

Ruthenium Assisted Reversible Proton Transfer from an Aromatic Carbon to a Hydride

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The functionalization of C–H bonds remains a problem of great current interest with many recent important advances.^{1–8} Murai has reported effective systems for the catalytic functionalization via cyclometalation of aromatic hydrocarbons containing a functional group able to coordinate to a metal (typically a ketone or an amino group).⁹ The mechanism of this reaction involves a C–H activation step to give an ortho-metalated species which appears to be the resting state of the catalyst.¹⁰ The activation process involves first the coordination of the C–H bond in an agostic configuration which is followed by a second step which can be an oxidative addition or a deprotonation of this agostic intermediate as recently proposed by Milstein et al.⁴ This step could be assisted by a hydride to give a dihydrogen complex as suggested by Albeniz and Crabtree,⁶ but no direct evidence for this process is currently available. Different fluxional processes involving agostic or ortho-metalated species have also been proposed to be assisted either by the metal or by a hydride.^{6–8}

As a result of our interest for the stoichiometric reactivity and catalytic applications of ruthenium complexes containing several coordinated σ -bonds,^{11–13} we have looked at the coordination of C–H bonds. A few complexes containing two coordinated C–H bonds were known prior to this work.¹⁴ In this paper we describe

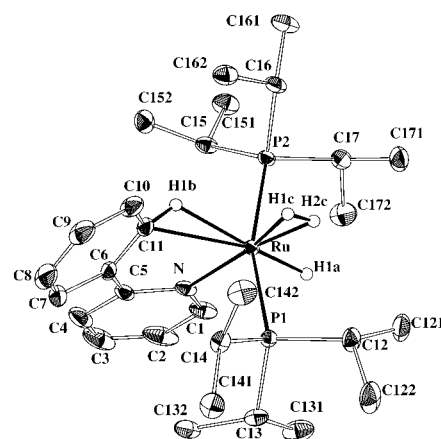


Figure 1. Molecular structure of **2**. Selected bond (Å) and angles (deg): Ru–P(1), 2.3889(9); Ru–P(2), 2.3671(9); Ru–N, 2.108(2); Ru–C(11), 2.528(3); Ru–H(1b), 1.924(33); Ru–H(1a), 1.528(20); Ru–H(1c), 1.564(20); Ru–H(2c), 1.547(21); H(1c)–H(2c), 0.82(4); P(2)–Ru–P(1), 163.56(3); N–Ru–P(2), 93.99(6); N–Ru–P(1), 96.24(6); H(1a)–Ru–H(1b), 163.54(14).

the synthesis of a novel hydrido dihydrogen complex containing an aromatic agostic C–H bond characterized by X-ray diffraction, as well as by multinuclear NMR and its equilibration with a dihydrogen ortho-metalated species.

We have recently described the synthesis of hydrido dihydrogen complexes containing an ortho-metalated phenylpyridine ligand, RuH(H₂)(*o*-C₆H₄py)(PR₃)₂ (R = ⁱPr, **1a**; R = Cy, **1b**).¹⁰ Protonation of **1a** by HBARf (HB[C₆H₃(CF₃)₂]₄) at –20 °C in THF yields [RuH(H₂)(*o*-C₆H₅py)(PⁱPr₃)₂][BARf] (**2**) isolated by crystallization in THF/Et₂O and fully characterized by classical techniques¹⁵ as well as by an X-ray crystal structure analysis carried out at 140 K (see Figure 1).¹⁶ The significant features are a cis geometry for the hydride and dihydrogen ligands, an H–H distance (0.82 (4) Å) significantly shorter than that found for **1a** (1.09 (4) Å)¹⁷, even if care must be taken when considering X-ray data, the agostic C–H interaction (Ru–H(1b) = 1.924 (33) Å, Ru–C(11) = 2.528 (3) Å, C(11)–H(1b) = 0.96 (3) Å), and a torsion between the phenyl and the pyridyl planes (27.5 (4)°).

The agostic interaction in **2** can be detected by ¹³C NMR spectroscopy (*d*⁸-THF, 173 K) by the presence of a peak at 111.2 ppm displaying a reduced coupling constant (*J*_{C–H} = 128 Hz) and by a 1D-gs-HMQC experiment. In ¹H NMR, a broad peak for both the hydride and the dihydrogen ligand is present at room temperature at –13.7 ppm. This signal displays a *T*_{min} of 16 ms at 243 K (*d*⁸-THF, 300 MHz). Below this temperature, a decoalescence is observed to give a triplet at –14.12 ppm (*J*_{P–H} = 18 Hz) for the hydride and a broad signal at –13.02 ppm for the dihydrogen ligand. The activation energy for this process was determined by line shape analysis to be Δ*G*[‡] = 42.0 ± 5.6

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(15) For full characterization of **2** and **3**, see Supporting Information.

(16) Crystal data for **2**: dark brown crystals, monoclinic, *P*₂₁/*n*, *a* = 15.232(3) Å, *α* = 90.26(3)°, *b* = 25.028(5) Å, *β* = 110.70(2)°, *c* = 19.142(4) Å, *γ* = 90.05(3)°; *V* = 6826(2) Å³; *Z* = 4; *R*[*I* > 2σ(*I*)] = 0.0357; GOF = 1.032.

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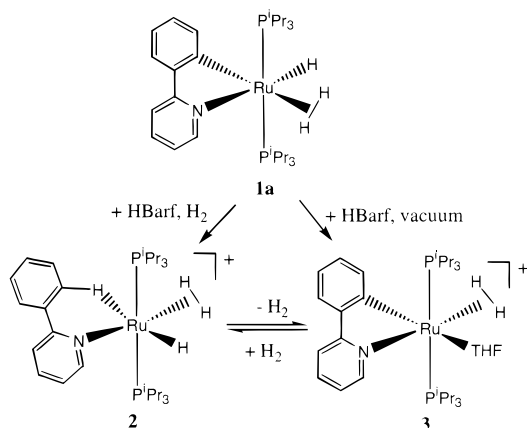
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Scheme 1. Protonation of **1a** in THF

$\text{kJ}\cdot\text{mol}^{-1}$ at 243 K. This is similar to what has been observed with **1a**, but in the present case, no exchange couplings are observed.¹⁰ Upon deuteration, a $J_{\text{H-D}}$ of 23 Hz can be estimated for coordinated H–D. In the aromatic region, broad peaks are observed at 6.18 and 7.95 ppm at room temperature. A decoalescence is observed below 243 K into peaks at 4.14 and 8.22 ppm and 7.87 and 8.30 ppm corresponding respectively to the protons H1b and H7 on one side and H8 and H10 on the other of the agostic phenyl ring. The chemical shift found for the frozen agostic proton H1b (4.14 ppm) is similar but shifted upfield compared to that observed by Crabtree in an agostic diphenylpyridine ligand (5.83 ppm).⁶ These data indicate that the phenyl ring rotates around the C5–C6 axis with an activation barrier of $\Delta G^\ddagger = 42.1 \pm 5.9 \text{ kJ}\cdot\text{mol}^{-1}$ (243 K). This value gives an upper limit for the bond dissociation energy of the agostic interaction, quite low in this case.

2 transforms into a new complex **3** if H_2 is removed from the THF solution by pumping or upon heating at ca. 65 °C in an NMR tube a d^8 -THF solution of **2** (Scheme 1). The reaction can be reversed when the resulting solutions are placed under an H_2 atmosphere or left standing for several hours at room temperature. We failed to isolate **3** but we could study its spectroscopic properties by NMR spectroscopy. **3** displays a broad hydride signal at -7.53 ppm (2H, $T_{1\text{min}} = 11 \text{ ms}$, d^8 -THF, 263 K, 300 MHz) and a characteristic ^{13}C NMR spectrum for an ortho-metalated phenylpyridine ligand ($\delta \text{C}(11)$: 169.0 ppm, br s).¹⁵ Upon deuteration, the hydride signal transforms into a 1:1:1 triplet ($J_{\text{H-D}} = 27 \text{ Hz}$) in agreement with the presence of an unstretched dihydrogen ligand. **3** results from the elimination of H_2 from **2** and from its probable replacement by THF. This reaction resembles both the proposal of Milstein,⁴ namely the deprotonation of an agostic aromatic C–H bond, here assisted by the presence of a hydride, and the proposed intermediate in the fluxional process of Crabtree.⁶ By placing **2** under a deuterium atmosphere, we observe the exclusive deuteration of the ortho positions of the phenyl ring of phenylpyridine hence demonstrating the presence of an equilibrium between the metalated and the agostic form of **2**.

DFT calculations (B3PW91) on these reactions have been carried out using PH_3 as an approximate quantum model.¹⁸ The optimized structure **4**, as a model for **2**, is in excellent agreement with the crystal structure of **2** (Figure 2). Most noticeably, the H_2 ligand ($\text{H}–\text{H} = 0.889 \text{ \AA}$) in **4** is cis to the agostic C–H bond as observed in **2**.

The optimized transition state, **TS**_{4,5}, for the proton-transfer reaction has an energy 25 $\text{kcal}\cdot\text{mol}^{-1}$ above the starting complex **4** due to the lengthening of the C–H bond and to the concomitant transfer of one proton from the H_2 ligand to the hydride. The transfer terminates with the formation of the bis dihydrogen intermediate **5** (Figure 2) lying 6.8 $\text{kcal}\cdot\text{mol}^{-1}$ above **4** and which

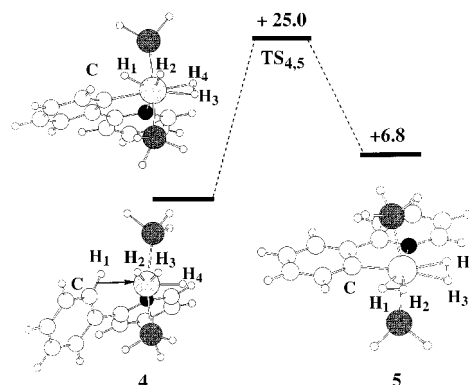


Figure 2. Calculated reaction pathway for the equilibrium between the hydrido dihydrogen agostic form (**4**) and the metalated bis(dihydrogen) form (**5**). Distances (Å): **4**, Ru–H1 2.105, C–H1 1.108, Ru–N 2.109, Ru–H2 1.702, H2–H3 0.887, Ru–H4 1.566, Ru–P 2.353; **5**, Ru–C 2.064, Ru–H1 1.720, H1–H2 0.855, Ru–N 2.087, Ru–H3 1.843, H3–H4 0.818, Ru–P 2.364.

therefore cannot accumulate. **TS**_{4,5} is formally a ruthenium(IV) derivative and hence the C–H activation proceeds through an oxidative addition. The complex resulting from H_2 dissociation from **4** has an energy 25.9 $\text{kcal}\cdot\text{mol}^{-1}$ above **4**, and therefore, a pathway involving proton transfer through this intermediate is ruled out. No pathway has been found for a direct transfer involving deprotonation of the agostic C–H bond.

The reaction $\mathbf{4} \rightleftharpoons \mathbf{5}$ and the easy rotation of dihydrogen¹⁹ allow the exchange between the agostic ortho hydrogens and all the hydrogen atoms bonded to Ru and hence D_2 scrambling. Complex **6**, $[\text{Ru}(\text{H}_2)(\text{Me}_2\text{O})(o\text{-C}_6\text{H}_4\text{py})(\text{PH}_3)_2]^+$ was optimized as a model for **3**. Me_2O (the model for THF) was located in place of the less bound dihydrogen ligand, H3–H4 (see Figure 2). The H–H distance in **6** is 0.867 Å and the equilibrium $\mathbf{4} + \text{Me}_2\text{O} \rightleftharpoons \mathbf{6} + \text{H}_2$ is endothermic by 4.8 $\text{kcal}\cdot\text{mol}^{-1}$. This study therefore suggests the presence of an equilibrium between **2** and an unobserved bis(dihydrogen) species which would readily react with an ether to substitute H_2 . This agrees with the above-described experimental observations and THF coordination is the driving force enabling the transformation of the agostic hydride complex **2** into the metalated dihydrogen species **3**.

In conclusion, we describe in this paper a novel complex, **2**, accommodating both a dihydrogen ligand and a weak agostic bond, for which no precedent is known. Complex **2** is in equilibrium with a metalated bis(dihydrogen) species which cannot be directly observed but a derivative of which (**3**), resulting from the substitution of one dihydrogen ligand by THF, can be stabilized. This process displays a low activation energy because of the simultaneous presence of cis hydride and dihydrogen ligands enabling the proton transfer although the activation step is a classical oxidative addition. The ease of this transformation can give rise to an interesting reactivity for aromatic hydrocarbon functionalization which is presently being studied.

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Supporting Information Available: Experimental section for the preparation of **2** and **3**, full spectroscopic data, computational details, and X-ray analysis of **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) The structure **5**_{perp}, where both H_2 ligands are rotated by 90°, has been optimized as a transition state only 1.5 $\text{kcal}\cdot\text{mol}^{-1}$ above **4**. Such small differences in energy have been found already for $\text{RuH}_2(\text{H}_2)_2(\text{PH}_3)_2$.^{19c} (a) Eckert, J. *Spectrochim. Acta* **1992**, *48A*, 363. (b) Clot, E.; Eckert, J. *J. Am. Chem. Soc.* **1999**, *121*, 8855. (c) Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Thoburn, J.; Ulrich, S.; Limbach, H. H.; Barthelat, J.-C.; Hussein, K.; Marsden, C. *Inorg. Chem.* **1998**, *37*, 3475. (d) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 834.

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