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1989, 540–544; (*b*) M. Paneque and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1989, 105–106.

12 Performing the reaction of **1a** with **2a** in THF-d_8 led to a slight preference for **4a**, accompanied by substantial formation of unidentified species.[8]

13 (*a*) J. Zhu, Z. Lin and T. B. Marder, *Inorg. Chem.*, 2005, **44**, 9384–9390; (*b*) H. Braunschweig, P. Brenner, A. Müller, K. Radacki, D. Rais and K. Uttinger, *Chem. – Eur. J.*, 2007, **13**, 7171–7176.

14 M. J. Frisch *et al.*, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford, CT, 2009.