X-Ray crystal structure of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$

Andrzej F. Borowski,[a] **Bruno Donnadieu,**[b] **Jean-Claude Daran,**[b] **Sylviane Sabo-Etienne**[b] **and Bruno Chaudret***[b]

[a] *Institute of Coal Chemistry, Polish Academy of Sciences, 5 Sowinskiego St., Gliwice, 44-121 Poland*
[b] *Laboratoire de Chimie de Coordination CNRS, 205 Route de Narbonne, F-31077 Toulouse Cedex 4, France.*
E-mail: Chaudret@lcc-toulouse.fr

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$RuH_2(H_2)_2(PCy_3)_2$, the first reported stable bis (dihydrogen) complex crystallizes in the *P*1 space group; the two dihydrogen ligands lie in the equatorial plane in a mutual *cis* position and are located *trans* to the hydride ligands; the H–H distances are *ca.* 0.85 Å, in agreement with the presence of unstretched dihydrogen ligands; these results are compared with previous theoretical calculations using density functional theory.

The chemistry of dihydrogen complexes has developed considerably since the first discovery of dihydrogen coordination without dissociation in 1984.[1] Many different compounds have now been isolated, characterized, in particular by X-ray crystallography, and have given rise to reactivity studies.[2]

The number of complexes containing more than one dihydrogen ligand remains, however, very limited.[3] No tris(dihydrogen) complex is known and only a few bis(dihydrogen) complexes have been isolated, namely $RuH_2(H_2)_2(PCy_3)_2$ **1**[4] and $LRuH(H_2)_2$ [L = hydridotris(3,5-dimethylpyrazolyl)borate, Tp*; L = hydridotris(3-isopropyl-4-bromopyrazolyl)borate, Tp']. [5] $RuH_2(H_2)_2(P^iPr_3)_2$ has been observed in solution following the same procedure as that used for preparing **1**[6] and recently isolated by Morris using a different procedure.[7] $Cr(CO)_4(H_2)_2$ has been observed in an argon matrix or in liquid xenon and characterized by IR spectroscopy.[8] Crabtree *et al.* have characterized the bis(dihydrogen) complex $[IrH_2(H_2)_2(PCy_3)_2]$+ in solution upon protonation of the neutral precursor $IrH_5(PCy_3)_2$.[9] Finally Caulton and coworkers have characterized a bis(dihydrogen) osmium derivative $[Os(H_2)_2(NCMe)_2(PPr^i{}_3)_2]^{2+}$ by protonation of $[OsH_3(NCMe)_2(P^iPr_3)_2]^+$.[10] A number of unstable bis(dihydrogen) ruthenium complexes have also been prepared when studying the reactivity of $RuH_2(H_2)_2(PCy_3)_2$.[11]

In a recent paper, we described the spectroscopic properties of $RuH_2(H_2)_2(PCy_3)_2$, in particular INS spectra demonstrating the presence of a low rotation barrier for the dihydrogen ligands and the results of DFT calculations showing that the most stable structure involved the presence of two mutually *cis* hydrides each of which was located *trans* to a dihydrogen ligand.[12] Complex **1** has proven to be important in ruthenium chemistry and has found applications as a starting material for a great variety of ruthenium dihydrogen complexes,[11,13,14] and complexes containing two σ-bonds.[15] It has also been used as a catalyst precursor for hydrogenation[13, 16] and silylation reactions[17] and as a precursor for carbene derivatives used in metathesis of alkenes, particularly ring closing metathesis.[18] Our synthesis involves the hydrogenation of Ru(cod)(cot) in the presence of the phosphine ligand PCy_3. This synthesis has proven over the years to be a high yield one, to be reproducible and to yield a very pure product.[4,13] An alternative synthesis has recently been proposed which is claimed to lead to a better yield but which produces a yellow complex, probably because of the presence of impurities mixed with **1**.[18]

We now describe the crystal structure of **1**, the first of a bis(dihydrogen) complex, including the location and refinement of all hydrogen atoms.

$RuH_2(H_2)_2(PCy_3)_2$ **1** was prepared as previously reported[13] by reacting a pentane solution of Ru(cod)(cot) and PCy_3 with dihydrogen (3 bar). After filtration, the white precipitate was dissolved in a minimum quantity of toluene by gentle warming under dihydrogen, concentrated in a dihydrogen stream and left standing at room temperature under a dihydrogen atmosphere. The resulting crystals were then mounted on a STOE diffractometer operating at 160 K under dinitrogen.†

The complex crystallizes in the *P*1 space group and the molecular structure is shown in Fig. 1. The environment of ruthenium consists of two phosphines located *trans* to each other [P–Ru–P 179.79(11)°] and displaying normal Ru–P distances (*ca.* 2.35 Å). In addition, two hydrides and two dihydrogen ligands are present in the equatorial plane. All Ru–H distances are within the range expected for such Ru–H and Ru–H_2 bonds (1.5–1.7 Å). The H–H distances within the

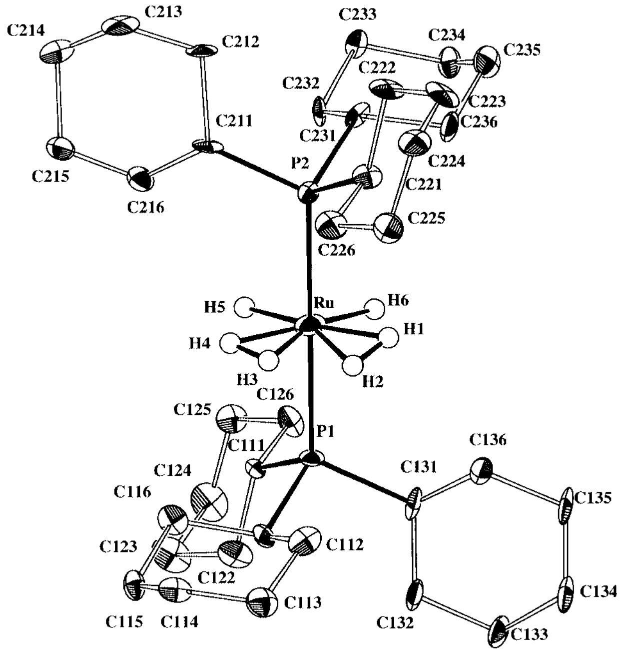

Fig. 1 Molecular structure of $RuH_2(H_2)_2(PCy_3)_2$. Selected bond lengths and interatomic distances (Å) : Ru1–H1 1.542(26), Ru1–H2 1.549(26), Ru1–H3 1.515(26), Ru–H4 1.529(26), Ru1–H5 1.708(38), Ru1–H6 1.687(37), H1–H2 0.848(37), H3–H4 0.864(38); H2–H3 1.405(65); H1–H6 2.152(57), H4–H5 2.080(55), Ru–P2 2.329(2); Ru–P1 2.347(2). Selected bond angles (°): P1–Ru1–P2 179.79(11), H1–Ru1–H2 31.84(14), H2–Ru1–H3 54.56(25), H3–Ru1–H4 32.96(14); H4–Ru1–H5 79.70(23); H5–Ru1–H6 78.92(24), H6–Ru1–H1 83.43(25).

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dihydrogen molecules are found to be *ca.* 0.85 Å, indicating the presence of an unstretched dihydrogen ligand (even taking into account the standard deviations, the H–H distances remain below 1 Å; see legend to Fig. 1)[2] and consistent with previous spectroscopic and theoretical studies carried out on this compound.[12] All the hydrogen atoms whether belonging to the hydride or dihydrogen ligands lie in the equatorial plane with no significant deviation from this plane. The distances between one hydride and the proton of the next dihydrogen molecule (*e.g.*; H6··H1 and H5··H4) are both > 2 Å and rule out the presence of any *cis*-interaction.[22] These data are consistent with the low rotation barrier found for the dihydrogen ligands in this complex by INS. However, it is interesting that the distance between the two dihydrogen ligands [H2··H3 1.405(65) Å] is relatively short, which may explain the structures found in the INS spectra, the origin of which was proposed to be the concerted rotation of both dihydrogen ligands.[12]

All these data are in complete agreement with previous DFT/B3LYP calculations.[12] In particular, the overall geometry of the complex, namely mutually *cis* disposition of the hydride and dihydrogen ligands, their coplanarity and the *trans* arrangement of the phosphines are well reproduced by the calculation. The Ru–P distances [2.311 Å by DFT/B3LYP calculations for the optimized most stable geometry *cf.* the experimental values of 2.329(2) and 2.347(2) Å] are very satisfactorily reproduced although the calculation was performed using PH_3 as a model for PCy_3. Steric interactions are presumably not important in this complex. The H–H distances within the dihydrogen molecule are also satisfactorily reproduced [0.853 Å by DFT/B3LYP; 0.848(37), 0.864(38) Å experimentally]. The only difference concerns the Ru–H distances which are found to be larger for the dihydrogen ligands than in the hydrides by X-ray diffraction, contrary to calculations. However, it is noteworthy that the X-ray technique only detects the electron density around the atoms. This density may be polarized towards ruthenium for these unstretched dihydrogen ligands which have a partially protonic character, much more than in the hydride ligands and may contribute to the present observation.

In conclusion, we report the first X-ray crystal structure of a bis(dihydrogen) complex with $RuH_2(H_2)_2(PCy_3)_2$ being first reported stable bis(dihydrogen) complex. It was originally formulated as a hexahydride and then correctly reformulated in 1988. Since its original preparation in 1982, this complex has proven to be very important in the chemistry of ruthenium. The confirmation of its structure by X-ray crystallography should induce a new interest for this bis(dihydrogen) complex and will provide renewed impetus for reactivity studies in our group.

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Notes and references

† *Crystal data*: $C_{36}H_{72}P_2Ru$ **1**, M = 667.94, crystal size 0.5 × 0.2 × 0.1 mm, triclinic, space group $P1$, a = 9.1781(13, b = 9.9339(17), c = 11.7055(3) Å, α = 76.183(19), β = 110.690(17), γ = 69.386(18)°, V = 864.2(2) Å^3, Z = 1, D_c = 1.283 mg m^{-3}, μ = 0.569 mm^{-1}, $F(000)$ = 362. Data were collected at 160 K on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream cooler device. 8219 reflections were collected (6009 unique, R_{int} = 0.0451). The structure was solved by direct methods using SIR92,[19] and refined by least-squares procedures on F^2 with the the aid of SHELXL97;[20] largest electron density residue: $\Delta\rho_{max}$ = 0.358, $\Delta\rho_{min}$ = −0.257 e Å^{-3}; $R(F)$ = 0.0308 [$I > 2\sigma(I)$] and $wR(F^2)$ = 0.0760. All hydrogen atoms were located on a difference Fourier map and refined with an idealized model, except the hydrides H5, H6 and the hydrogen atoms H1, H2, H3, H4 of the two dihydrogen ligands which were refined with a fixed isotropic thermal parameter. All non-hydrogen atoms were anisotropically refined and in the last cycles of refinement a weighting scheme was used. A drawing of the molecule was generated with the program ZORTEP[21] with 50% probability displacement ellipsoids for non-hydrogen atoms. CCDC 182/1553. See http://www.rsc.org/suppdata/cc/a908567j/for crystallographic files in .cif format.

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