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Bifunctional Ruthenium(II) Hydride Complexes with Pendant Strong Lewis Acid Moieties: Structure, Dynamics, and Cooperativity

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Supporting Information

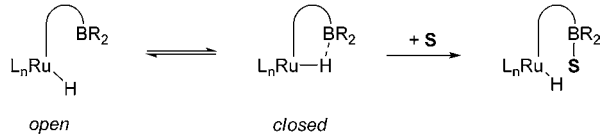
ABSTRACT: The synthesis of a novel class of bifunctional ruthenium hydride complexes incorporating Lewis acidic BR_2 moieties is reported. Determination of the molecular structures in the solid state and in solution provided evidence for tunable interaction between the two functionalities. Cooperative effects on the reactivity of the complexes were demonstrated including the activation of small Lewis basic molecules by reversible anchoring at the boron center.

Transition metal complexes containing multiple reactive sites hold great opportunities for the future development of homogeneous catalysis. In particular, this relates to the combination of metal hydrides and Lewis or Brønsted acidic sites to facilitate networks of bond-breaking and -forming events as required for cooperative small molecule activation.[1] Nature uses this concept in various enzymes to facilitate highly selective multistep transformations under mild conditions.[2] In heterogeneous catalysis, the combination of hydrogenation active transition metal particles with acidic sites in the support materials is also a well-established principle, used on a large scale for example in hydrocarbon reforming.[3]

In sharp contrast, there are only very few examples for late transition metal hydride complexes containing Lewis acidic groups within the same molecule and little is known about possible synergistic effects.[4] Hill and Owen reported examples of late transition metal hydride complexes functionalized with pendant di- and triaza borane units facilitating hydride transfer reactions.[5] In 1995, Baker, Marder and co-workers isolated a complex with a Ru−H−B unit by hydroboration of the cyclometalated $[RuH(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)]$ complex with H-9-BBN and already, in 1990, a related Ir-complex.[6] Most recently, a nickel complex with integrated borane function was shown to enable heterolytic cleavage of dihydrogen.[7]

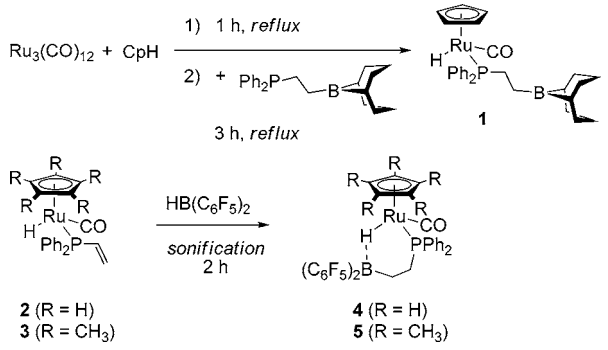
In the present study, we focus on bifunctional ruthenium hydride complexes with BR_2 groups as the Lewis acidic sites. Ruthenium hydride complexes are known to serve as active intermediates in numerous hydrogen transfer processes. By systematic variation of the ligand environment at the metal and the Lewis acidity of the borane moiety, we wanted to explore (i) whether an interaction between the hydride ligand and the borane group occurs; (ii) how such an interaction might affect the reactivity of the Ru−H moiety; and (iii) whether the Lewis acid could serve as an anchor group to activate small molecules in the vicinity of the reactive Ru−H function (Scheme 1).

Scheme 1. Bifunctional Ruthenium Hydride Complexes Bearing Borane-Based Lewis Acid Sites: Possible Intramolecular Interaction and Substrate (S) Activation



A series of new ruthenium hydride complexes based on the $[CpRu(H)(CO)(PR_3)]$ framework with pendant boron-based Lewis acid moieties were synthesized as shown in Scheme 2.

Scheme 2. Synthesis of Bifunctional Ru−H/Lewis Acid Complexes 1, 4, and 5



Complex **1** was obtained in 76% yield in a two-step one-pot reaction starting from commercially available $Ru_3(CO)_{12}$ by treatment with cyclopentadiene and the phosphane-9-BBN ligand[8] in refluxing *n*-heptane.[9] This method cannot be applied for the incorporation of the stronger Lewis acidic $B(C_6F_5)_2$-group, as the corresponding free phosphine ligand is not accessible due to B−P Lewis base pair formation. We therefore synthesized the new diphenylvinylphosphane complexes **2** and **3** as above and then, in a second step, conducted the hydroboration with Piers' borane[10] at the ligand within the coordination sphere. Under ultrasound irradiation, the Cp (**4**) and Cp* (**5**) complexes were obtained in good yields of 87% and 71%, respectively.

The new complexes **1**, **4**, and **5** are yellow crystalline solids, and the molecular structures obtained from single crystal X-ray are depicted in Figure 1. The hydride ligands could be fully

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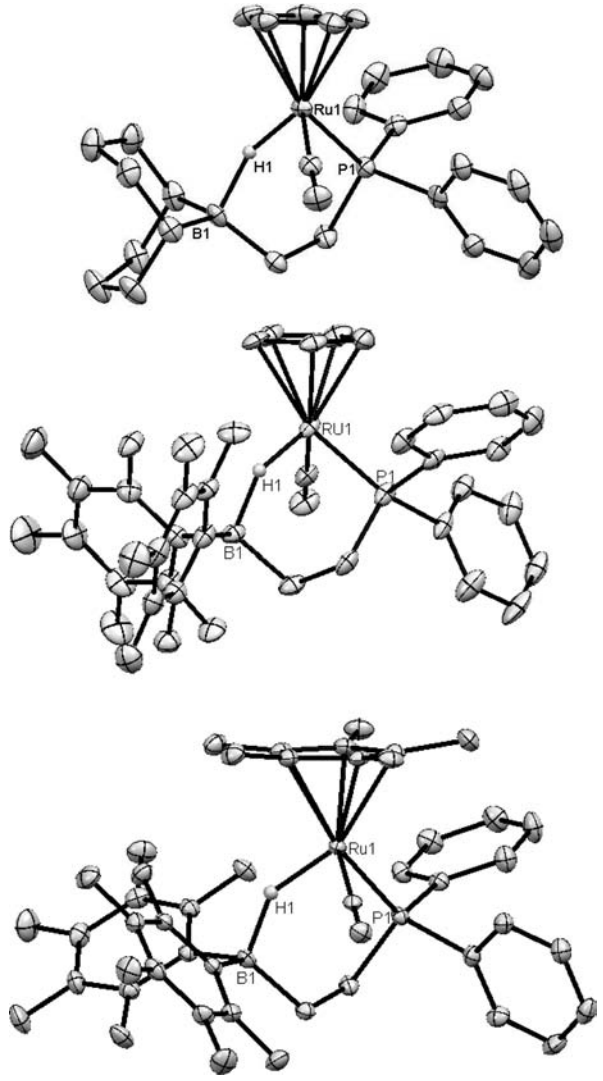

Figure 1. Molecular structures of complexes **1** (*top*), **4** (*middle*), and **5** (*bottom*) as obtained from single crystal X-ray diffraction. Hydrogen substituents except H1 were omitted for clarity. Thermal ellipsoids are at the 50% probability level.

refined on the basis of the corresponding electron density, providing a reliable determination of their positions (see Supporting Information (SI)). In the solid state, all three compounds reveal a cyclic conformation with the Ru···B and B—H distances indicative of a Lewis acid/Lewis base interaction similar to that for comparable structures.[6b,11] Both distances are shorter by about 10 pm for **4** and **5** as compared to **1**, reflecting the stronger Lewis acidity of the $B(C_6F_5)_2$-group (Table 1). The Ru···B distance in **5** is also slightly longer than that in **4**. This may occur from increased steric repulsion between the Cp* and the $B(C_6F_5)_2$ groups, as the B—H distances remain largely identical in both complexes.

Table 1. Structural Parameters of Complexes 1, 4, and 5

complex	*d*(B—H)/pm	*d*(Ru—H)/pm	*d*(Ru···B)/pm	*d*(C≡O)/pm
1	152(6)	159(5)	301.9(6)	115.3(7)
4	143(6)	160(6)	289.5(6)	115.3(6)
5	141(3)	168(2)	292.2(3)	114.9(3)

In solution, the B—H interaction is strongly dependent on the Lewis acidity of the BR_2 group: At room temperature, NMR spectroscopy shows evidence of only a very weak boron—hydride interaction for complex **1** bearing the 9-BBN moiety. The ^{11}B resonance is found in the typical region of three-coordinated boron at 65.7 ppm. The hydride signal appears as two sharp doublets at −13.88 and −13.90 ppm (both $^2J_{HP}$ = 26.8 Hz) in the ratio 4:1 (Figure 2b, Table 2). This can be

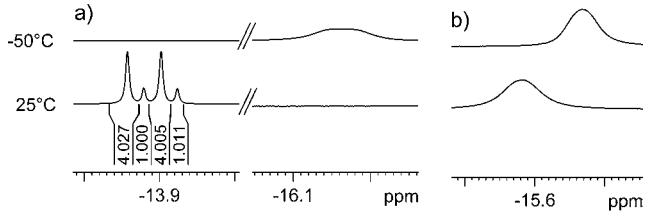

Figure 2. Hydride region of the ^1H NMR spectra of complexes **1** (a) and **4** (b) at 25 °C (*lower line*) and −50 °C (*upper line*). Solvents were C_6D_6 or CD_2Cl_2.

Table 2. Selected ^1H NMR Data of the Neutral Complexes 1, 4, and 5 and the Cationic Complexes 6, 7, and 8

compl.	$\delta(H)^a$/ppm	$T1(H)^b$/ms	compl.	$\delta(H_2^+)^b$/ppm	$T1(H_2^+)^b$/ms
1	−13.8[c]	443	**6**	−7.2	15
4	−15.4	205	**7**	−7.2	25
5	−13.9	230	**8**	−6.9	808

[a]Rt in C_6D_6. [b]−50 °C in CD_2Cl_2. [c]Two doublets (4:1).

attributed to an isotope-induced chemical shift $^1\Delta^{10/11}B(^1H)$ arising from a very weak interaction with $^{10/11}B$ in analogy to other $^n\Delta^{10/11}B(X)$ shifts where the equilibrium lies on the side of the threefold coordination.[12] The observation of the isotopic shift reflects the long relaxation time T1 in the typical range for terminal Ru—H groups.[13] By lowering the temperature to −50 °C this signal shifts to −16.2 ppm appearing as a broad singlet ($h_{1/2}$ = 47 Hz) indicative of formation of an internal Lewis base adduct (Figure 2a).

In contrast, complexes **4** and **5** bearing the strong Lewis acidic $B(C_6F_5)_2$ group show broad hydride signals already at room temperature appearing at −15.4 and −13.9 ppm, respectively (Figure 2a, Table 2). With T1 values of about 200 ms the relaxation times of the hydride signals of **4** and **5** are considerably shortened, reflecting the interaction with the quadrupole nucleus ^{11}B, whose signals appear at −4.2 and −4.1 ppm in the typical region of four-coordinated boron. Furthermore, the ^{19}F NMR spectra of **4** and **5** exhibit two sets of three individual signals, resulting from the diastereotopic C_6F_5 substituents next to the chiral-at-metal $CpRu(CO)(PR_3)H$ unit.[14] Raising the temperature to 70 °C for **4** and to 100 °C for **5** results in a coalescence of the ^{19}F NMR signals indicating a dynamic process that can be associated with the weakening of the B—H interaction (see SI for figure).

Upon protonation of the Ru—H unit, the boron hydride interaction was cleaved for all three complexes as indicated by ^{11}B signals in the three-coordinate region. Treatment of **1** and **4** with HBF_4 in ether resulted in the formation of the cationic dihydrogen complexes **6** and **7**, whereas complex **5** gave the dihydride **8** as can be seen by comparison of the T1 values (Scheme 3, Table 2).[15] This is fully consistent with the corresponding reactivity of the nonfunctionalized Cp(*)Ru—H

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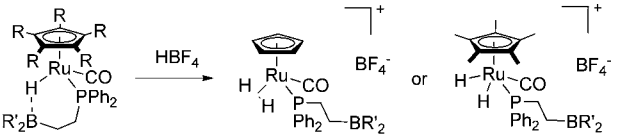
Scheme 3. Protonation of Complexes 1, 4, and 5 To Give Cationic Dihydrogen Complexes 6 and 7 or Dihydride 8



1 (R = H, R' = 9BBN)
4 (R = H, R' = C_6F_5)
5 (R = CH_3, R' = C_6F_5)

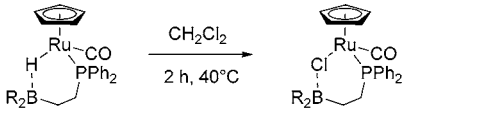
6 (R' = 9BBN)
7 (R' = C_6F_5)

8 (R' = C_6F_5)

units, indicating that the Lewis acid group has no interaction with the cationic complexes, as expected.

The different strengths of the interactions in the neutral monohydrides are, however, clearly reflected by their reactivity toward chlorinated hydrocarbons (Scheme 4). The hydride

Scheme 4. Reactivity towards Chlorinated Hydrocarbons



1 (R = 9-BBN)
4 (R = C_6F_5)

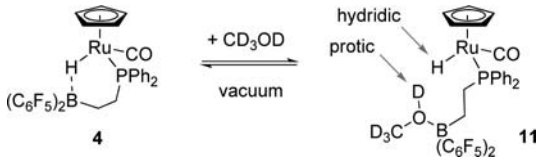
9 (R' = 9-BBN) quant.
10 (R' = C_6F_5) **no reaction**

ligand of the 9-BBN complex **1** is exchanged for chloride to quantitatively yield **9** within 2 h at 40 °C in CD_2Cl_2 solution.[9] In contrast, no H/Cl exchange was observed with complexes **4** and **5** even after 24 h at 40 °C. Thus, the boron hydride interaction appears to shield the Ru−H group preventing the substitution process.

Finally, the behavior of complexes **1** and **4** toward external Lewis bases was investigated. In the case of complex **1**, no changes in the ^{11}B NMR data associated with adduct formation at the weakly Lewis acidic 9-BBN group could be observed in the presence of acetonitrile, tetrahydrofurane, or pyrrolidine. In contrast, complex **4** with the strong Lewis acidic $B(C_6F_5)_2$ moiety was found to bind these molecules under opening of the Ru−H interaction. The ^{11}B NMR signals at −3 to −6 ppm clearly indicate the four-coordinate boron. The sharp hydride resonances at −11.9 to −12.0 ppm in the ^1H NMR with a doublet splitting of $^2J_{HP}$ = 32 Hz together with the appearance of only one set of signals in the ^{19}F NMR rule out an internal interaction with the hydride ligand, confirming the binding of the external Lewis base. The adduct formation was fully reversible and the parent complex **4** was reformed upon removing the Lewis bases in vacuum.

Most significantly, the potential for cooperative activation of external Lewis bases was revealed by the reactivity of complexes **1** and **4** toward methanol (Scheme 5). Again, the NMR data showed reversible binding of MeOH only for complex **4**. In deuterated methanol, a fast exchange within seconds of the

Scheme 5. Reversible Adduct Formation with Methanol and Activation for H/D Exchange



4 **11**

Ru−H for deuterium was observed for this species. For complex **1**, however, H/D exchange was not complete even after two weeks under identical conditions. This is most consistent with the formation of species **11**, where the binding at the strong Lewis acid site $B(C_6F_5)_2$ enhances the acidity of the MeOH molecule in close proximity to the hydridic Ru−H moiety, whose signal appears at −11.9 ppm in the adduct. This arrangement holds great potential for catalytic heterolytic reduction of polar groups via an outer sphere mechanism, in the presence of appropriate hydrogen donors.[16]

In summary we reported the synthesis, structure, and reactivity of a novel class of bifunctional ruthenium hydride/borane complexes. The results provide evidence for synergistic interactions between the hydridic and Lewis acid moieties: Whereas the principal bonding situation at the Ru−H unit is mainly controlled by the ancillary ligands (here Cp and Cp*), additional control factors are provided by the incorporation of a sufficiently strong Lewis acidic site such as the $B(C_6F_5)_2$ function. This includes modulation of the reactivity of the M−H group as well as coordination and activation of small molecules in close proximity to a hydride ligand. Thus, further investigations toward the application of this new class of bifunctional complexes in catalysis appear highly promising and are currently under investigation in our group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization 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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