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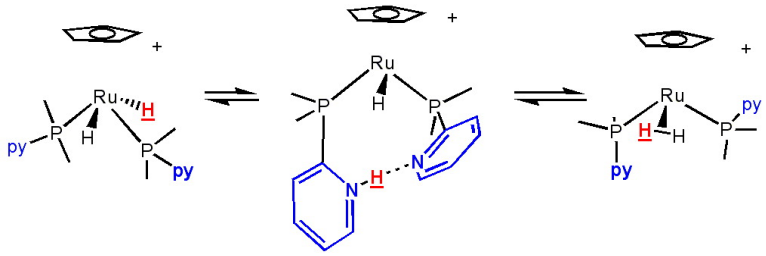

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Facile Ru−H_2 Heterolytic Activation and Intramolecular Proton Transfer Assisted by Basic N-Centers in the Ligands

Félix A. Jalón,*,† Blanca R. Manzano,† Agustín Caballero,† M. Carmen Carrión,† Lucía Santos,‡ Gustavo Espino,§ and Miquel Moreno⊥

Departamento de Química Inorgánica, Orgánica y Bioquímica, IRICA, Departamento de Química Física, Universidad de Castilla-La Mancha, Avda. C. J. Cela 10, 13071 Ciudad Real, Spain, Facultad de Ciencias, Universidad de Burgos, Pza. Misael Bañuelos s/n, 09001 Burgos, Spain, and Departamento de Química, Edifici Cn, Universidad Autònoma de Barcelona, 08193 Bellaterra, Spain

Received July 28, 2005; E-mail: Felix.Jalon@uclm.es

Cationic dihydride derivatives of formulas $[Cp'RuH_2L_2]^+$ and $[Cp'Ru(H_2)L_2]^+$ have proven to be particularly useful complexes concerning proton-transfer reactions and the dihydride/dihydrogen tautomerism.[1] From the classical work of Chin and Heinekey,[2] some conclusions were obtained that nowadays are considered as solidly established, namely, (i) at low temperature, the proton transfer to the derivatives $[Cp'RuHL_2]$ (L = phosphine) gives first the nonclassical dihydrogen isomer under kinetic control; (ii) upon increasing the temperature, the *trans*-$[Cp'RuH_2L_2]$ (classical hydride) is formed either in equilibrium with the *cis* form or as the sole species; (iii) although the proposed mechanism for this isomerization process is only speculative, its intramolecular character is well established. In this context, our goal was the design of monohydride and dihydride complexes of this type bearing basic and uncoordinated centers that could favor proton-transfer processes[3] and offer new perspectives and information in this field. With this proposal, we have used the phosphine PPh_2py (py = pyridine) that, according with our experience, favors intramolecular proton-transfer reactions.[4]

The reaction of $[Cp^*RuCl_2]_n$ with PPh_2py and zinc gave $[Cp^*Ru(\kappa^2\text{-}P,N\text{-}PPh_2py)(PPh_2py)]Cl$ (**1**). This complex reacted with KBH_4 to give $[Cp^*RuH(PPh_2py)_2]$ (**2**), whose hydride appears at −12.35 ppm (t, J_{HP} = 32.8 Hz) in the ^1H NMR spectrum.

Proton-transfer reactions over **2**, using HBF_4 as acid, in complex: acid molar ratios of 1:1 and 1:2 were carried out in acetone-d_6 at −80 °C (see Scheme 1). D/H isotopic exchange with the solvent was not observed.

Products **3** and **4** showed singlet ^{31}P NMR resonances. In the ^1H NMR spectrum, a broad resonance for each compound, assigned to the hydride groups (2H), appeared around −6 ppm. Significantly, the broad hydride resonance of **3** (but not that of **4**) resolves as a triplet between −80 and −30 °C with J_{HP} = 20.7 Hz and is unaffected by the temperature. The most remarkable difference between **3** and **4** was the existence of a broad resonance at 12.90 ppm in **4** (1H) that could be assigned to a (py)N*H* group. For both complexes, a broadening of the hydride resonance and also that of N*H* for **4** was observed as the temperature increased. At room temperature, the slow release of H_2 was detected. The T_1(min) of **3** and **4** and that of **2** were determined using a 500 MHz spectrometer. The values found were 414 ms at 0 °C (**2**), 400 ms at −45 °C (**3**), and 203 ms at −20 °C (**4**). The stated J_{HP} coupling constant for the hydride of **3** and this high T_1(min) allows one to conclude that **3** is the classical dihydride *trans*-$[Cp^*RuH_2(PPh_2py)_2]BF_4$. This result contrasts with the previously reported behavior of the proton transfer over $[Cp^*RuH(PPh_3)_2]$ that at low temperature is transformed into the nonclassical *cis*-$[Cp^*Ru(H_2)(PPh_3)_2]BF_4$.[1,2] The observed decrease of the T_1(min) in **4** with respect to **3** and two other experimental observations concerning **4**, namely, (i) the identical T_1's measured for the hydrides and the N*H* resonances in all the range of temperature studied, and (ii) the significantly broadening of these two resonances when the temperature increases, are indicative of the existence, in **4**, of a dihydrogen bond RuH···HN with a rapid proton-hydride exchange.[5] The two hydrides and the two N(py) centers of **4** must alternate in this bond since their respective resonances are equivalent in the NMR.

Scheme 1

$$[Cp^*RuH(PPh_2py)_2],\ \mathbf{2} \xrightarrow{HBF_4} \textit{trans}\text{-}[Cp^*RuH_2(PPh_2py)_2]BF_4,\ \mathbf{3}$$

$$\xrightarrow{HBF_4} [Cp^*RuH\overline{(PPh_2pyH)}(PPh_2py)](BF_4)_2,\ \mathbf{4}$$

Considering that in a piano stool structure, very probably, only one pyridine fragment can be involved in the possible RuH···Hpy interaction (see below), and subtracting the contribution of the N(py) atom to the excess of relaxation in **4** with respect to **3**, we have calculated[6] an H···H distance of 1.64 Å, which is very close to that expected for a dihydrogen bond.[7]

Complexes **3** and **4** give rise, after the release of hydrogen, to products with a ^{31}P NMR pattern very similar to that of **1** (**1′** and **5**, respectively). The more remarkable difference between **1′** and **5** is the presence of a N*H* resonance for **5** at 12.27 ppm. Therefore, we ascribe the formula $[Cp^*Ru(\kappa^2\text{-}P,N\text{-}PPh_2py)(PPh_2py)]BF_4$ for **1′** and $[Cp^*Ru(\kappa^2\text{-}P,N\text{-}PPh_2py)(PPh_2pyH)](BF_4)_2$ for **5**.

Both **2** and **3** were used as catalysts in a deuterium labeling experiment of H_2 monitored by ^1H NMR using methanol-d_4 as deuterium source at room temperature. Complex **3** is particularly active since 50% of the initial H_2 is labeled after 7 min. After 4 h, H_2 has practically disappeared from the spectrum, and HD and D_2 are in an equimolecular ratio. However, the instability of **3** at room temperature prevents this process at longer times. Complex **2** is not so active (see Figure 1). However, **2** is more stable than **3**, and after 15 h of activity, when practically only D_2 was present in the solution, **2** was unaffected. Only the deuteration of the hydride ligands of **2** and **3** was detected.

These results show that labile dihydrogen compounds, able to heterolytically activate H_2, are accessible from **2** and **3** in methanol-d_4. This conclusion is especially striking since for **3** no evidence of such species had been observed in the NMR spectra and, more notably, because the *trans*-to-*cis* isomerization was considered to be a very unfavorable process.

To shed light on the mechanism of this process, we have carried out a theoretical study at a DFT (B3LYP) level. First, the geometry

† Dpto. Q.I.O.B., Universidad C-LM, IRICA.
‡ Dpto. O.F., Universidad C-LM.
§ Universidad de Burgos.
⊥ Universidad Autònoma de Barcelona.

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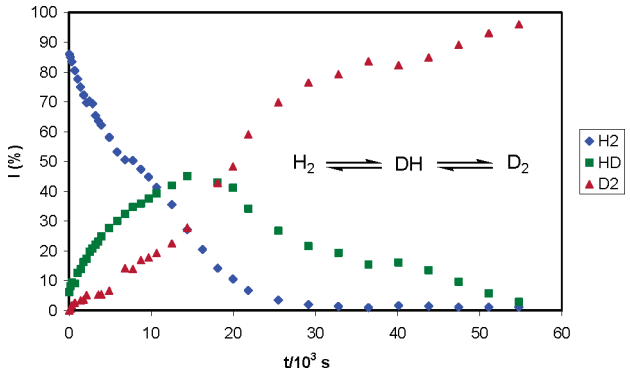

Figure 1. $H_2/HD/D_2$ ratio versus time in the D^+-H_2 exchange with **2**/methanol-d_4 at room temperature.

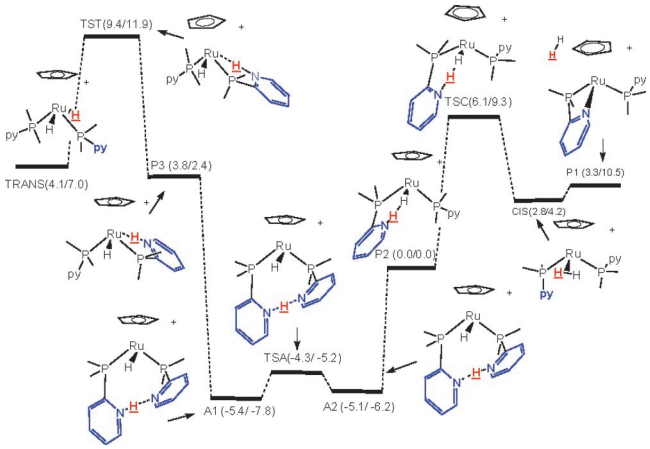

Figure 2. Calculated reaction profile (kcal/mol) for the proton transfer over $[CpRuH_2(PMe_2py)_2]^+$. Energy values are given in brackets in kcal/mol (vacuum/acetone).

for the model compound $[CpRuH(PMe_2py)_2]$ was optimized. The starting parameters for this structure were based on the X-ray structure of $[CpRuH(PPh_3)_2]$.[8] Theoretical results are depicted in Figure 2 (see also Supporting Information), where the geometries of the located stationary points are shown along with a scheme of their relative energy (values in kcal/mol in brackets).

The energy was calculated in vacuum and also by introducing acetone as solvent correction through the PCM cavity method.[9] The energy levels in the figure and the data in the discussion refer to the vacuum calculations, but the conclusions in acetone are similar. These results reveal the existence of both the dihydrogen (CIS) and the dihydride (TRANS) structures, which are very close in energy (CIS 1.3 kcal/mol more stable than TRANS). As seen in the left part of Figure 2, a proton transfer transforms the TRANS structure into another minimum labeled P3 that exhibits an intramolecular hydrogen bond, Ru···H−N(py). Fortunately, we were able to find the transition state (TST) between these two minima. The energetic accessibility of TST ensures that deprotonation of the TRANS form to give P3 is theoretically possible. Another proton-transfer process is presented on the right of Figure 2 that goes from the CIS minimum to a dihydrogen-bridged structure termed P2. The participation of unconventional hydrogen bonds, as those found in P2 and P3, in proton-transfer processes has been previously proposed.[10] Again, a low-energy transition state TSC was found linking CIS and P2 minima. This fact implies that not only the proton transfer from a fragment pyH to a Ru−H bond is feasible but also the reverse process of heterolytic breaking of the coordinated H_2 molecule in CIS, thanks to the participation of the pyridine moiety. A combination of Ru−P and P−C(py) bond rotations, from both P3 and P2, allowed the optimization of the other two minima, denoted as A1 and A2 in Figure 2, that are the most stable structures along the whole process. These minima possess a hydrogen bond between the two pyridines. The proton transfer from one pyridine group to the other connects A1 and A2 and takes place through TSA, which is just 1.1 kcal/mol above A1. The existence of A1 and A2 is one of the most important results of this DFT study because it connects the two proton-transfer processes. In this way, the protonation of one *N*(py) center could be the initial step in the proton transfer. The low-energy cost allows the proton transfer both to the Ru (TRANS) and to the Ru−H bond (CIS) that could interconvert through A1−A2. The existence of **3** (TRANS) as a sole species at −80 °C in acetone solution could be the consequence of an unexplored additional stabilization at low temperature of this tautomer. To the best of our knowledge, this mechanism, including all the necessary TS's, has never been theoretically seen.

The reaction scheme is completed with the minimum energy structure P1, obtained by H_2 release from CIS and formation of a Ru−py bond. In terms of free energy, P1 will be probably very favored due to the increase of entropy that supposes the loss of H_2. This fact would support the experimental evolution of **3** to give **1′**. The full sequence represented in Figure 2 also supports our labeling experiments. Accepting that the release of dihydrogen is a reversible process and that the involvement of acid species of pyridinium as A1, A2, P2, and P3 allows the incorporation of deuterons from methanol-d_4, the labeling of external H_2 must be a feasible process.

In conclusion, the substitution of PPh_3 by PPh_2py dramatically changes the behavior of $[Cp^*RuHP_2]$ against proton-transfer processes. In contrast with the PPh_3 derivative, **2** gives a *trans* dihydride even at low temperature. Probably the kinetic control is suppressed at this temperature due to the easy intramolecular proton transfer favored by the presence of the N(py) basic centers. At room temperature, the *cis*-(H_2) tautomer must be easily formed (H_2 release) and a heterolytic activation of H_2 takes place. A complete theoretical study, including all of the transition states for the proton-transfer processes, supports all of the experimental observations.

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Supporting Information Available: Experimental section, and computational details (22 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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