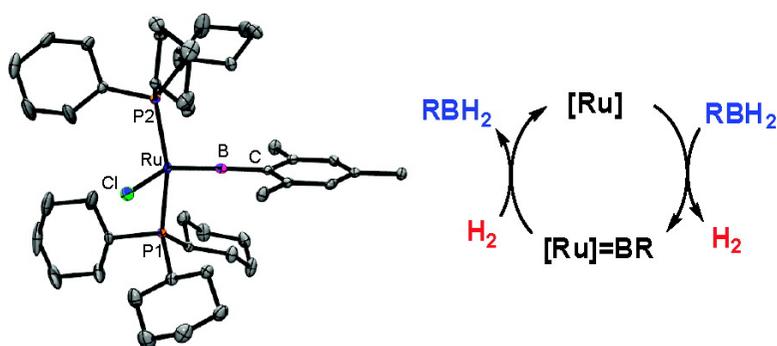


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## A Terminal Borylene Ruthenium Complex: From B–H Activation to Reversible Hydrogen Release

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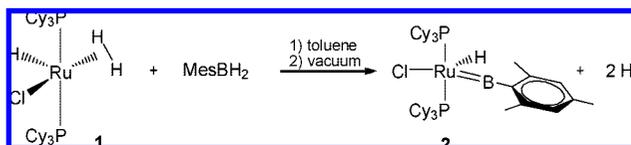
Since the first structurally characterized terminal borylene complex reported in 1998,<sup>1</sup> important findings have been regularly disclosed concerning the chemistry of metal–boron double bond complexes.<sup>2–6</sup> With a stabilized B–R unit (R = amino, alkyl, aryl, silyl, metal fragment) in the coordination sphere of the metal, this class of complexes of general formulation  $L_nM=B-R$  is mostly limited to early transition metals (V, Cr, Mo, W) and Mn for neutral complexes. Four additional examples with late transition metals (Fe, Pt, and Ir) are reported so far.<sup>7–10</sup> Their reactivity is dominated by addition of metal bases, borylene transfer, metathesis, and insertion reactions. The lack of simple and viable synthetic approaches still hampers their promising development, the syntheses being restricted to salt elimination from suitable dihaloboranes and homoleptic carbonylmetallates, photoinduced intermetallic borylene transfer, phosphine-induced cleavage of a bimetallic bridged borylene complex, and halogen abstraction from B-halogenoboryl complexes in the case of terminal cationic borylene complexes.<sup>6,11</sup>

As part of our broad program on the chemistry of  $\sigma$ -complexes and more particularly on  $\sigma$ -borane complexes,<sup>12,13</sup> we have recently reported the isolation of the ruthenium complex  $RuH_2(\eta^2:\eta^2-H_2BMe_s)(PCy_3)_2$  in which mesitylborane is coordinated to the metal through two geminal  $\sigma$ -B–H bonds.<sup>14</sup> Here we report the reaction of mesitylborane with a chlorohydrido(dihydrogen) ruthenium complex leading to the isolation of the first terminal borylene ruthenium complex that can serve as a model for reversible dihydrogen storage.<sup>15</sup>

Reaction of  $RuHCl(H_2)(PCy_3)_2$  (**1**) in toluene with 1.5 equiv of mesitylborane is carried out at room temperature. After evaporation of the solvent under vacuum and workup, a yellow powder analyzed as  $RuHCl(BMes)(PCy_3)_2$  (**2**) was isolated (80% yield) (scheme 1) and fully characterized by NMR and X-ray diffraction crystallography.<sup>16</sup>

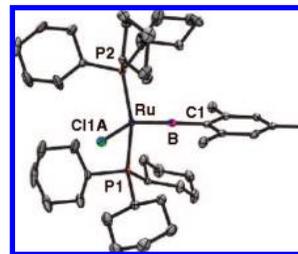
The  $^{11}B\{^1H\}$  NMR spectrum shows a broad signal centered at  $\delta$  106.0 in a region characteristic of two-coordinated boron atom<sup>2,6</sup> and strongly downfield of that of mesitylborane dimer. The  $^1H$  NMR spectrum exhibits in the hydride region a well-resolved triplet at  $\delta$  –14.88 ( $J_{PH} = 18.1$  Hz) that collapsed into a singlet upon phosphorus decoupling. Boron decoupling experiments confirm that the hydride is not coupled to the boron (Figure S1). The mesityl group exhibits five sharp signals, two for the aryl protons and three for the methyl groups, respectively, clearly indicating hindered rotation around the B–C<sub>ipso</sub> bond. The 1:1:1 integration ratio for the hydride triplet and the two nonequivalent aromatic CH protons are in agreement with a species bearing one mesityl group and one hydride around the ruthenium center.

### Scheme 1. Synthesis of the Borylene Complex 2



The X-ray structure of **2** was determined at 110 K (Figure 1). The Ru atom is in a distorted trigonal bipyramid environment with the phosphines in axial positions (P1–Ru–P2 164.44(3) Å). The coordination sites in the equatorial plane are occupied by the boron and the chlorine atoms, whereas the hydride could not be located as a result of some disorder. The boron atom is two-coordinated and linearly bound to its neighboring Ru and C atoms (Ru–B–C1 178.1(3) Å). The Ru–B distance of 1.780(4) Å is among the shortest metal–B bonds ever reported, 7 pm shorter than the Pt–B bond in the terminal mesityl cationic platinum complex (1.859(3) Å)<sup>9</sup> but comparable to the metal–B bonds in cationic mesityl iron (1.792(8) Å)<sup>7</sup> and neutral *tert*-butyl manganese borylene complexes (1.809(9) Å), respectively.<sup>11</sup>

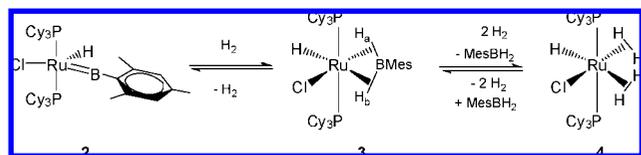
Electron-deficient  $d^6$  *trans*-ML<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub> complexes are known to be stabilized by  $\pi$ -donating ligands, and depending on the donor abilities of the ligands, the complexes have either a square-pyramidal (T-shaped) or a distorted trigonal bipyramidal (Y-shaped) geometry.<sup>17</sup> If BMes is considered as a neutral ligand, it is formally equivalent to CO with two  $\pi$ -accepting orbitals and a T-shaped structure would be expected as in  $RuHCl(CO)(PCy_3)_2$  which exhibits a T-shaped geometry with *trans* Cl and CO, the hydride being *trans* to the vacant site.<sup>18</sup> But, even though the hydride position was not refined in **2**, the X-ray structure clearly indicates that the  $\pi$ -donor Cl and the  $\pi$ -acceptor BMes are not mutually *trans* and the geometry is better defined as a pseudo Y-shaped structure. To shed more light on this special feature and to securely locate the hydride, ONIOM (B3PW91/UFF) calculations have been performed on **2** (see Supporting Information (SI) for Computational Details). Two different isomers, **2Y** and **2T**, were optimized



**Figure 1.** X-ray crystal structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ru–B 1.780(4), B–C1 1.558(5), B–Ru–Cl(1A) 113.76(12), Ru–B–C1 178.1(3), P1–Ru–P2 164.44(3).

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**Scheme 2.** Reaction of the Borylene Complex **2** with H<sub>2</sub>

(Figure S2). B3PW91 single-point calculations on the ONIOM geometries resulted in **2Y** being 41.6 kJ mol<sup>-1</sup> more stable than **2T**. There is thus a clear energetic preference for **2Y**. Even though the geometry of **2Y** is in better agreement with experiment than that of **2T** (Table S1), there is a close contact between the hydride and the boron (1.548 Å, Figure S2) that could cast some doubt on the description of **2** as a true borylene. The isomer **2Y** was thus optimized at the B3PW91 level to check if the close contact pertained. At this better level of theory, the geometry obtained for **2Y-DFT** is in very good agreement with experiment (Ru–B = 1.793 Å (1.780(4) Å), Ru–B–Cl = 177.7° (178.1(3)°), B–Ru–Cl = 127.3° (113.76-(12)°), **2Y-DFT** (2-X-ray)),<sup>19</sup> and there is no direct contact between the hydride ligand and the boron (H···B = 2.142 Å, Figure S3).

To further confirm the borylene nature of **2**, an NBO analysis of the electronic structure of **2Y-DFT** was carried out. If the phosphine ligands define the *z* axis and Ru–B defines the *x* axis, then back-donation from Ru is expected from d<sub>xz</sub> and d<sub>xy</sub> (see Table S2 in the SI for composition of selected NLMO for **2Y-DFT**). The NBO procedure yielded three lone pairs on Ru as expected for a d<sup>6</sup> Ru<sup>II</sup> complex. This agrees with the idea that the BMes ligand is a neutral L-ligand with two π-accepting orbitals. In **2Y-DFT** back-donation contributions from d<sub>xy</sub> and d<sub>xz</sub> are similar as illustrated by the magnitude of the B content in the NLMO (12.5%). The BMes ligand thus behaves similarly to CO in such a geometry. The preference for a Y-shaped geometry in **2** results probably from similar σ-donating influences for hydride and borylene. Interestingly, there is some participation of B (5.3%) in the σ(Ru–H) NLMO even though the hydride boron distance is long. Finally, the Wiberg bond indices around Ru in **2Y-DFT** confirm the description of **2** as a true borylene complex (Ru–B, 1.49; Ru–H, 0.58; Ru–Cl, 0.30; Ru–P, 0.46).

Pressurization of a C<sub>6</sub>D<sub>6</sub> solution of **2** with dihydrogen (3 bar) at room temperature leads to the complete disappearance of the ruthenium borylene signal as monitored by <sup>31</sup>P{<sup>1</sup>H} NMR. The formation of two new complexes **3** and **4** in variable ratio exhibiting a resonance signal at δ 59.1 and 53.7, respectively, was observed (Scheme 2).

Interestingly, after drying the mixture of **3** and **4** under vacuum, the resulting solid was characterized as the borylene complex **2**. Such a process could be repeated several times by successive H<sub>2</sub> pressurization (3 bar in C<sub>6</sub>D<sub>6</sub> solution)/vacuum cycles. Complex **4** was identified as RuHCl(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> on the basis of multinuclear NMR data by comparison to an authentic sample prepared from direct reaction of **1** with H<sub>2</sub>.<sup>20</sup> In solution, an equilibrium is established as a result of mesitylborane/dihydrogen exchange. The intermediate complex **3** can be described as a mesitylborane adduct onto a RuHCl(PCy<sub>3</sub>)<sub>2</sub> fragment on the basis of NMR data.<sup>21</sup> Two different B–H bond activation levels are observed as a result of two different *trans* ligands (H vs Cl). The hydrogen transfer process with release of mesitylborane was ascertained by trapping it as a pyridine adduct. Indeed, reaction of **2** with pyridine under a dihydrogen atmosphere led to the mesitylborane–pyridine adduct fully characterized by NMR spectroscopy.<sup>22</sup>

In conclusion, complex **2** is the first borylene ruthenium complex synthesized by simple addition of a dihydrogenoborane and

concomitant evolution of dihydrogen. Remarkably, the dihydrogen release can be reversed. In view of these preliminary results, one can expect a versatile reactivity from this new borylene at ruthenium by analogy to the tremendous development of carbene ruthenium chemistry.<sup>23,24</sup>

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**Supporting Information Available:** X-ray crystallographic files for **2** (CIF), NMR spectra, computational details, Cartesian coordinates for the calculated structures. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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- A toluene solution (2 mL) of MesBH<sub>2</sub> (17 mg, 0.129 mmol) was added to a toluene solution (2 mL) of **1** (59 mg, 0.084 mmol) and stirred at room temperature for 17 h. After removal of the solvent and drying under vacuum, pentane was added and the precipitate was separated from the supernatant and dried under vacuum leading to **2** (53 mg, 80%). Selected NMR (C<sub>6</sub>D<sub>6</sub>) data for **2**: <sup>1</sup>H NMR (298 K, 400.13 MHz) δ: –14.88 (t, 1H, <sup>2</sup>J<sub>PH</sub> = 18.1 Hz, RuH), 1.11–2.48 (m, 66H, Cy), 1.98 (s, 3H, *p*-CH<sub>3</sub> Mes), 2.83 and 3.19 (2×s, 2×3H, *o*-CH<sub>3</sub> Mes), 6.62 and 6.68 (2×s, 2×1H, CH Mes). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, 161.975 MHz) δ: 50.75 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (298 K, 128.377 MHz) δ: 106.0 (bs).
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- NMR data are in full agreement with those obtained for an authentic sample prepared separately from a stoichiometric amount of mesitylborane and pyridine. NMR (C<sub>6</sub>D<sub>6</sub>) data: <sup>1</sup>H NMR (298 K, 400.13 MHz) δ: 2.37 (s, 3H, *p*-CH<sub>3</sub> Mes), 2.62 (s, 6H, *o*-CH<sub>3</sub> Mes), 4.25 (bs, 2H, BH<sub>2</sub>), 6.12 and 8.08 (2×m, 2×2H, CH pyridine), 6.50 (m, 1H, CH pyridine), 7.10 (s, 2H, CH Mes). <sup>11</sup>B{<sup>1</sup>H} NMR (298 K, 128.38 MHz) δ: –6.7 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, 100.61 MHz) δ: 21.77 (*p*-CH<sub>3</sub> Mes), 24.37 (*o*-CH<sub>3</sub> Mes), 125.00, 128.91, 138.30, 135.66, 146.91, 143.79 (CH and C, Mes + py).
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