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Synthesis and Reactivity of a Stable Hydrido Bis(dihydrogen) Derivative in a Nitrogen Donor Environment $LRuH(H_2)_2$ (L = HB(3,5-Me_2-pz), HB(3-iPr,4-Br-pz))

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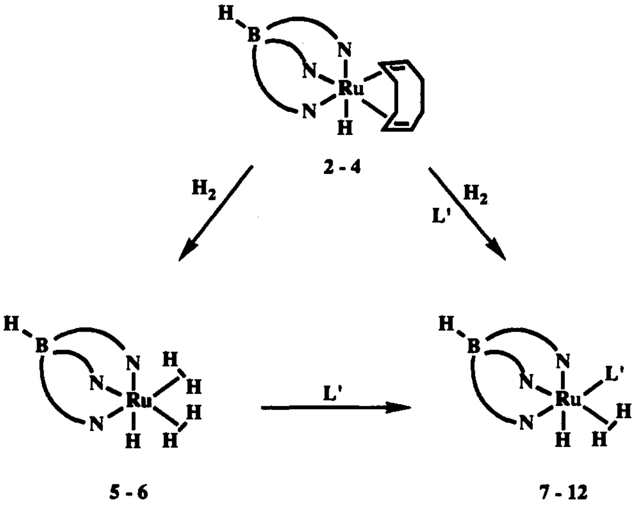
The discovery of dihydrogen coordination without dissociation by Kubas in 1984[1] stimulated an intense research effort during the past decade. Coordination of dihydrogen has now been found on many transition metals and in different ligand environments.[2] However, almost all such known complexes contain phosphorus or, in certain cases, CO donor ligands.[1,2] Three exceptions have been discovered, all containing a nitrogen donor environment.[3–5] $TpRhH_2(H_2)$ was the first such complex.[3] The mode of bonding of dihydrogen is now well understood[6] and is very sensitive to the nature of the other ligands in the coordination sphere. In particular, the stretching of the dihydrogen ligand is highly dependent on the back-donation from the metal to the σ^* orbitals of H_2.[2d]

Although many dihydrogen derivatives are known, only one thermally stable bis(dihydrogen) derivative, $RuH_2(H_2)_2(PCy_3)_2$, has been isolated.[7] It shows a high reactivity, leading, for example, to the 16-electron dihydrogen derivatives $RuHX(H_2)(PCy_3)_2$ (X = Cl, I)[8] and to dihydrogen substitution to give $RuH_2(H_2)(HER_3)(PCy_3)_2$ (E = Si, Ge).[9] All these species are highly reactive but not very stable. In searching for the stabilization of polydihydrogen derivatives of ruthenium, we considered hydridotris(pyrazolyl) borate ligands[10] and recently reported the synthesis of $TpRuH(H_2)(PCy_3)$ Tp = hydridotris(pyrazolyl) borate.[11] We have now found a more general route toward tris(pyrazolyl) borate ruthenium derivatives using RuHCl(COD)(bpm) (**1**) as starting material (bpm = bis(pyrazolyl)methane; COD = 1,5-cyclooctadiene),[12] and we describe in this communication the preparation of novel hydridobis(dihydrogen) derivatives, fully characterized by sequential deuteration, and some of their chemistry.

Scheme 1. Synthesis and Reactivity of $LRuH(H_2)_2$[a]



[a] $L = H\text{-}B(\frown N)_3$. **2**, L = Tp; **3**, L = Tp*; **4**, L = Tp′; **5**, L = Tp*; **6**, L = Tp′; **7**, L = Tp*, L′ = PCy_3; **8**, L = Tp′, L′ = PCy_3; **9**, L = Tp*, L′ = py; **10**, L = Tp′, L′ = py; **11**, L = Tp*, L′ = THT; **12**, L = Tp′, L′ = THT.

The reaction of **1** with KL (L = Tp; Tp* = hydridotris(3,5-dimethylpyrazolyl) borate; Tp′ = hydridotris(3-isopropyl-4-bromopyrazolyl) borate) produced selectively LRuH(COD) (L = Tp, **2**;[13] L = Tp*, **3**; L = Tp′, **4**) in high yield.[14] Complexes **2**–**4** were isolated and characterized by microanalysis, mass spectrometry, and ^{1}H and ^{13}C NMR. **2** was reluctant to undergo hydrogenation in any conditions, whereas **3** reacted slowly (15 h) with dihydrogen (3 bar) at room temperature in pentane, and both **3** and **4** reacted rapidly in the presence of PtO_2 (Adams catalyst) to yield new complexes of stoichiometry $LRuH_x$ (L = Tp*, **5**; Tp′, **6**). The ^{1}H NMR spectra of **5** and **6** show the hydridotris(pyrazolyl) borate ligand L and "hydrides" only as a sharp singlet at δ −11.26 (**5**) or −11.85 (**6**). The "hydride" signal remained a sharp single line down to 177 K in both cases.

The number of ruthenium-bound hydrogen atoms was deduced first from integration in ^{1}H NMR (on one scan or using large repetition delays, *i.e*, 30 s) which was consistent with the presence of five hydrogen atoms. Partial deuteration was carried out either by bubbling D_2 in a solution of **5** in $C_6D_5CD_3$ or by allowing **5** or **6** to undergo H/D exchange with C_6D_6 or $C_6D_5CD_3$ over several hours or days. It was then possible to observe the stepwise exchange of hydrogen for deuterium in the "hydride" signal and to identify sequentially all isotopomers, namely $LRuH_4D$, $LRuH_3D_2$, $LRuH_2D_3$, and $LRuHD_4$, as respectively nonbinomal triplet (1:1:1), quintet (1:2:3:2:1), septet (1:3:6:7:6:3:1), and nonet (1:4:10:16:19:16:10:4:1) (see Figure 1). This observation unambiguously demonstrates the presence of five ruthenium-bound hydrogen atoms in **5** and **6**. Finally, a mass spectrum (DCI) showing the presence of $[Tp^*RuH_4]^+$ was obtained for **5**.[14]

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[14] Selected data for compounds **5**–**6**. **5**: ^{1}H NMR ($C_6D_5CD_3$, 250 MHz) δ −11.26 (s, 5H), 2.31 (s, 9H, 3CH_3), 2.32 (s, 9H, 3CH_3), 5.73 (s, 3H, Tp*CH); T_1 at 177 K, 31 ms. **6**: ^{1}H NMR (C_6D_6, 300 MHz) δ −11.82 (s, 5H), 1.38 (d, J = 7.08 Hz, 18H, 6CH_3), 3.66 (sept, 3H, H^{iPr}), 7.25 (s, 3H, Tp′CH); T_{1min} ($C_6D_5CD_3$) at 182 K, 28 ms. For more details and for data for compounds **3**–**12**, see supplementary material.

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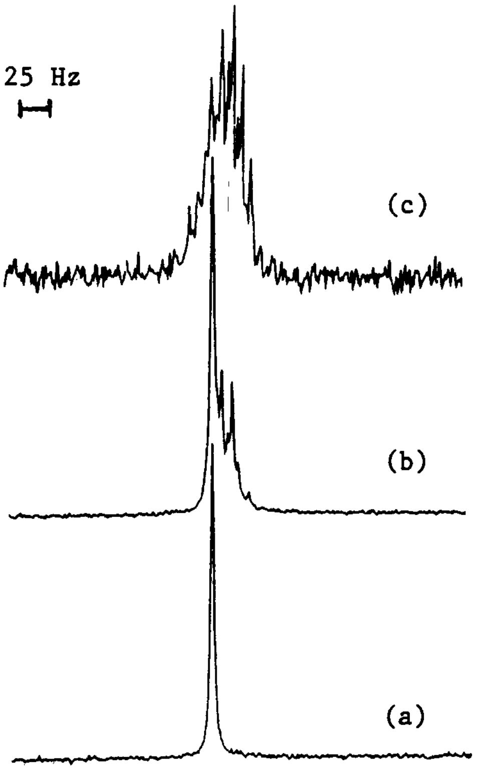

Figure 1. Modification of the high-field signal of **5** upon stepwise deuteration. (a) Initial spectrum, Tp*RuH_5; (b) after 5 min bubbling D_2, a mixture of Tp*RuH_5, Tp*RuH_4D and Tp*RuH_3D_2; (c) after 24 h under D_2, Tp*$RuHD_4$ and some Tp*RuH_2D_3.

The number of coordinated dihydrogen molecules was deduced first from measurements of the relaxation time T_1, which showed a minimum of 28 ms at 182 K (300 MHz) for **6** and no minimum but the smallest observed value of 31 ms at 177 K (250 MHz) for **5**. These values are in agreement with the presence of at least one dihydrogen molecule in **5** and **6**. The deuteration experiment allows the two possible formulations $LRuH_3(H_2)$ and $LRuH(H_2)_2$ to be distinguished. Hence all the observed multiplets show a J_{H-D} coupling constant of 5.5 Hz in the case of **5** and 5.2 Hz in the case of **6**. Assuming that a fast exchange will lead to a statistical repartition of isomers of a given isotopomer (*viz.* $LRuH_4D$) and that in each isomer a mean J_{H-D} value is observed, we can calculate the J_{H-D} value corresponding to the coordinated dihydrogen molecule(s).[15] The values found are near 50 Hz for a mono(dihydrogen) formulation and near 27 Hz for a bis(dihydrogen) one (27.5 Hz for **5**; 26 Hz for **6**). This experiment therefore demonstrates unambiguously the presence of two dihydrogen molecules in **5** and **6**. The J_{H-D} coupling constants are furthermore in the range observed for unstretched dihydrogen complexes for which a high reactivity is expected.

Upon hydrogenating **3** or **4** in the presence of 1 equiv of a ligand L′ or upon reacting **5** or **6** with 1 equiv of L′, a series of new hydrido(dihydrogen) derivatives of general formulation $LRuH(H_2)L'$ can be prepared [L = Tp*, L′ = PCy_3, **7**; L′ = py (pyridine), **9**; L′ = THT (tetrahydrothiophene), **11**; L = Tp′, L′ = PCy_3, **8**; L′ = py, **10**; L′ = THT, **12**]. The characterizations of the compounds are given in the supplementary material. All complexes **7–12** show a hydrido(dihydrogen) structure. The chemical shift of the "hydride" signal in ^1H NMR increases upon substitution of H_2 by PCy_3, THT, and py (respectively in the Tp* series from −11.26 to −10.7, −9.6, and −8.2 ppm). The chemical shift of the metal-bound hydrogen atoms is, in general, related to the metal–hydrogen distance (d-orbitals shielding). This variation could therefore roughly reflect the amount of stretching of the coordinated dihydrogen molecule, which should decrease in agreement with the values found for the T_{1min} (**5**, <31 ms at T < 177 K; **7**, 22 ms at 218 K; **9**, 19 ms at 233 K; **11**, 19 ms at 223 K; all 250 MHz).

Finally preliminary reactivity studies show that displacement of H_2 from **5** or **6** is facile. This leads in deuterated aromatic solvent to a relatively fast H–D exchange between the "hydrides" and the solvent at room temperature, which indicates a reactivity higher than that of $RuH_2(H_2)_2(PCy_3)_2$.

In conclusion, we report in this communication the second example of a thermally stable bis(dihydrogen) derivative, the unambiguously characterization of the first by direct spectroscopic methods, and a rare case of a "polyhydride" in a nitrogen donor environment.[3,16] These molecules are reactive, allowing substitution of H_2 by classical ligands of hydride chemistry (PCy_3) but also by more unusual ones such as THT or pyridine. Of special interest are the C–H activation reactions occurring at room temperature, which are unusual for such complexes. Finally, it is noteworthy that these compounds represent the first general entry into a hydridotris(pyrazolyl) borate ruthenium chemistry.[17]

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Supplementary Material Available: Spectroscopic and analytical data for compounds **3–12** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(15) The calculation was carried out as follows, using the following definitions: $J_{H-D(obs)}$, observed value; $J_{H-D(NC)}$, H–D coupling constant in a coordinated hydrogen deuteride molecule; and $J_{H-D(C)}$, coupling constant between a hydride and a deuteride. The couplings between a deuteride and coordinated dihydrogen and between a hydride and coordinated H–D are assumed to be zero. Assuming a trihydrido(dihydrogen) structure, a statistical treatment implying an average over all D-position isomers of the mean J_{H-D} values found for each isomer leads to $J_{H-D(NC)} = 10J_{H-D(obs)} - 3J_{H-D(C)}$; then for **5**, $J_{H-D(NC)} = 55 - 3J_{H-D(C)}$. The classical coupling constant $J_{H-D(C)}$ being at most 3 Hz, the $J_{H-D(NC)}$ value is greater than that found for free hydrogen deuteride. However, assuming the presence of two dihydrogen molecules, we find $J_{H-D(NC)} = 5J_{H-D(obs)} = 27.5$ Hz, a reasonable value in this chemistry. The statistical treatment can be done over all isotopomers and leads to the same result. For similar treatments, see ref 2b and Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

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