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A Ru−η^6-Arene Complex as a C-Based Lewis Acid in the Activation of Hydrogen and Hydrogenation Catalysis

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S Supporting Information

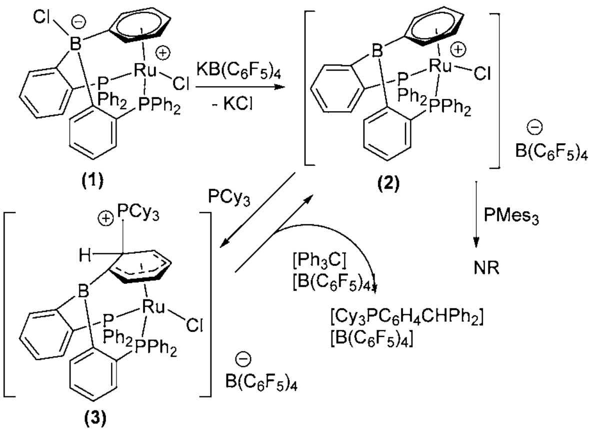
ABSTRACT: The PBP ligand $(Ph_2PC_6H_4)_2BPh$ was used to prepare $((Ph_2PC_6H_4)_2B(Cl)(\eta^6\text{-}Ph)RuCl$ (**1**) and subsequently $[((Ph_2PC_6H_4)_2B(\eta^6\text{-}Ph))RuCl][B(C_6F_5)_4]$ (**2**). The latter species exhibited Lewis acidity on the η^6-Ph ring, as reaction with Cy_3P gave the donor−acceptor adduct $[(Ph_2PC_6H_4)_2B(\eta^5\text{-}C_6H_5\text{-}o\text{-}PCy_3)RuCl][B(C_6F_5)_4]$ (**3**). Steric frustration of this binding was seen with Mes_3P, and yet the combination of **2** and Mes_3P reacted with H_2 to give a 2:1 mixture of **5-*o*** and **5-*p***, two isomers of $[(Ph_2PC_6H_4)_2B(\eta^5\text{-}C_6H_6)RuCl]$ (**5**), along with $[Mes_3PH][HB(C_6F_5)_3]$. Compound **2** behaves as C-based Lewis acid and thus can also be used for catalytic hydrogenation of aldimines at room temperature via a frustrated Lewis pair mechanism.

The advent of "frustrated Lewis pairs" (FLPs) in 2006 has enabled the heterolytic activation of H_2 by nonmetal systems.[1] Such systems can be exploited to activate H_2 and deliver H^- and H^+ to a substrate, thereby effecting catalytic hydrogenation.[2−9] While much effort has focused on the range of substrates to which this strategy can be applied, the range of Lewis bases and acids used in work to date has largely been limited to group-15 (P, N)/group-13 (B, Al) combinations.[10−16] The use of group-14 species in related chemistry has drawn less attention. In 2007, Bertrand and co-workers[17] reported the reaction of monoamino carbenes with H_2, and computations supported the role of the carbene carbon as both a Lewis acid and a Lewis base. Our group[18] and that of Tamm[19] have described the use of carbenes as Lewis bases in FLP H_2 activation. Efforts to exploit carbon-based Lewis acids have also been described. In a highly creative effort by Alcarazo and co-workers,[20,21] the use of electron-deficient allenes to effect the heterolytic cleavage of disulfides was presented. Although Müller and co-workers[22] reported the activation of H_2 by silylium cation/phosphine combinations, the corresponding reactions of trityl cations with phosphine resulted in phosphine substitution at the aryl carbon para to the central carbon of the cation. In 2011, Arduengo and co-workers[23] reported the activation of H_2 by trityl cation and a bulky di-*tert*-butyl carbene, demonstrating the first example of the use of a C-based Lewis acid for H_2 activation. In this work, we exploited an ancillary metal center to enhance the Lewis acidity of aromatic carbons, generating a C-based Lewis acid that can participate in FLP activation of H_2 as well as act as a C-based hydrogenation catalyst for the reduction of aldimines.

The species $(Ph_2PC_6H_4)_2BPh$ reacted with $(Ph_3P)_3RuCl_2$ in CH_2Cl_2 to give an orange solution that upon isolation yielded the zwitterion $((Ph_2PC_6H_4)_2BCl)(\eta^6\text{-}Ph)RuCl$ (**1**) in 76% yield. The $^{31}P\{^1H\}$ spectrum of **1** displayed a low-field resonance at 26.4 ppm, while the ^{11}B NMR spectrum exhibited a resonance at 1.5 ppm. The ^1H NMR spectrum showed resonances at 6.17, 6.05, and 4.65 ppm, suggesting an arene−metal interaction. The X-ray crystallographic data for **1** confirmed this coordination mode (see the Supporting Information), in which the boron atom adopts a pseudo-tetrahedral geometry and the PBP ligand binds to Ru via the two phosphorus donors and an η^6 interaction of the boron-bound phenyl group. The present binding mode of the PBP ligand in **1** results in a Ru−B distance of 3.221(5) Å. Earlier this year, Peters and co-workers described similar η^6 binding of the B-bound phenyl ring to Fe(0) species.[24] This zwitterionic compound is reminiscent of ambiphilic ligand complexes of Au, Ni, Pd, Pt, and Ru described by the Bourissou[25] and Tilley[26] groups as well as our group.[27] In addition, it is noteworthy that PBP ligands have also been shown by several groups to exhibit z-type binding,[28−39] while related compounds displaying B−H−M interactions for Rh[40] and Ni[41] species have also been observed.

The reaction of **1** with $K[B(C_6F_5)_4]$ resulted in halide abstraction, affording the red product $[((Ph_2PC_6H_4)_2B(\eta^6\text{-}Ph))RuCl][B(C_6F_5)_4]$ (**2**) in 88% yield (Scheme 1). Compound **2** exhibited a $^{31}P\{^1H\}$ resonance at 32.8 ppm and ^{11}B resonances at 48.0 and −16.6 ppm. These data together

Scheme 1. Synthesis and Reactivity of 2 and 3



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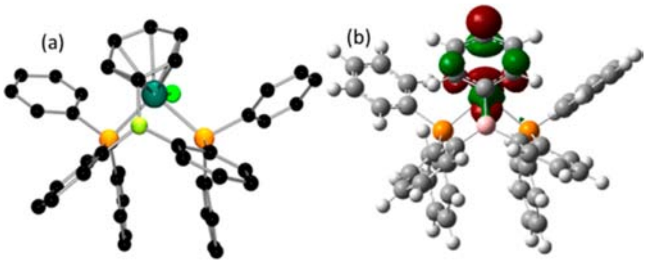


Figure 1. (a) POV-ray depiction of the cation of **2**. H atoms have been omitted for clarity. Atom colors: Ru, teal; P, orange; B, yellow-green; Cl, green; C, black. (b) Depiction of the LUMO of the cation of **2**.

with the X-ray data for **2** (Figure 1a) confirmed the removal of the Cl atom from B of the PBP ligand, resulting in a Ru−B distance of 2.647(2) Å. Despite this approach, the sum of the angles about boron is 360.0°. This Ru−B distance in **2** is longer than the formal Rh−B bond length of 2.306(3) Å reported for $[((Ph_2PC_6H_4)_2BPh)RhCl]_2$.[30]

In stark contrast to the related Ni and Rh species,[34−40] no reaction occurred upon exposure of **2** to H_2. However, compound **2** did react instantaneously with Cy_3P, resulting in a color change. Subsequent workup afforded a yellow crystalline product, $[(Ph_2PC_6H_4)_2B(\eta^5\text{-}C_6H_5\text{-}o\text{-}PCy_3)RuCl][B(C_6F_5)_4]$ (**3**), in 92% yield (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum revealed three doublets of doublets at 40.4 ppm ($^2J_{PP}$ = 25 Hz, $^4J_{PP}$ = 7 Hz), 34.1 ppm ($^2J_{PP}$ = 25 Hz, $^4J_{PP}$ = 9 Hz), and 23.1 ppm ($^4J_{PP}$ = 9 Hz, $^4J_{PP}$ = 7 Hz), consistent with three inequivalent and coupled phosphorus environments. The ^{11}B NMR spectrum showed a resonance at 35.0 ppm, inferring retention of the three-coordinate B center in the ligand backbone. In addition, a resonance appeared at −16.6 ppm, consistent with the presence of the $B(C_6F_5)_4^-$ counteranion. These data and a crystallographic study confirmed that **3** resulted from phosphine attack at a phenyl carbon ortho to boron (Figure 2); quaternization of C2 resulted in typical P−C and C−C single bonds, while the other C−C distances within the B-bound arene ring remained shorter [1.388(4)−1.444(4) Å], consistent with η^5 binding to Ru. Interestingly, the Ru−B bond shortened significantly to 2.509(4) Å, reflecting the increase in electron density at Ru.

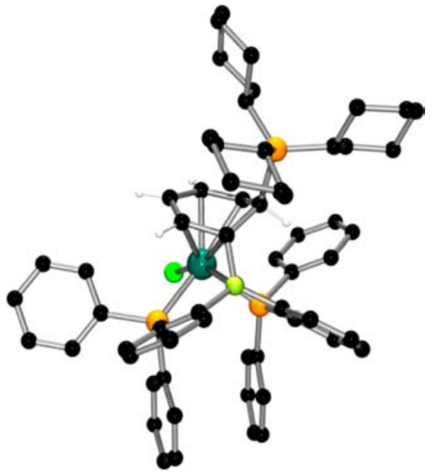
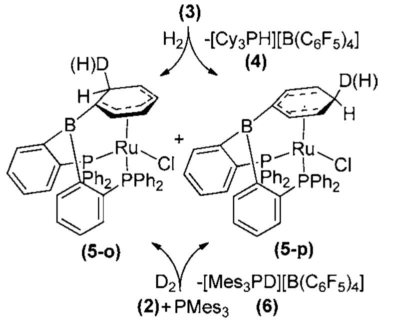


Figure 2. POV-ray depiction of the cation of **3**. H atoms except for those on the η^5-bound arene ring have been omitted for clarity. Atom colors: Ru, teal; P, orange; B, yellow-green; Cl, green; C, black.

The formation of **3** is perhaps surprising in view of the presence of the trigonal-planar boron center in **2**. However, this experimental observation is consistent with the computed lowest unoccupied molecular orbital (LUMO) of **2** (Figure 1b), in which the major components reside on the ortho carbons of the B-bound η^6 phenyl ring, with minor components on the boron and para carbon atoms.

The reaction of **3** with $[Ph_3C][B(C_6F_5)_4]$ resulted in the capture of phosphine, affording the known species $[p\text{-}Cy_3P(C_6H_5)CPh_2][B(C_6F_5)_4]$[42] and regenerating **2**. This finding demonstrates that the formation of the donor−acceptor adduct **3** is reversible, suggesting that an equilibrium governs the formation of **3**. In probing this aspect, **3** was subjected to 4 atm H_2 at 45 °C for 72 h. This resulted in the formation of two new products, **4** and **5** (Scheme 2). The ^{11}B NMR spectrum contained resonances at 34.8 and −16.6 ppm. The latter peak, together with the $^{31}P\{^1H\}$ NMR singlet at 33.5 ppm ($^1J_{PH}$ = 444 Hz) was consistent with the presence of $[Cy_3PH][B(C_6F_5)_4]$ (**4**). In addition, the $^{31}P\{^1H\}$ NMR spectrum also showed doublets at 42.3 ppm ($^2J_{PP}$ = 22 Hz) and 39.3 ppm ($^2J_{PP}$ = 22 Hz) as well as a peak at 50.2 ppm. These data infer heterolytic cleavage of H_2 to afford the cation of **4** and hydride delivery to the arene ring to give the species $[(Ph_2PC_6H_4)_2B(\eta^5\text{-}C_6H_6)RuCl]$ (**5**). The ^1H NMR data revealed the presence of two isomers of **5**. Resonances at 5.20, 5.04, 4.05, 2.59, 1.90, and 1.77 ppm were consistent with hydride addition to one of the ortho carbons to afford **5-*o***, while signals at 3.97, 3.22, 3.01, and 2.70 ppm infer hydride addition at the para position to give **5-p**. Interestingly, the ratio of these two isomers varied with reaction stoichiometry. A 1:1 Ru:P ratio afforded a mixture with **5-*o***:**5-*p*** = 2:1. Altering the initial Ru:P ratio to 1:10 resulted in almost exclusively the **5-*p*** isomer, although in this case the reaction was much slower, taking 1 week at room temperature to go to completion. Monitoring this mixture over time showed no change in this ratio, demonstrating that there is a thermodynamic barrier to interconversion of these isomers.

Scheme 2. Reactions of 3 with H_2 and 2 + $PMes_3$ with D_2



The analogous combination of **2** with the phosphine Mes_3P resulted in no reaction. This FLP reacted upon exposure of the mixture to 4 atm H_2 at room temperature for 4 h. The reaction proceeded in a fashion similar to that for **3**, affording two products: the phosphonium salt $[Mes_3PH][B(C_6F_5)_4]$ (**6**) and a mixture of the Ru complexes **5-*p*** and **5-*o*** in a ratio of 2:1, as identified by NMR data. Exhaustive efforts to grow crystals of **5** were unsuccessful, but exchange of the chloride on Ru in **5-*o*** to bromide via reaction with Me_3SiBr gave crystals of **5-*o*-Br**. X-ray diffraction studies (Figure 3) confirmed the formulation and demonstrated the hydride delivery to the carbon ortho to the planar boron atom. While related complexes in which hydride is

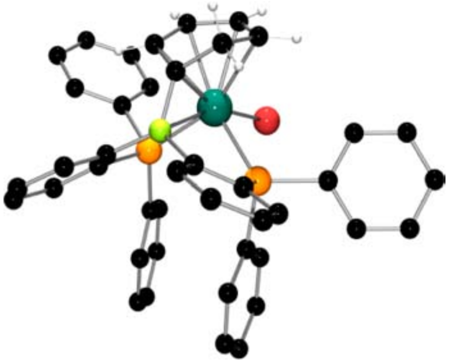
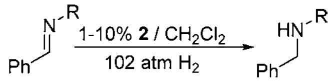
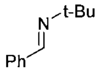
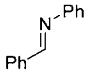


Figure 3. POV-ray depiction of **5-*o*-Br**. H atoms except for those on the η^5-bound arene ring have been omitted for clarity. Atom colors: Ru, teal; P, orange; B, yellow-green; Br, red; C, black; H, white.

Table 1. Hydrogenation of Imines Using 2



Entry	Substrate	mol%	T (°C)	t(h)	% yield[b]
1[a]		10	45	144	99
2		5	25	2	99
3		2.5	25	4	99
4		1	25	8	99
5		5	25	4	99
6		2.5	25	8	97
7		1	25	8	83

[a] 4 atm H_2. [b] NMR yields.

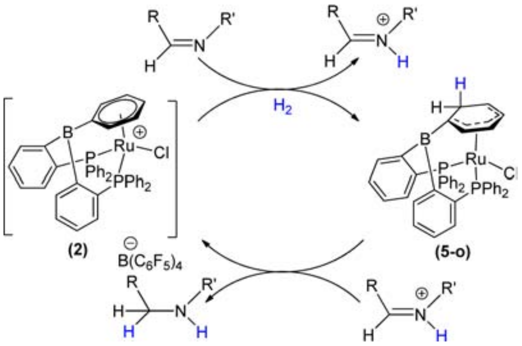
added to an aromatic fragment have been described, such as $[Ru(Me_3tacn)(\eta^6\text{-}C_6H_6)](OTf)_2$,[43] the present reaction represents the first in which such a species is derived from the activation of H_2 and not harsh hydride sources such as $[Li][HBEt_3]$ or $LiAlH_4$.[44−47]

The corresponding reaction of **2** and Mes_3P with D_2 resulted in the formation of the analogous products **5-d_1** and **6-d_1** (Scheme 2). In the case of **5-d_1**, the ^1H, ^2H and correlation spectroscopy (COSY) NMR data confirmed the exclusive formation of the isotopomer in which the deuteride occupies the exo position on the methylene carbon of the six-membered-ring substituent of B that is η^5-bound to Ru. These data are contrary to an intramolecular mechanism involving hydride delivery from Ru. Preliminary kinetic data were found to be consistent with a rate law that is first order in Ru, thus also eliminating a bimolecular mechanism involving hydride delivery from Ru. Thus, this heterolytic cleavage of H_2 is proposed to proceed by the action of the phosphine and the Lewis acidic carbon in an "FLP-type" reaction. While C-based Lewis acids have been described in FLP activations of disulfides and H_2 with the trityl cation or allenes and bulky carbenes, this is the first FLP system to effect H_2 activation by means of an aromatic C-based Lewis acid.

Density functional theory calculations were performed on **5-*o*** and **5-*p***. The energy difference is small, favoring **5-*o*** by only 2.5 kcal/mol. In addition, the energy of $((Ph_2PC_6H_4)_2B(H)(\eta^6\text{-}Ph))RuCl$ (**7**) in which the hydride is located on the boron center was computed, and **7** was found to be ∼18 kcal/mol higher in energy than **5-*o*** or **5-*p***. These data further support the description of **3** as a C-based Lewis acid in which the "ancillary" metal center enhances the Lewis acidity of the aromatic carbons.

Treatment of the mixture of **5-*o*** and **5-*p*** with $[Ph_3C][B(C_6F_5)_4]$ resulted in hydride abstraction from the aromatic ring and regeneration of **2**. This prompted an examination of **5-*o*** and **5-*p*** as hydride sources for the hydrogenation of aldimines. Mixing a stoichiometric amount of **2** with *N*-benzylidene-*tert*-butylamine (PhCH═N*t*Bu) resulted in no reaction. However, exposure of the mixture to H_2 resulted in the formation of **5-*o*** and **5-*p*** along with the amine $PhCH_2NH$*t*Bu. This reduction could also be effected in a catalytic fashion. With 10 mol % **2** under 4 atm H_2, the hydrogenation of PhCH═N*t*Bu was sluggish but reached completion in 144 h at 45 °C (Table 1). Using a higher H_2 pressure (102 atm) and 5 mol % **2** greatly accelerated the reduction of PhCH═N*t*Bu at room temperature, resulting in quantitative reduction to the corresponding amine in 2 h. Reducing the catalyst loading slowed the conversion (Table 1). In a similar fashion, PhCH═NPh was reduced to $PhCH_2NHPh$ under 102 atm H_2 using 5 mol % **2** in 4 h (Table 1). The slower reduction of the latter imine is attributed to its lower basicity. It is noteworthy that NMR spectra of the reaction mixtures following reduction showed evidence of only the products and the species **5-*o***, **5-*p***, and **2**. This is consistent with a proposed FLP-type hydrogenation mechanism in which the imine and **2** act as an FLP to split hydrogen, with subsequent hydride delivery to the generated iminium cation (Scheme 3).

Scheme 3. Proposed Mechanism for the Catalytic Reduction of Imines Using 2 and H_2 (Only the 5-*o* Isomer of the Intemediate Is Shown)



In summary, coordination of an arylborane to Ru and generation of the Ru cation in a coordinatively saturated complex, **2**, that is highly Lewis acidic at the ortho and para carbon centers has been described. The sterically less demanding phosphine PCy_3 reacted with **2** to form the Lewis acid−base adduct **3** via coordination to the ortho carbon; this adduct formation was found to be reversible. Also, **3** reacted further with H_2 to effect heterolytic splitting of H_2. While mixing the bulkier phosphine $PMes_3$ with **2** resulted in no adduct, this combination behaved as an FLP to effect H_2 splitting with hydride delivery to either the ortho or para position of the coordinated arene. This system is a unique example in which an aryl carbon center acts as a Lewis acid in the FLP activation of H_2 and stands in contrast to the mechanism of hydrogenation described for Ni−PBP species.[40] Finally, **2** was used for catalytic hydrogenation of imines under H_2 at room temperature with catalyst loadings as low as 1 mol %. The further reactivity of such unusual systems in which metals act as ancillary groups to enhance Lewis acidity are currently the subject of ongoing studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic, spectroscopic, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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