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Maxime Boudjelel, Sonia Mallet-Ladeira, Ghenwa Bouhadir, Didier Bourissou. Strong metal-borane interactions in low-valent cyclopentadienyl Rhodium complexes. *Chemical Communications*, 2019, 55 (85), pp.12837-12840. 10.1039/C9CC06639J . hal-02398800

HAL Id: hal-02398800

<https://hal.science/hal-02398800>

Submitted on 8 Dec 2019

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Strong metal-borane interactions in low-valent cyclopentadienyl Rhodium complexes

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ABSTRACT. The first examples of half-sandwich Rh(I) complexes stabilized by borane coordination have been prepared and structurally characterized. As substantiated by NMR spectroscopy and single-crystal x-ray diffraction, the phosphine-borane ligand *i*Pr₂P-(*o*-C₆H₄)-BFxyl₂ **1** [Fxyl = 3,5-(F₃C)₂C₆H₃] engages in tight η³-BCC or η¹-B coordination, depending on the metal environment.

Transition metal complexes featuring Lewis acid ligands have garnered considerable interest over the last two decades. Initially considered as a chemical curiosity, the ability of Lewis acids to behave as σ-acceptor (Z-type) ligands has in fact proven quite general.¹ Besides the fundamental interest associated with TM→LA interactions,² Lewis acid ligands open a new way to modulate the properties and reactivity of metal complexes.³

Low-valent electron-rich metal fragments are particularly well-suited partners for Lewis acids.¹⁻⁴ In this context, we report here the first example of metal→borane interactions in low-valent half-sandwich Rh complexes. Phosphine cyclopentadienyl (Cp) Rh(I) complexes are known to be highly reactive and their faculty to activate a variety of σ-bonds has been extensively investigated.⁵⁻⁷ Due to their strong Lewis basic character, [(Cp)Rh] fragments readily engage into TM→LA interactions with heavier group 13 elements. The first such Al and Ga compounds **A** and **B** were reported by Mayer and Fisher, respectively (Chart 1).⁸ Recently (Cp)L₂Rh→AlX₃ complexes **C** (L = PMe₃) were also obtained by Braunschweig using transmetalation or disproportionation reactions.⁹ In addition, Rivard showed that heavier group 14 Lewis acids such as PbCl₂ can form similar donor-acceptor adducts **D**.¹⁰ However, to the best of our knowledge, no related complex has been described so far with boron-based Lewis acids. Conversely, B(Fxyl)₃ [Fxyl = 3,5-(F₃C)₂C₆H₃] was found to react at the Cp ring to give the zwitterionic Rh(III) hydride species **E**.¹⁰

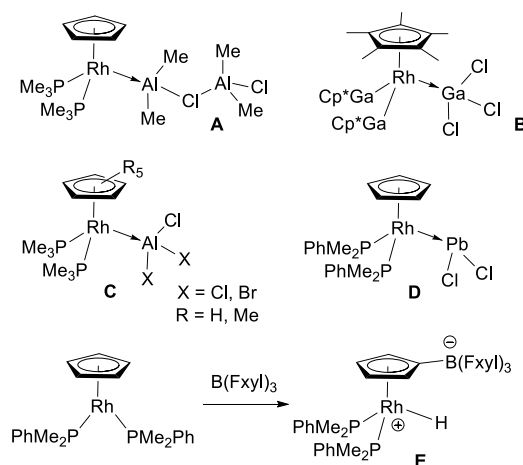


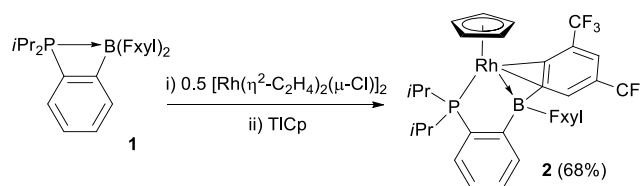
Chart 1 Low-valent cyclopentadienyl rhodium complexes stabilised by Rh→LA interactions.

Because of their chelating character and modulable structure, ambiphilic phosphine-boranes are particularly efficient in supporting M→B interactions.¹¹ In this context, we took advantage here of the phosphine-borane *i*Pr₂P-(*o*-C₆H₄)-BFxyl₂ **1**. As shown in our previous work,¹² compound **1** adopts a closed structure with strong but geometrically constrained P→B interaction. As a result, it behaves as a dormant Lewis pair and proved to efficiently catalyse the dehydrogenation of a variety of amine and diamine-boranes under mild conditions. Here, (Cp)Rh complexes of **1** have been investigated and the borane moiety was found to engage in η³-BCC and η¹-B coordination, as substantiated by NMR and X-ray diffraction analyses.

The direct coordination of **1** to the [(Cp)Rh] fragment was first attempted by reacting it with the ethylene precursor [(η⁵-Cp)Rh(η²-C₂H₄)₂] in refluxing toluene. The solution turns progressively dark purple but the displacement of ethylene at Rh by the phosphine-borane was very slow (it is incomplete even after 10 days) and not

clean, several side-products being formed concomitantly. The desired complex **2** was obtained much more efficiently *via* a two-step procedure (Scheme 1).¹³ The (P,B) ligand **1** was first treated with the dimeric Cl-bridged Rh precursor $[\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2(\mu\text{-Cl})_2]$ in toluene. Within a few hours at room temperature, the mixture takes a blood red color. One equivalent of TICp was added afterwards. The solution rapidly turned dark purple and TICl crashed out of solution. $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring revealed a complete and clean reaction within 4 hours of time. According to High Resolution Mass Spectrometry (HRMS) ($m/z = 798.0980$), the formed complex **2** results from the coordination of the phosphine-borane **1** to the $[(\text{Cp})\text{Rh}]$ fragment. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a doublet signal at $\delta 79.6$ ppm with a diagnostic $^1J_{\text{PRh}}$ coupling constant (173 Hz). No ^{11}B NMR signal could be resolved, but the participation of the $\text{B}(\text{FxyI})_2$ moiety in the coordination was clearly apparent from the loss of symmetry of the Fxyl groups observed in the ^{19}F , ^1H and ^{13}C NMR spectra. The ^{19}F NMR spectrum displays three CF_3 signals of relative integrations 1:1:2 at $\delta -64.20$, -63.99 and -63.06 ppm indicating that the two aryl groups are not interchanging and that only one freely rotates. One of the *ortho* C–H group of the desymmetrized Fxyl group displays very shielded ^1H and ^{13}C NMR signals ($\delta 3.53$ and 61.43 ppm, respectively), as deduced from HSQC $^{19}\text{F}/^{13}\text{C}$ and HSQC $^1\text{H}/^{13}\text{C}$ experiments.¹³ These features suggest that one of the Fxyl group is engaged in direct unsymmetric coordination to Rh.

Crystals of **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of a concentrated pentane solution at room temperature. The complex adopts a piano-stool structure (Fig. 1). Besides phosphorus, the phosphine-borane **1** binds to Rh *via* the boron center and one of the Fxyl ring resulting in tight η^3 -BCC coordination.¹⁴ The Rh–B distance is short at $2.409(4)$ Å and falls in the same range than those we observed in square-pyramidal diphosphine-borane Rh(I) complexes.¹⁵ Consistently, the boron environment is pyramidalized (the sum of C–B–C bond angles $\Sigma\alpha\text{B}$ is 353.6°). The *ipso* carbon atom and one of the *ortho* carbon atoms of a Fxyl group also show short contacts to Rh at $2.191(4)$ and $2.255(4)$ Å, respectively. Most noticeable is the pyramidalization of the respective C_{ortho} atom (H_{ortho} deviates out of the Fxyl plane by 0.333 Å)¹⁶ and the partial dearomatization of the Fxyl ring (as apparent from the alternation of short and long CC bonds).¹⁷



Scheme 1 Synthesis of the (Cp)Rh(P,B) complex **2**.

The highly Lewis acidic BFxyl_2 moiety of **1** is thus engaged in tight η^3 -BCC coordination, providing thermodynamic and kinetic stability to the low-valent $[(\text{Cp})\text{Rh}(\text{P,B})]$ complex **2**. Of note, Emslie and co-workers previously reported η^3 -BCC coordination of a BPh moiety to Rh in the heterobimetallic complex $[(\text{TXPB})\text{Rh}(\mu\text{-CO})_2\text{Fe}(\text{CO})\text{Cp}]$, where TXPB is a rigid phosphine-borane derived from thioxanthene.¹⁸ The found Rh–B, Rh– C_{ipso} and Rh– C_{ortho} distances [$2.63(2)$, $2.33(2)$ and $2.46(2)$ Å, respectively] are all substantially longer than in **2**, indicating weaker coordination of the B–aryl moiety. The difference between the two systems is also apparent in solution by NMR. In the $[(\text{TXPB})\text{Rh}(\mu\text{-CO})_2\text{Fe}(\text{CO})\text{Cp}]$ complex, broad signals were observed at room temperature for the BPh_2 moiety due to fluxional behavior.¹⁹ High-field ^1H NMR signals diagnostic of aryl coordination and loss of symmetry were observed at low temperature (-75°C). In contrast, complex **2** adopts an unsymmetric frozen structure at room temperature and according to variable-temperature ^{19}F NMR experiments upon heating,¹³ the two CF_3 signals of the coordinated Fxyl group coalesce only at *ca* 80°C . The activation barrier of this process, which may involve the slippage of the Fxyl ring or rotation around the B– C_{ipso} bond, was estimated to 18.0 kcal/mol.¹³ Note that the two Fxyl groups remain inequivalent up to the highest accessible temperature, *ie* 100°C .

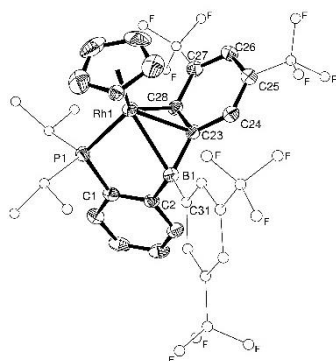
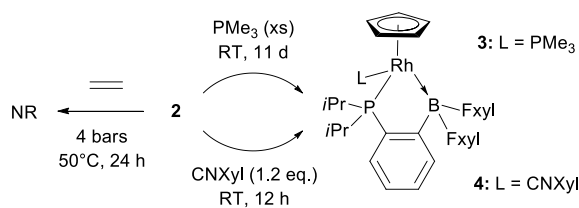


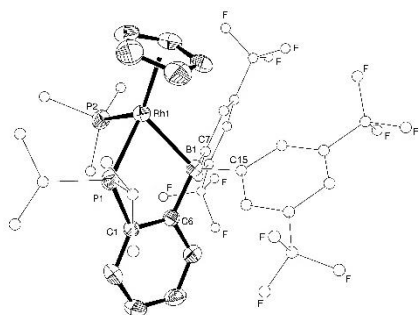
Fig 1 Molecular structure **2** as determined by X-Ray diffraction analysis. Ellipsoids are shown at 50% probability; *i*Pr and free Fxyl are simplified, and H atoms omitted for clarity. Selected bond distances (Å) and angles (°): P1–Rh1 2.282(1), Rh1–B1 2.409(4), Rh1–C23 2.191(4), Rh1–C28 2.255(4), C23–C28 1.439(6), C28–C27 1.450(5), C27–C26 1.355(5), C26–C25 1.420(6), C25–C24 1.359(5), C24–C23 1.440(5), C2–B1–C31 117.3(3), C31–B1–C23 120.3(3), C23–B1–C2 116.0(3).

The possibility to displace the Fxyl group from Rh and to shift the coordination mode of the borane moiety from η^3 -BCC to η^1 -B was then investigated. To this end, complex **2** was reacted with donor ligands, *ie* an alkene, a phosphine and an isonitrile (Scheme 2). Complex **2** proved completely inert towards ethylene, even after prolonged heating under pressure (4 bars, 50°C, 24 hours). With PMe_3 , some reaction occurred, but ^{31}P NMR monitoring showed very slow conversion of **2**. Using a large excess of phosphine, the formation of the $[(\text{Cp})(\text{Me}_3\text{P})\text{Rh}(\text{P},\text{B})]$ complex **3** reached completion after 11 days at room temperature. Comparatively, the reaction of **2** with CNXyl [Xyl = 2,6-(H_3C) $_2\text{C}_6\text{H}_3$] was much faster and the ensuing complex **4** was obtained in high yield (85%) within 12 hours using only a slight excess of isonitrile.²⁰ The $^{31}\text{P}\{^1\text{H}\}$ NMR signature of complex **3** is characteristic with two doublets of doublets at δ –2.45 and 81.22 ppm featuring large $^1J_{\text{PRh}}$ couplings (170 and 180 Hz, respectively) as well as $^2J_{\text{PP}}$ coupling (50.3 Hz). Complex **4** gives a doublet at δ 84.5 ppm ($^1J_{\text{PRh}}$ 170 Hz), very similar to that of **2**. Distinct ^{11}B NMR signals were observed for complexes **3** and **4** at δ 4.6 and 8.8 ppm, respectively. Combined with the inequivalence and free rotation of the two Fxyl groups (as apparent from the ^{19}F , ^1H and ^{13}C NMR spectra), this is indicative of η^1 -coordination *via* Rh→B interaction of the borane moiety. The NC stretch of the isonitrile in complex **4** (2119 cm^{-1}) is very close to that of free XylNC (2122 cm^{-1}).

To further analyse the bonding situation in **3** and **4**, single crystals were grown and X-ray diffraction studies were performed (Figure 2). Both complexes adopt piano-stool structures with P→Rh→B bridging coordination of the ambiphilic ligand. Upon coordination of PMe_3 and CNXyl to Rh, the borane shifts from η^3 -BCC to η^1 -B coordination. This is accompanied by some shortening of the Rh–B distance [from 2.409(4) Å in **2**, to 2.377(3) and 2.349(3) Å in **3** and **4**, respectively] and further pyramidalization of the boron environment ($\Sigma\alpha\text{B} = 353.6^\circ$ in **2** vs 332.0 and 333.0° in **3** and **4**, respectively). Conversely, the P–Rh–B bite angle remains almost unchanged upon binding of the additional donor ligand to Rh [77.2(1)° in **2** vs 80.90(9) and 79.83(6) in **3** and **4**, respectively].



Scheme 2 Synthesis of the $[(\text{Cp})\text{LRh}(\text{P},\text{B})]$ complexes **3** and **4** (Xyl = 2,6-(H_3C) $_2\text{C}_6\text{H}_3$).



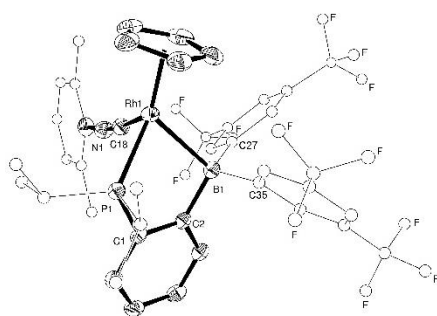
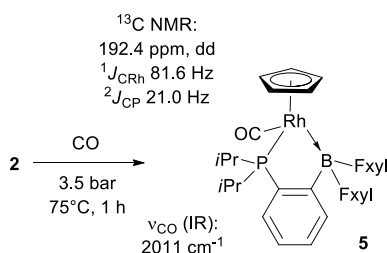


Fig 2 Molecular structure **3** (top) and **4** (bottom) as determined by X-Ray diffraction analysis. Ellipsoids are shown at 50% probability; *i*Pr, Fxyl and Xyl are simplified, and H atoms omitted for clarity. Selected bond distances (Å) and angles (°). **3**: P1–Rh1 2.254(1), Rh1–P2 2.266(1), Rh1–B1 2.377(3), C6–B1–C7 114.0(3), C7–B1–C15 111.1(3), C15–B1–C6 106.9(3). **4**: P1–Rh1 2.272(1), Rh1–B1 2.349(3), Rh1–C18 1.893(2), C2–B1–C27 113.4(2), C27–B1–C35 110.6(2), C35–B1–C2 109.0(2).

Finally, to assess the withdrawing effect of the Rh→B interaction, we studied the reaction of **2** with CO with the aim to obtain the [(Cp)(OC)Rh(P,B)] complex **5** (Scheme 3). According to $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the reaction was slow at room temperature but proceeded readily at 75°C under 3.5 bars of pressure. The NMR features of the (P,B) ligand in **5** (^{31}P : δ 84.5 ppm, doublet, $^1J_{\text{PRh}} = 173$ Hz; ^{11}B : δ 14.0 ppm; symmetry of the Fxyl groups in ^{19}F , ^1H and ^{13}C) are indicative of P→Rh→B bridging coordination, by analogy to complexes **3** and **4**. In addition, the ^{13}C NMR signal observed at δ 192.4 ppm (doublet of doublet due to $^1J_{\text{CRh}}$ and $^2J_{\text{CP}}$ couplings of 81.6 and 21.0 Hz, respectively) is diagnostic for the coordination of CO to Rh. The $\nu(\text{CO})$ stretching frequency of complex **5** is found at 2011 cm^{-1} in the infrared spectrum, shifted to higher wavenumbers by as much as 50–100 cm^{-1} compared to those of related Rh complexes free of borane.^{21,22} In line with relatively strong Rh→B interaction, the highly Lewis acidic BFxyl₂ borane thus depletes electron density from Rh in complex **5** and thereby significantly weakens the Rh→CO backdonation.



Scheme 3 Synthesis and key spectroscopic data of the [(Cp)(OC)Rh(P,B)] complex **5**.

In summary, the first examples of low-valent half-sandwich Rh complexes stabilized by borane coordination have been prepared and structurally characterized. The phosphine-borane ligand **1** is able to stabilize both [(Cp)Rh] and [Cp(L)Rh] fragments thanks to the faculty of the BFxyl₂ moiety to shift from η^3 -BCC to η^1 -B coordination. Shifts in the coordination mode of aryl-boranes to transition metals are very rare. Of note, Cowie and Emslie recently evidenced exchanges between η^3 -BCC, η^2 -BC and η^1 -B coordination in platinum(0) complexes of a BPh₂-appended diphosphine.²³ The fact that *i*Pr₂P-(*o*-C₆H₄)-BFxyl₂ displays such flexibility in complexes **2–5**, despite the tight η^3 -BCC and η^1 -B coordination to Rh, is noteworthy.

The unique properties of the Fxyl group²⁴ make phosphine-boranes such as **1** very appealing ambiphilic ligands. Future work in our group will aim to develop further this chemistry, in particular reactivity and catalysis involving M→B cooperation.³

Financial support from the Centre National de la Recherche Scientifique and the Université de Toulouse is acknowledged.

We thank Pierre Lavedan (ICT, Toulouse) for helpful assistance with the HSQC { ^{13}C ; ^{19}F } and variable temperature NMR experiments.

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