Exchange Couplings between a Hydride and a Stretched Dihydrogen Ligand in Ruthenium Complexes

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Over 10 years after the Kubas discovery, the chemistry of dihydrogen has proven to be far more complex than originally thought. Thus coordinated dihydrogen can be unstretched, stretched, electrophilic, or even superacidic.[1] The study of the reactivity of stretched dihydrogen derivatives, which are known in particular in the chemistry of rhenium, ruthenium, and osmium, has remained relatively unexplored.[1c,2] We have studied for a few years the reactivity of ruthenium dihydrogen complexes and have demonstrated that, whereas dihydrogen substitution and hydrogen transfer is easy on $RuH_2(H_2)_2(PCy_3)_2$ (**1**),[3] the related complexes $RuH(H_2)(LX)(PCy_3)_2$ (LX = $o\text{-}OC_5H_4N$, pyO, **2**; LX = $o\text{-}NHC_5H_4N$, pyNH, **3**) which accommodate a stretched dihydrogen ligand are found to be much less reactive.[4] In addition, stretched dihydrogen ligands may experience a high rotation barrier[5] that we have demonstrated, at least in the case of tantalum[6] and niobium,[7] to be related to the existence of large quantum mechanical exchange couplings.[6,8,9]

Exchange couplings have been previously observed in di- and trihydride complexes[8,9] and in tantalum[6] and niobium[7] dihydrogen complexes. We now report the synthesis of a series of hydrido orthometalated dihydrogen complexes showing exchange couplings as well as preliminary catalytic activity for the coupling of ethylene to functional arenes (Murai's reaction).[10]

Phenylpyridine reacts rapidly at room temperature in pentane with **1** to yield the new compound $RuH(H_2)(Ph\text{-}py)(PCy_3)_2$ (Ph-py = $o\text{-}C_6H_4C_5H_4N$, **4**) as a slightly soluble orange powder (see Scheme 1). The analogous and more soluble triisopropylphosphine derivative $RuH(H_2)(Ph\text{-}py)(P^iPr_3)_2$ (**5**) could be prepared directly from Ru(COD)(COT) (COD = 1,5 cyclooctadiene, COT = 1,3,5-cyclooctatriene), P^iPr_3, and dihydrogen.[11] Substitut-

Scheme 1. New Orthometalated Ruthenium Complexes
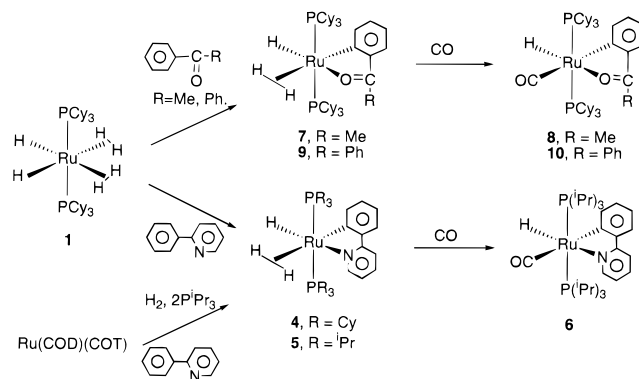
ing H_2 by CO in **5** leads to $RuH(CO)(ph\text{-}py)(P^iPr_3)_2$ (**6**). Full characterization of the complexes is given in the Supporting Information. The similarity of ^{31}P and ^{13}C NMR data (triplets for metalated carbon respectively at 197.0 ppm, $J_{P–C} = 10.6$ Hz and 192.0 ppm, $J_{P–C} = 13.1$ Hz) demonstrates that **5** and **6** are isostructural. The only difference is their high-field ^1H NMR spectra: broad triplet at −8.59 ppm for **5** ($J_{P–H} = 12.3$ Hz, 3 H; $T_{1 min} = 22$ ms at 258 K, 400 MHz, C_7D_8) and sharp triplet at −12.50 ppm ($J_{P–H} = 24.6$ Hz, 1 H; $T_{1 min} = 202$ ms at 233 K, 250 MHz, C_7D_8) for **6**. The calculation of the H−H bond length in **5**, using **6** as a reference for all effects other than H−H distance,[12] gives a value of 1.08 Å (slow rotation hypothesis, 0.83 Å for rapid rotation hypothesis), close to that found by X-ray and NMR for $RuHI(H_2)(PR_3)_2$ (R = Cy, ^iPr), 1.03 Å,[11,13] and much less than that found for **2** and **3**, ca.1.3 Å.[4] In the ^1H NMR spectra of **4** and **5** we observe at low temperature the decoalescence of the high-field signal into an AB_2 spin system at −12.1 and −6.1 ppm ($\Delta G^\ddagger$ 39.8 kJ mol^{-1}) displaying quantum mechanical exchange couplings clearly visible for **5** between 218 K ($J_{HA–HB} = 308$ Hz) and 188 K ($J_{HA–HB} = 141$ Hz; see Figure 1). After the decoalescence, the relaxation time of H_A is always observed to be longer than that of H_B (198 K: H_B $\delta_{-6.1}$, 69 ms; H_A $\delta_{-12.1}$, 87 ms; 208 K: H_B $\delta_{-6.2}$, 34 ms; H_A $\delta_{-12.2}$, 38 ms) but both signals remain in exchange as evidenced by T_1 averaging.[14] **4** displays similar features, but they are more difficult to observe because of low solubility and the large correlation time of PCy_3 complexes. As stated above, complexes **5** and **6** display very

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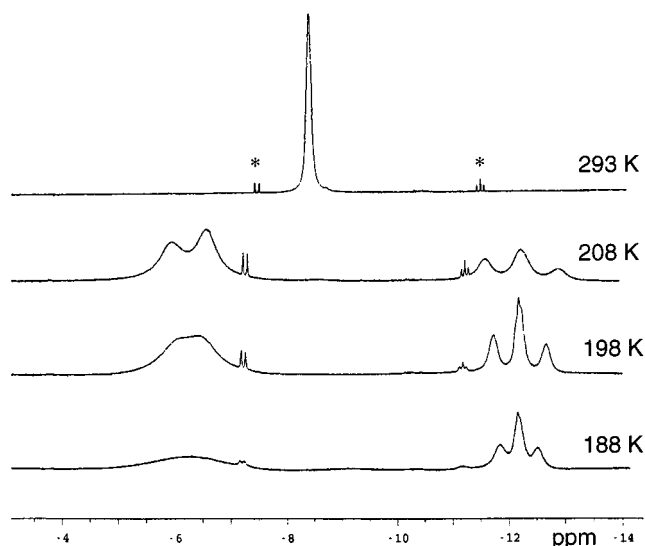
Figure 1. High-field $\{^{31}P\}^1H$ NMR spectrum of **5** (400 MHz, C_7D_8) at variable temperatures (asterisks denote impurities).

similar spectroscopic features. The chemical shift after decoalescence and, more importantly, the H–P coupling constant of H_A (−12.1 ppm, t, J_{P-H} = 22.5 Hz for **5**) are also very similar to those of the hydride of **6**, which suggests that the H_A signal in **4** and **5** is due to the hydride. The H_B signal would result from the coordinated dihydrogen molecule, in agreement with the lower T_1 measured for H_B compared to H_A below the decoalescence temperature. The calculated H–P coupling constant of H_B (ca. 7 Hz) is also in agreement with this proposal. The origin of this novel phenomenon is the presence of an exchange process between the hydride and one of the hydrogens of the dihydrogen molecule, the barrier for this process being 39.8 kJ·mol^{-1}. A possibility for explaining it involves the presence of a weak bonding interaction between the hydride and the coordinated dihydrogen molecule as previously proposed by Eisenstein et al.[15]

Compounds **4**–**6** are reminiscent of the intermediates proposed by Murai for the insertion of olefins into aromatic C–H bonds located in ortho position relative to a coordinating group such as ketone, amine, or pyridine.[10] A similar reaction has recently been used by Trost et al. for elaborating conjugated alkenes.[16] A mechanism is proposed which involves the intermediacy of an orthometalated species but which has not been substantiated by the isolation of any intermediate.[17] Such a chemistry can find useful applications in organic synthesis.[18,19] These studies led us to prepare the analogous complexes using acetophenone and benzophenone, namely $RuH(L)(o\text{-}C_6H_4X)(PCy_3)_2$ (X = C(O)Me;

L = H_2, **7**; L = CO, **8**; X = C(O)Ph, L = H_2, **9**; L = CO, **10**). Whereas **7** reacts stoichiometrically with triethoxyvinylsilane at room temperature to give the monoinsertion product $MeC(O)\text{-}C_6H_4(CH_2)_2Si(OEt)_3$, catalytic insertion of ethylene (20 bar) is achieved *at room temperature* with both acetophenone and benzophenone using **1** or **7** as the catalyst precursor (see eq 1).[20−22] Acetophenone gave selectively the monoinsertion product, whereas benzophenone led mainly to the bis-insertion product, 2,2′-diethylbenzophenone. Up to 19 turnovers could be achieved in 48 h in the case of benzophenone. Interestingly, complex **10** does not show any stoichiometric or catalytic activity, which substantiates the suggestion by Trost that CO must be excluded from the complex during the reaction.[16]
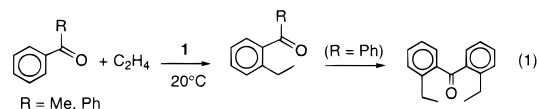
In conclusion, we describe the synthesis of a new series of ruthenium hydride and dihydrogen derivatives which, besides being a rare case of a dihydrogen complex incorporating a sp^2 metal carbon σ bond,[23] displays two novel features. After decoalescence of the hydride and dihydrogen signals,[24] it is possible to observe in these complexes, for the first time, exchange couplings between a hydride and protons of a coordinated dihydrogen molecule. The second novel feature is the coupling of ethylene to functional arenes which is catalytic at room temperature in the presence of our complexes (Murai's reaction occurs at 135 °C). The mild conditions could significantly increase the scope of this reaction and confirm that complexes such as **7** are true intermediates in the catalytic cycle postulated by Murai.

Supporting Information Available: Experimental data for compounds **4**−**10**, ^1H NMR spectra of the partially deuterated **5**, and scheme showing the exchange process in **5** (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

(14) It was possible to determine on the spectrum that the line width of the HD signal was larger than that of the H signal in RuH(HD)-(Ph-py)(P^{i}Pr$_3$)$_2$ and was compatible with an H–D coupling of up to ca. 25 Hz. Furthermore, it was possible to determine that under the same conditions (C$_7$D$_8$, 400 MHz) at 188 and 193 K the J_{H-H} couplings were respectively ca. 124 and 149 Hz for RuH(HD)(Ph-py)(P^{i}Pr$_3$)$_2$ and ca. 141 and 168 Hz for RuH(H$_2$)(Ph-py)(P^{i}Pr$_3$)$_2$. It is noteworthy that the influence of partial deuteration on exchange couplings is the reverse of the usual observation in dihydridodeutero complexes of iridium or ruthenium.[9] (a) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909. (b) Manzano, B.; Jalon, F.; Matthes, J.; Sabo-Etienne, S.; Chaudret, B.; Ulrich, S.; Limbach, H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3153.

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