



Communication

***Tert*-butylborane: A bis (σ -B–H) ligand in ruthenium hydride chemistry**

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ABSTRACT

The reaction of *tert*-butylborane with the bis(dihydrogen) complex $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2$ leads to the corresponding bis σ -borane complex which is the first example of a monoalkylborane ruthenium bis σ -complex. An alternative route involves the reaction of $\text{RuHCl}(\eta^2\text{-H}_2)(\text{PCy}_3)_2$ with lithium *tert*-butylborohydride.

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1. Introduction

Boranes are key compounds in a wide variety of metal mediated organic transformations such as hydroboration, borylation [1–3], boron transfer reactions [4] or dehydrogenation of ammonia borane [5,6]. Metal boron chemistry is thus an active field of investigation dominated by reactivity studies with disubstituted boranes HBRR' ($\text{R}, \text{R}' = \text{pinacol, catechol, alkyl}$) [7]. More recently, this area has attracted considerable attention with the development of hydrogen storage materials and the potential reversibility of hydrogen-release reactions from amineborane compounds [8–11]. Although the formation of hydrido boryl species in a final B–H bond activation stage has been well documented [12,13] isolated σ -borane complexes remain quite rare since the first report in 1996 by Hartwig et al. [14]. These complexes often represent key intermediates in the boundary oxidative addition/reductive elimination steps of metal catalyzed reactions [15–18]. More evidence is now in favour of σ -B–H coordinated intermediates as observed in catalyzed borylation processes, thus supporting the recent metathesis mechanism termed σ -CAM for late transition metals (σ -complex assisted metathesis) and involving metal induced dynamic rearrangements of E–H bonds at constant oxidation state [19].

The situation can prove different in the presence of polyhydride metal precursors. Depending first on the nature of the ligands coordinated to the metal fragment and also on the Lewis acidity of the boron atom, dihydroborate coordination resulting from an interaction of the boron with a neighbouring hydride can be favoured [15,20–22]. As part of our ongoing program on B–H bond activation

of less-common borane reagents, we started to explore the coordination of monosubstituted boranes RBH_2 . The use of mesitylborane allowed us to isolate the first bis σ -borane complex $\text{RuH}_2(\eta^2\text{-H}_2\text{BMes})(\text{PCy}_3)_2$ (**4**) [23]. In this complex, the mesitylborane displays a unique coordination mode with two geminal σ -B–H bonds. It is noteworthy that such a bonding mode is limited to mesitylborane with only two other complexes presenting a similar coordination: $\text{RuHCl}(\eta^2\text{-H}_2\text{BMes})(\text{PCy}_3)_2$, the precursor to the first terminal borylene ruthenium complex [24], and the cationic complex $[\text{Cp}^*\text{Ru}(\text{PiPr}_3)(\text{BH}_2\text{Mes})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ [25]. We now report the reaction of *tert*-butylborane with a polyhydride ruthenium center leading to the corresponding bis σ -borane complex as the first example of a monoalkylborane bis σ -complex. In this communication, we mainly focus on spectroscopic and structural data in order to evaluate the influence of the boron substituent on the coordination of the borane to the ruthenium center.

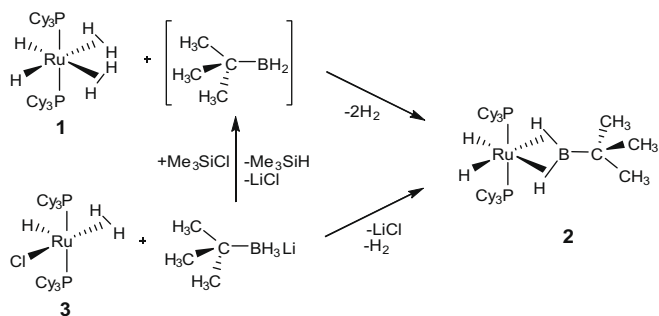
2. Results

An ethereal solution of ${}^t\text{BuBH}_2$ *in situ* generated from ${}^t\text{BuBH}_3\text{Li}$ and Me_3SiCl was reacted at room temperature with a stoichiometric amount of $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2$ (**1**) in toluene. After workup, yellow crystals of $\text{RuH}_2(\eta^2\text{-H}_2\text{-H}_2\text{B}^t\text{Bu})(\text{PCy}_3)_2$ (**2**) were isolated. Complex **2** resulting from the substitution of two labile σ -H₂ ligands was fully characterized by multinuclear NMR and X-ray diffraction crystallography. As previously reported in the case of **4**, an alternative synthetic route could also be obtained by stoichiometric reaction of $\text{RuHCl}(\eta^2\text{-H}_2)(\text{PCy}_3)_2$ (**3**) with lithium *tert*-butylborohydride (Scheme 1).

NMR data are consistent with a bis- σ coordination mode. The ${}^1\text{H}$ NMR spectrum of **2** in C_6D_6 at 298 K, in the hydride region

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Scheme 1. Synthetic routes to the ruthenium *tert*-butylborane bis- σ complex (**2**).

consists of a sharp triplet and a broad singlet in a 1:1 integration ratio at $\delta -10.99$ and $\delta -6.48$, respectively, the signals slightly deshielded compared to the ones in $\text{RuH}_2(\eta^2\text{-H}_2\text{-H}_2\text{BMe}_3)(\text{PCy}_3)_2$ (**4**). The triplet ($J_{\text{P-H}} = 27.0$ Hz) collapsed into a singlet upon phosphorus decoupling whereas the singlet sharpened upon boron decoupling. T_1 measurements on the hydride resonances are reminiscent of the ones obtained in the case of the mesitylborane bis σ complex **4** and rule out the presence of any ($\eta^2\text{-H}_2$) ligand in **2** [23]. The integrals of the hydrides and the *tert*-butyl resonances also confirm the presence of one *tert*-butyl group and four hydrogen atoms around the ruthenium. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum exhibits a broad signal at $\delta 69$ deshielded ($\Delta\delta + 10$) compared to the resonance of **4**, still in a region characteristic of a tricoordinated boron atom [15].

The X-ray structure of **2** was determined at 110 K (Fig. 1 and Table 1). The Ru atom is in a pseudo-octahedral environment with the two tricyclohexylphosphine ligands in axial position and the equatorial plane occupied by four coplanar hydrogen atoms (H_{1-4}).

The Ru–B bond distance of 1.934(2) Å is shorter than the sum of the covalent radii (2.09 Å) and very close to that of **4** (1.938(4) Å) suggesting a similar interaction between the metal center and the boron atom. With 1.582(3) Å, as expected for a $\text{C}_{\text{sp}^3}\text{-B}$, the B–C1 bond distance is slightly longer than the one in **4** (1.543(5) Å) but lies in the range quoted for *tert*-butylboranes (1.61 Å) [26,27]. Interestingly, the Ru–H₃ and Ru–H₄ bond distances (1.55(2) and 1.53(3) Å) are comparable to the ones in **4** (1.59(3) and 1.61(3) Å). The B–H bond distances (1.23(2) and 1.25(3) Å) are slightly elongated compared to free boranes (1.20 Å) and similar to those found in **4**. In these two complexes, the bis σ -coordination mode is thus of the same nature and results from the σ -donation from $\sigma(\text{BH})$ to Ru and π -back-donation from Ru into the vacant p orbital on B.

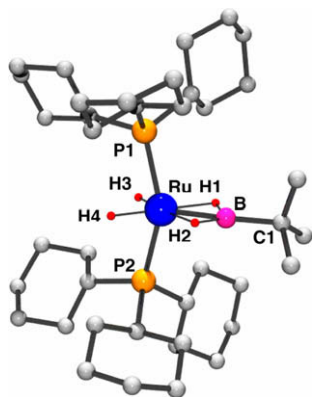


Fig. 1. X-ray crystal structure of $\text{RuH}_2(\eta^2\text{-H}_2\text{-H}_2\text{B}^t\text{Bu})(\text{PCy}_3)_2$ (**2**).

Table 1

Comparison between selected geometrical parameters (distances in Å, angles in °) from the X-ray structures of **2** and **4**.

	2	4
Ru–B	1.934(2)	1.938(4)
Ru–P1	2.3159(4)	2.3186(9)
Ru–P2	2.3059(4)	2.2952(9)
B–C1	1.582(3)	1.543(5)
Ru–H3	1.55(2)	1.61(3)
Ru–H4	1.53(3)	1.59(3)
Ru...H1	1.73(2)	1.73(3)
Ru...H2	1.69(2)	1.77(3)
B–H1	1.23(2)	1.24(3)
B–H2	1.25(2)	1.29(3)
H1–B–H2	120.8(16)	123(2)
P1–Ru–P2	151.691(16)	150.87(3)
P1–Ru–B	106.01(6)	108.89(11)
P2–Ru–B	101.79(6)	100.19(11)
Ru–B–C1	173.29(17)	177.1(3)
P1–Ru–B–P2	174.6	178.3

3. Conclusion

Examples of σ -coordinated alkyl substituted boranes are scarce. Only three examples involving Mn or Ni and a very limited number of dialkylboranes R_2BH (R = Cy, Me, Et) have been reported so far [28,29]. The use of monosubstituted boranes (RBH_2) as a ligand is even more limited and restricted to mesitylborane ligated in a bis- σ coordination mode to a ruthenium center [23–25]. In this communication, we report the first example of a monoalkylborane bis- σ complex involving *tert*-butylborane ligated to a dihydride ruthenium fragment. NMR and X-ray data tend to indicate that irrespective of the substituent on boron, alkyl in **2** or aryl in **4**, the borane is coordinated to the metal in a similar fashion. Computational studies are currently being undertaken to analyze in more detail the *tert*-butylborane coordination *via* the electronic structure of **2** and reactivity studies are in progress.

4. Experimental

4.1. Synthesis of $\text{RuH}_2(\eta^2\text{-H}_2\text{-H}_2\text{B}^t\text{Bu})(\text{PCy}_3)_2$ (**2**)

All the manipulations were performed in a glove box under an atmosphere of argon. The solvents were dried with a solvent purification system MBraun SPS-800 Series. The NMR spectra were recorded on Bruker AV-300 or AV-500 MHz spectrometers.

Me_3SiCl (0.42 mL, 3.309 mmol) was added to an ethereal solution (4 mL) of lithium *tert*-butylborohydride (12.2 mg, 0.157 mmol) [30] at room temperature and stirred for 5 h. The resulting suspension was transferred to a toluene solution (5 mL) of $\text{RuH}_2(\eta^2\text{-H}_2)(\text{PCy}_3)_2$ (**1**) (104.3 mg, 0.156 mmol) and stirred for 3 h. After removal of the solvent and addition of pentane, the suspension was filtrated over Celite® and the solvent evaporated. An impure yellow powder resulted from which suitable crystals of **2** were obtained after solubilisation in the minimum amount of pentane and standing at -35 °C. Yield: 73% as estimated by ^{31}P NMR integration on the crude yellow powder.

NMR data for **2**: ^1H NMR (C_6D_6 , 298 K, 300.131 MHz) δ : -10.99 (t, 2H, $^2J_{\text{HP}} = 27.0$ Hz, H_{3-4}), -6.48 (br, 2H, H_{1-2}), 1.40 (s, 9H, ^tBu), 1.00–2.50 (m, 66H, Cy). T_1 min (C_7D_8 , 253 K, 500.33 MHz) δ : -11.01 (327 ms), -6.60 (160 ms). $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6 , 298 K, 121.495 MHz) δ : 84.03 (s). $^{11}\text{B}\{^1\text{H}\}$ (C_7D_8 , 293 K, 160.526 MHz) δ : 69 (br). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 298 K, 75.467 MHz) δ : 27.00 (CH_2 Cy), 29.21 (CH_3 ^tBu), 30.79 (CH_2 Cy), 38.97 (CH Cy). The C^{IV} (^tBu) was not observed.

4.2. Crystal structure determination and refinement

Data were collected at low temperature (110 K) on a Bruker Kap-pa Apex II diffractometer using a graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters have been obtained by means of a least-squares refinement performed on a set of 9567 well measured reflections. The structures have been solved by Direct Methods using SIR92 [31], and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL97 [32] included in the software package WINGX version 1.63 [33]. The Atomic Scattering Factors were taken from International tables for X-ray crystallography [34]. All the hydrogen atoms were located geometrically, and refined by using a riding model, except for Hy1, Hy2, Hy3 and Hy4 which were found by calculating Fourier difference maps of the electronic density observed at small theta ($<18^\circ$). The disorder on C2, C3 and C4 of the *tert*-butyl group was treated using the option 'Part' in the SHELX97 refinement program. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights were calculated from the following formula:

$$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \quad \text{where } P = (F_o^2 + 2F_c^2)/3.$$

For a question of clarity the atoms C2B, C3B and C4B of the disordered *tert*-butyl were not represented.

4.3. Crystallographic data and refinement data for compound 2

	Compound 2
Empirical formula	C ₄₀ H ₇₉ BP ₂ Ru
Formula weight	733.85
Temperature (K)	110
Wavelength λ (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	10.7272(6)
<i>b</i> (Å)	12.2520(7)
<i>c</i> (Å)	16.8196(10)
α (°)	94.984(3)
β (°)	96.829(2)
γ (°)	112.051(2)
Volume (Å ³)	2013.5(2)
Z, calculated density (g/cm ⁻³)	2, 1.210
Absorption coefficient (mm ⁻¹)	0.494
$F(000)$	796
Crystal size (mm)	0.2 × 0.12 × 0.07
Theta range for data collection (°)	1.23–28.28
Limiting indices	–14 ≤ <i>h</i> ≤ 8 –16 ≤ <i>k</i> ≤ 16 –22 ≤ <i>l</i> ≤ 22
Reflections collected/unique	60610/9858 [$R_{\text{int}} = 0.0324$]
Completeness to theta = 28.28	98.6%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.975 and 0.889
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9858/6/422
Goodness-of-fit on F^2	1.136
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0254$, $wR_2 = 0.0660$
R indices (all data)	$R_1 = 0.0313$, $wR_2 = 0.0783$
Largest difference peak and hole (e Å ⁻³)	0.875 and –0.913

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|.$$

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Appendix A. Supplementary material

CCDC 718699 contains the supplementary crystallographic data for 2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.03.020](https://doi.org/10.1016/j.jorganchem.2009.03.020).

References

- [1] H. Chen, S. Schlecht, T.C. Semple, J.F. Hartwig, *Science* 5460 (2000) 1995–1997.
- [2] J.F. Hartwig, K.S. Cook, M. Hapke, C.D. Incarvito, Y. Fan, C.E. Webster, M.B. Hall, *J. Am. Chem. Soc.* 8 (2005) 2538–2552.
- [3] N. Miyaoura, in: A. Togni, H. Grützmaier (Eds.), *Catalytic Heterofunctionalization*, Wiley-VCH, Weinheim, Germany, 2001, pp. 1–45.
- [4] C.E. Anderson, H. Braunschweig, R.D. Dewhurst, *Organometallics* 24 (2008) 6381–6389.
- [5] V. Pons, R.T. Baker, *Angew. Chem., Int. Ed.* 50 (2008) 9600–9602.
- [6] F.H. Stephens, V. Pons, R.T. Baker, *Dalton Trans.* 25 (2007) 2613–2626.
- [7] T.B. Marder, Z. Lin, *Contemporary Metal Boron Chemistry I. Borylenes, Boryls, Borane s-Complexes, and Borohydrides*, vol. 130, Springer, Berlin/Heidelberg, 2008, p. 218.
- [8] N. Blaquiére, S. Diallo-Garcia, S.I. Gorelsky, D.A. Black, K. Fagnou, *J. Am. Chem. Soc.* 43 (2008) 14034–14035.
- [9] M.C. Denney, V. Pons, T.J. Hebdén, D.M. Heinekey, K.I. Goldberg, *J. Am. Chem. Soc.* 37 (2006) 12048–12049.
- [10] C.W. Hamilton, R.T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* 1 (2009) 279–293.
- [11] R.J. Keaton, J.M. Blacquiére, R.T. Baker, *J. Am. Chem. Soc.* 7 (2007) 1844–1845.
- [12] H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem., Int. Ed.* 32 (2006) 5254–5274.
- [13] 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, L.J. Wright, *Chem. Rev.* 8 (1998) 2685–2722.
- [14] J.F. Hartwig, C.N. Muhoro, X. He, O. Eisenstein, R. Bosque, F. Maseras, *J. Am. Chem. Soc.* 44 (1996) 10936–10937.
- [15] G. Alcaraz, S. Sabo-Etienne, *Coord. Chem. Rev.* 21–22 (2008) 2395–2409.
- [16] M.V. Campian, E. Clot, O. Eisenstein, U. Helmstedt, N. Jasim, R.N. Perutz, A.C. Whitwood, D. Williamson, *J. Am. Chem. Soc.* 13 (2008) 4375–4385.
- [17] G.J. Kubas, *Metal Dihydrogen and Sigma-Bond Complexes*, Kluwer Academic/Plenum Publishers, New York, 2001, p. 444.
- [18] G.J. Kubas, *Chem. Rev.* 10 (2007) 4152–4205.
- [19] R.N. Perutz, S. Sabo-Etienne, *Angew. Chem., Int. Ed.* 15 (2007) 2578–2592.
- [20] K. Essalah, J.-C. Barthelat, V. Montiel, S. Lachaize, B. Donnadieu, B. Chaudret, S. Sabo-Etienne, *J. Organomet. Chem.* 1–2 (2003) 182–187.
- [21] S. Lachaize, K. Essalah, V. Montiel-Palma, L. Vendier, B. Chaudret, J.C. Barthelat, S. Sabo-Etienne, *Organometallics* 12 (2005) 2935–2943.
- [22] V. Montiel-Palma, M. Lumbierres, B. Donnadieu, S. Sabo-Etienne, B. Chaudret, *J. Am. Chem. Soc.* 20 (2002) 5624–5625.
- [23] G. Alcaraz, E. Clot, U. Helmstedt, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* 28 (2007) 8704–8705.
- [24] G. Alcaraz, U. Helmstedt, E. Clot, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* 39 (2008) 12878–12879.
- [25] K.D. Hesp, M.A. Rankin, R. McDonald, M. Stradiotto, *Inorg. Chem.* 17 (2008) 7471–7473.
- [26] U. Flierler, M. Burzler, D. Leusser, J. Henn, H. Ott, H. Braunschweig, D. Stalke, *Angew. Chem., Int. Ed.* 23 (2008) 4321–4325.
- [27] H.N. Ralf Littger, *Eur. J. Inorg. Chem.* 7 (2000) 1571–1579.
- [28] M.G. Crestani, M. Munoz-Hernandez, A. Arevalo, A. Acosta-Ramirez, J.J. Garcia, *J. Am. Chem. Soc.* 51 (2005) 18066–18073.
- [29] S. Schlecht, J.F. Hartwig, *J. Am. Chem. Soc.* 39 (2000) 9435–9443.
- [30] M. Srebnik, T.E. Cole, P.V. Ramachandran, H.C. Brown, *J. Org. Chem.* 26 (1989) 6085–6096.
- [31] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* 3 (1993) 343–350.
- [32] G.M. Sheldrick, SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] – Programs for Crystal Structure Analysis (Release 97-2), Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- [33] L.J. Farrugia, *J. Appl. Crystallogr.* 4 (1999) 837–838.
- [34] A.J.C. Wilson (Ed.), *International Tables Vol. C Tables 4.2.6.8 and 6.1.1.4*, International Tables for Crystallography, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995.