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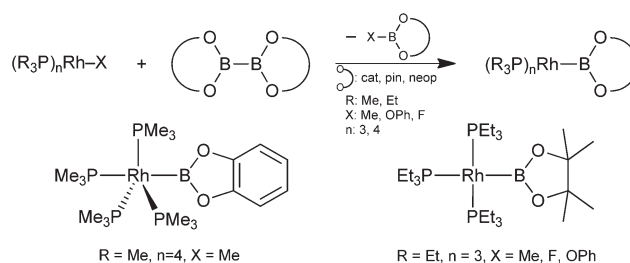
Selective B–B bond activation in an unsymmetrical diborane(4) by [(Me₃P)₄Rh–X] (X = Me, OtBu): a switch of mechanism?†

C. Borner, K. Brandhorst and C. Kleeberg*

The unsymmetrical diborane(4) pinB–B((RN)₂(C₆H₄)) (R = Me, Bn) reacts with [(Me₃P)₄Rh–X] (X = Me, OtBu) giving predominantly either [(Me₃P)₄Rh–Bpin] or [(Me₃P)₃Rh–B((RN)₂(C₆H₄))] depending on X. At low temperatures in the presence of excess PMe₃ the unprecedented equatorial boryl complex [(Me₃P)₄Rh–B((MeN)₂(C₆H₄))] 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} tris-boryl complexes or, more recently, their use as subunits in boryl pincer complexes.^{1–4} In particular, rhodium boryl complexes of the type [(R₃P)_nRh–B(OR')₂] (R = Me, Et; n = 3, 4; (OR')₂ = OCMe₂–CMe₂O (pin), 1,2–O₂C₆H₄ (cat), OCH₂CMe₂CH₂O (neop)) have been explored (Scheme 1).^{2,3} These complexes are accessible by the reaction of a precursor complex [(Me₃P)_nRh–X] and a symmetrical diborane(4) derivative (B₂(OR)₂) (Scheme 1).²

Marder and co-workers have studied in some detail the chemistry of [(Me₃P)₄Rh–B(OR)₂] complexes and especially their formation from [(Me₃P)₄Rh–Me] (**1a**) and B₂(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 fluoro (X = F) complexes [(Et₃P)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)₂C₁₀H₆) 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



Scheme 1 General synthesis and two examples of [(R₃P)_nRh–B(OR)₂] complexes.²

accessible unsymmetrical diborane(4) derivatives of the type pinB–B((NR)₂C₆H₄) (R = Me (**2a**), Bn (**2b**), TMS) and demonstrated their utility as precursors for diamino-boryl 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 [(Me₃P)₄Rh–X] (X = Me (**1a**), OtBu (**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 [(Me₃P)₄Rh]Cl and KOtBu 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 [(Me₃P)₂Rh–CH₂–PMe₂]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 ³¹P NMR spectrum at low temperatures shows a doublet of quartets and a doublet of doublets as the AM₃ part of an AM₃X spin system indicative of a five-coordinate, approximately trigonal-bipyramidal rhodium complex with the alkoxido ligand occupying an apical position.⁸

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

Technische Universität Carolo-Wilhelmina zu Braunschweig, Hagenring 30, 38106 Braunschweig, Germany. E-mail: ch.kleeberg@tu-braunschweig.de

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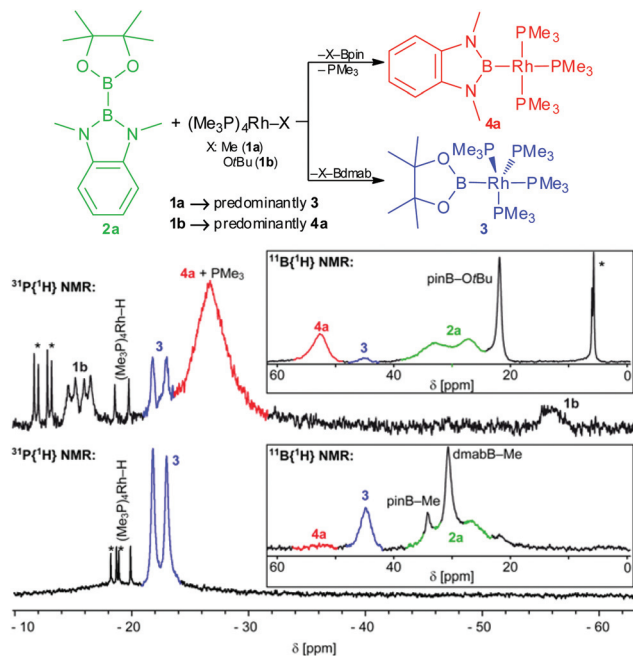


Fig. 1 Reaction pathways and *in situ* $^{31}\text{P}\{^1\text{H}\}$ and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the reaction of **2a** with **1a** (bottom, in C_6D_6 after 20 h at rt) and **1b** (top, in THF-d_8 after 20 h at rt) (rt, 122 MHz/96 MHz, *unidentified impurities).^{10,11}

^{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-OtBu**, respectively ($\delta_{11\text{B}}$: 34, 31 and 22 ppm; these compounds, as well as **dmabB-OtBu**, 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 $^{31}\text{P}\{^1\text{H}\}$ 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 $[(\text{Me}_3\text{P})_4\text{Rh-Bpin}]$ (**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 $[(\text{Me}_3\text{P})_3\text{Rh-Bdmb}]$ (**4a**) in rapid exchange with free PMe_3 (*vide infra*).⁸ In addition, for both reactions, small amounts of by-products/impurities (especially $[(\text{Me}_3\text{P})_4\text{Rh-H}]$) 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** + *KOtBu* then addition of $[(\text{Me}_3\text{P})_4\text{Rh}]\text{Cl}$) as well as the reaction of an isolated

alkoxide adduct of **2a**, $[(18\text{-C-6})\text{K}][\text{dmabB-B}(\text{OtBu})\text{pin}]$, with $[(\text{Me}_3\text{P})_4\text{Rh}]\text{Cl}$ 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 $[(\text{Me}_3\text{P})_2\text{Rh-CH}_2\text{-PMe}_2]_2$. 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-OtBu** and **dmabB-OtBu** 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 *OtBu*⁻ to form the anionic $\text{sp}^2\text{-sp}^3$ diboron species of the type $[\text{dmabB-B}(\text{OtBu})\text{pin}]^-$. 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 $[(\text{R}_3\text{P})_3\text{Rh-X}]$ (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 $[(\text{Me}_3\text{P})_3\text{Rh-Bdbab}]$ (**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, $^1J_{\text{Rh-P}} = 107$ Hz, $^2J_{\text{P-P}} = 33$ Hz, $\Delta\omega_{1/2} = 11$ Hz; -12.8 ppm, 2 P, dd, $^1J_{\text{Rh-P}} = 148$ Hz, $^2J_{\text{P-P}} = 33$ Hz, $\Delta\omega_{1/2} = 3$ Hz). Towards ambient temperature both signals broaden, the latter ($\Delta\omega_{1/2} = 7$ Hz) much less than the first one which loses any fine-structure ($\Delta\omega_{1/2} = 194$ 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. Noteworthy, 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 $P2_1/n$ and is situated on the two-fold axis exhibiting C_2 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



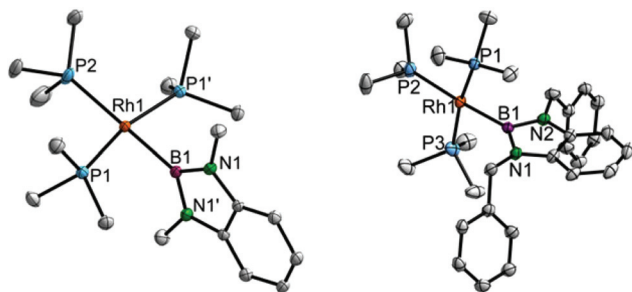


Fig. 2 Molecular structures of **4a** (left) and **4b** (right) at 100 K. Selected bond lengths and angles for **4a**: B1–Rh1 2.074(3) Å, P1–Rh1 2.2697(5) Å, P2–Rh1 2.3194(7) Å, B1–Rh1–P2 180°, B1–Rh1–P1 83.73(1)°, P1–Rh1–P1' 167.46(2)°, P1–Rh1–P2 96.27(1)° (symmetry equivalent atom denoted by a prime (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 [(Me₃P)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 BN₂C₆H₄ moiety) and the coordination plane (defined by the RhP₃B 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 [(Et₃P)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 diamino-boryl 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 [(Me₃P)₄Rh–H] as well as dmabB–Ph along with B₂dmab₂ and further unidentified species.⁸ It can be stated that the C–H bond activation of C₆H₆ (and C₆D₆) by **4a** is a comparably slow process and that NMR measurements of **4a** may be conducted in C₆D₆ within a few hours.⁸

To gain insight into the fundamental coordination chemistry of **4a** its reaction with PMe₃ was investigated. Upon addition of PMe₃ to a solution of **4a** the colour changes from red-orange to yellow and the resulting ³¹P NMR spectrum exhibits only one broad signal (Fig. 3, bottom).⁸ The chemical shift of this signal changes with the relative amount of PMe₃ added and is well described by the weighted average of the ³¹P NMR

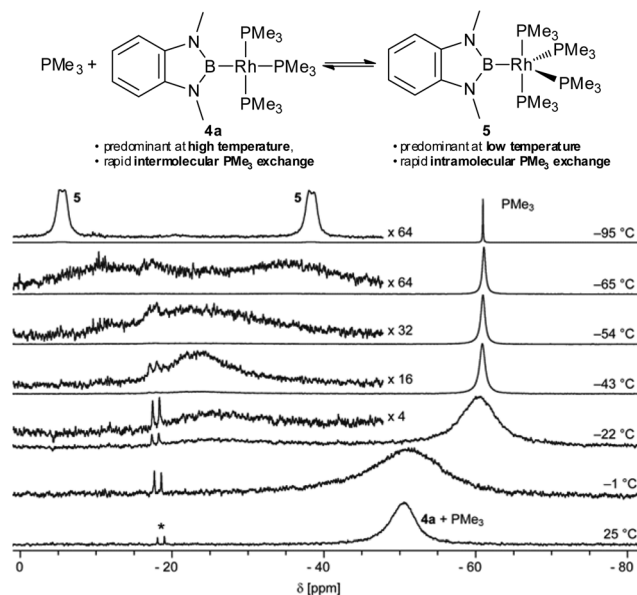


Fig. 3 Selected ³¹P{¹H} VT-NMR spectra of **4a** in the presence of 10.2 eq. of PMe₃ (THF-d₈, 162 MHz, *denotes an impurity of [(Me₃P)₄Rh–H]).^{8,11}

chemical shifts of **4a** and PMe₃, whilst the ¹¹B NMR shift does not change noticeably.⁸ This indicates that, at ambient temperature, the PMe₃ ligands in **4a** are in rapid exchange with free PMe₃, whilst other species, in particular [(Me₃P)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 PMe₃ (–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, Δ*w*_{1/2} = 400 Hz, and –38.4 ppm, Δ*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 PMe₃ with coordinated PMe₃ 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 PMe₃.

A likely candidate for the novel species observed at low temperature is the tetrakis-trimethylphosphine complex [(Me₃P)₄Rh–Bdmab] **5**, though, the intensity of the ³¹P NMR signals imply a trigonal-bipyramidal structure with an equatorial boryl ligand that is unprecedented amongst related complexes such as [(Me₃P)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 PMe₃ at low temperatures lead repeatedly to a yellow crystalline material. However, these crystals decompose upon removal from the mother liquor and the



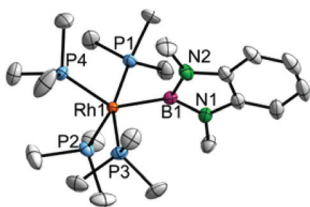


Fig. 4 Molecular structures of **5** at 175 K. Selected bond lengths and angles B1–Rh1 2.109(3) Å, P1–Rh1 2.2765(7) Å, P2–Rh1 2.3396(7) Å, P3–Rh1 2.2660(7) Å, P4–Rh1 2.3616(7) Å, B1–Rh1–P1 79.20(8)°, B1–Rh1–P2 130.45(8)°, B1–Rh1–P3 80.02(8)°, B1–Rh1–P4 121.15(8)°, P1–Rh1–P2 96.04(3)°, P1–Rh1–P3 158.92(3)°, 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 $\text{P}_{\text{eq}}\text{-Rh}$ distances compared to the *cis* boryl $\text{P}_{\text{ax}}\text{-Rh}$ distance are observed.^{2a,8} Noteworthy are the small ($\sim 80^\circ$) 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

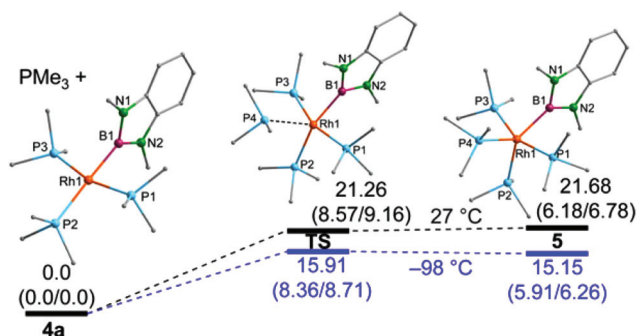


Fig. 5 Calculated structures and relative energies $\Delta G(\Delta H/\Delta E)$ in kcal mol^{-1} for **4a**, **5** and the respective transition states for the two temperatures 27 °C and –98 °C at the B3LYP/6-311G(d,p) level of theory; for further details see ESI.†⁸

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.

Conclusions

The regioselectivity of B–B bond activation of the unsymmetrical diborane(4) derivative $\text{pinB-B}((\text{MeN})_2(\text{C}_6\text{H}_4))$ by $[(\text{Me}_3\text{P})_4\text{Rh-X}]$ (X = Me, *Ot*Bu) (**1a,b**) is controlled by the nature of X. Either the dialkoxido boryl complex $[(\text{Me}_3\text{P})_4\text{Rh-Bpin}]$ (**3**) for X = Me or, accompanied by dissociation of a PMe_3 ligand, the diamino boryl complex $[(\text{Me}_3\text{P})_3\text{Rh-B}((\text{MeN})_2(\text{C}_6\text{H}_4))]$ (**4a**) for X = *Ot*Bu is obtained predominantly. This strongly suggests that two fundamentally different mechanisms are operating for B–B activation. The expected penta-coordinate product $[(\text{Me}_3\text{P})_4\text{Rh-B}((\text{MeN})_2(\text{C}_6\text{H}_4))]$ (**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.

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- 11 The formation of small amounts of $[(\text{Me}_3\text{P})_4\text{Rh}-\text{H}]$ 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.
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