Influence of Hydrogen Bonding on the Spectroscopic Properties and on the Reactivity of Ruthenium Hydrido Dihydrogen Complexes

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The reaction of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with L−X in pentane at room temperature yields new hydrido derivatives of ruthenium accommodating a stretched H−H bond, namely $RuH(H_2)(L-X)(PCy_3)_2$ (L−X = C_5H_4N-O, **2**; L−X = C_5H_4N-NH, **3**). NMR studies show that hydrogen bond donors (substituted phenols, hexafluoro-2-propanol, etc.) interact with the hydrides in the case of **2**, whereas for **3** an equilibrium with the cation $[RuH(H_2)(py\text{-}NH_2)(PCy_3)_2]^+$ is attained. The latter species has been isolated in the form of the $[B(C_6F_5)_4]$ salt, **4**, independently prepared by addition of $(PhNMe_2H)[B(C_6F_5)_4]$ to **3**. These phenomena explain the difference of reactivity with olefins between **2** and **3** in nonpolar media or in the presence of alcohols.

The presence of hydrogen bonds between a transition metal hydride and a hydrogen bond donor containing an O−H or an N−H group has recently been established intramolecularly by Crabtree[1] and Morris[2] and intermolecularly by Crabtree in the solid state[3] and Epstein and Berke in solution.[4] We have been interested in studying the modification of the spectroscopic properties of the hydrides induced by the presence of hydrogen bonds. In this respect, we have recently shown that hydrogen bonding to $Cp^*(PCy_3)RuH_3$ leads in solution to an enhancement of the exchange couplings present in this complex[5] and have suggested that exchange couplings are good sensors for the establishment of hydrogen bonds. A further step was to study the modification of reactivity induced by the presence of such interactions. This proved possible in the case of the mixture of *trans*- and *cis*-$RuH_2(dppm)_2$. Thus both isomers of this dihydride give hydrogen bonds to alcohols and phenol but only the hydrogen-bonded *trans*-isomer gives rise to an equilibrium with a hydrido dihydrogen complex.[6]

A system incorporating both a hydride and a stretched dihydrogen ligand should be particularly interesting for this study, given the sensitivity of dihydrogen coordination to small modification of the electronic density on the metal. However when a complex incorporates other functional groups, the establishment of hydrogen bonds with other ligands can also occur and have an influence on dihydrogen coordination.

We have described recently in a preliminary communication[7] the synthesis of a series of complexes accommodating stretched dihydrogen ligands,[8,9] with calculated H−H distances near 1.3 Å. We present here full details on the synthesis of two of these complexes, namely $RuH(H_2)(py\text{-}O)(PCy_3)_2$ (**2**) and $RuH(H_2)(py\text{-}NH)(PCy_3)_2$ (**3**) as well as their reactivity toward hydrogen bond donors and protonation.

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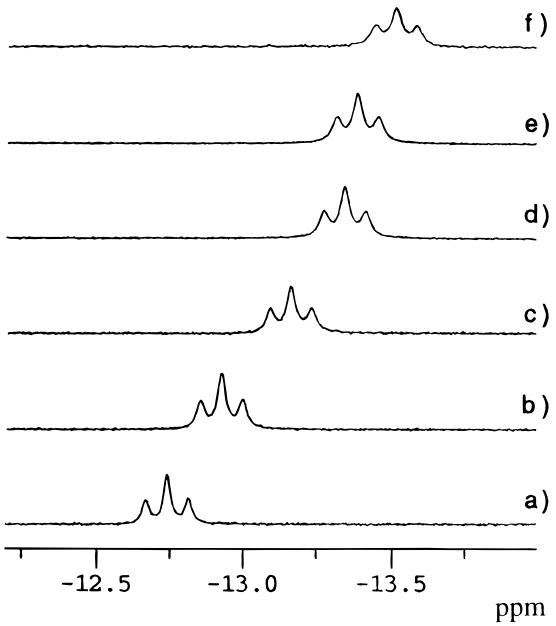
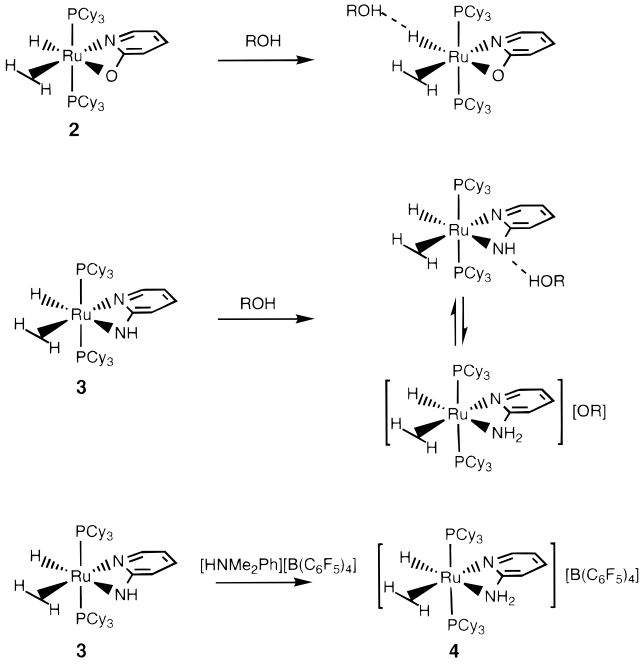


Figure 1. Evolution of the ^{1}H NMR spectrum of **2** in the hydride region: (a) **2**; (b) **2** + 0.55 equiv of HFP; (c) **2** + 1.86 equiv of HFP; (d) **2** + 3.0 equiv of HFP; (e) **2** + 6.0 equiv of HFP; (f) **2** + large excess of HFP.

Scheme 1



Results and Discussion

Synthesis of the Complexes. The reaction of a suspension of **1** in pentane with 1 equiv of L−XH [L = C_5H_4N (py); X = O, NH] yields solids analyzing for $RuH(H_2)(L-X)(PCy_3)_2$ (L−X = py−O, **2**; L−X = py−NH, **3**) (see Scheme 1). A high-field triplet is observed at −12.64 ppm (J_{PH} = 14.3 Hz, **2**) and −11.90 ppm (J_{PH} = 14.6 Hz, **3**) in the ^{1}H NMR, together with the characteristic resonances of the PCy_3 ligands and peaks for the heterocyles between 6 and 8 ppm. The presence of three ruthenium bound hydrogens is deduced both from the careful integration of the high-field signal and from partially decoupled ^{31}P NMR spectra (in which only the alkyl protons of the phosphines are irradiated). The latter displays a quartet pattern near 49 ppm. The relaxation times (T_1) of the hydride signals were measured (250 MHz, C_7D_8), and the minimum was found to be respectively 33 ms at 243 K for **2** and 36 ms at 233 K for **3**. Both complexes exchange readily H_2 by D_2, but only in the case of **3** did we succeed in measuring a J_{H-D} value which was found to be near 3 Hz. This value can be in agreement with a classical trihydride structure or the presence of a very stretched dihydrogen ligand for which a J_{HD} of 9 Hz within the coordinated HD molecule would be calculated by assuming no IPR effects. In that case, using the empirical equation developed by Morris, the corresponding H−H distance would be 1.27 Å.[10] Furthermore using relaxation data and as a reference the hydrido vinylidene complex $RuH(C{=}C(H)SiEt_3)(L-X)(PCy_3)_2$,[7] we could calculate distances of 1.28 and 1.30 Å for the dihydrogen ligands of **2** and **3** in agreement with their large elongation.[11]

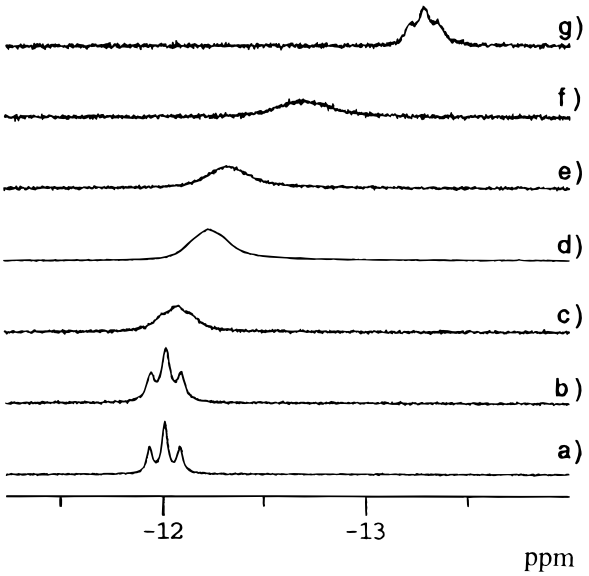


Figure 2. Evolution of the ^{1}H NMR spectrum of **3** in the hydride region: (a) **3**; (b) **3** + 0.45 equiv of HFP; (c) **3** + 0.8 equiv of HFP; (d) **3** + 1.5 equiv of HFP; (e) **3** + 2.0 equiv of HFP; (f) **3** + 3.5 equiv of HFP; (g) **3** + 4.5 equiv of HFP; (h) **3** + large excess of HFP.

Addition of Hydrogen Bond Donors. Addition of various hydrogen bond donors [trifluoroethanol, phenol, 4-iodophenol, 4-(trifluoromethyl)phenol, and hexafluoro-2-propanol (HFP)] at room temperature to complexes **2** or **3** leads to an upfield shift of the "hydride" signal of these complexes (the signal corresponding to the rapid interconversion of the hydride and dihydrogen ligands) in ^{1}H NMR as well as to a modification of the ^{31}P NMR spectrum. Tables 1 and 2 and Scheme 1 summarize the different observations. The shift can be related to the hydrogen bond donor ability of each alcohol which is linked but not simply to the acidity of the proton involved in hydrogen bonding.[5,12] Furthermore, the data reveal a significant difference between the chemical shift variations in the complexes, much larger in the case of **2** than in the case of **3**.

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Table 1. NMR Data for **2** in the Presence of Alcohol

alcohol	equiv of alcohol	δ (Ru−H) (ppm (Hz))	$\Delta\delta$(H) (ppm)	δ(P) (ppm)	$\Delta\delta$(P) (ppm)	δ(H) (ppm) for L−X (d/pt/d/pt)
		−12.74 (14.0)		49.12		8.06/7.11/6.28/6.23
phenol	2.20	−13.06 (14.0)	0.32	47.64	1.48	8.00/7.14/6.46/6.27
4-iodophenol	1.00	−13.00 (14.0)	0.26	48.07	1.05	8.01/7.07/6.32/6.27
	1.60	−13.08 (13.8)	0.34	47.69	1.43	8.00/7.05/6.36/6.27
	6.00	−13.20 (13.8)	0.46	47.24	1.88	7.97/7.03/6.40/6.27
4-(trifluoromethyl)phenol	1.00	−13.04 (14.0)	0.30	47.81	1.31	8.06/7.11/6.28/6.23
hexafluoro-2-propanol	0.55	−12.93 (14.2)	0.19	48.26	0.86	8.06/7.11/6.28/6.23
	1.86	−13.16 (13.8)	0.42	47.07	2.05	8.06/7.11/6.28/6.23
	3.00	−13.35 (14.0)	0.61	46.07	3.05	7.90/7.03/6.37/6.25
	6.00	−13.39 (13.8)	0.65	45.91	3.21	7.89/7.03/6.38/6.25
	>>	−13.52 (13.3)	0.78	45.6	3.52	7.89/7.03/6.38/6.25

Table 2. NMR Data for **3** in the Presence of Alcohol

alcohol	equiv of alcohol	δ(Ru−H) (ppm) (J_{H-P} (Hz))	$\Delta\delta$(H) (ppm)	δ(P) (ppm)	$\Delta\delta$(P) ppm	δ(H) (ppm): L−X (d/t/t/d); NH (s)
		−12.01 (14.7)		49.57		8.00/6.90/5.98/5.61; 3.74 (br)
1,1,1-trifluoroethanol	3.00	−12.03 (13.8)	0.01	49.57		7.99/6.89/5.98/5.62
phenol	3.00	−12.10 (br)	0.09	49.53	0.04	8.00/6.89/6.03/5.65; 4.63 (br)
hexafluoro-2-propanol	0.45	−12.01 (14.7)		49.55	0.02	8.00/6.90/5.98/5.61; 3.74
	0.80	−12.02 (14.7)	0.01	49.55	0.02	8.00/6.90/5.98/5.61; 3.74
	1.50	−12.07 (br)	0.05	49.33	0.24	8.00/6.90/5.98/5.61; 3.74
	2.0	−12.22 (br)	0.21	48.80	0.73	7.94/6.96/6.07/6 (br); 4.55 (br)
	3.5	−12.31 (br)	0.30	48.41	1.16	7.94/6.96/6.07/6 (br); 4.55 (br)
	4.5	−12.66 (br)	0.65	47.67	1.90	7.94/6.96/6.07/6 (br); 4.55 (br)
	>>	−13.26 (13.0)	1.25	44.81	4.76	7.94/6.96/6.07/6 (br); 4.55 (br)

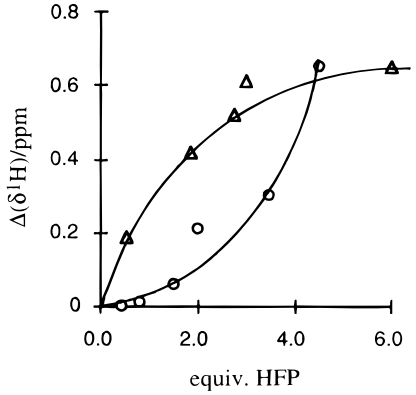

Figure 3. Plot of the ^{1}H NMR chemical shift variations of the hydride signal of **2** (△) and **3** (○) versus HFP concentration.

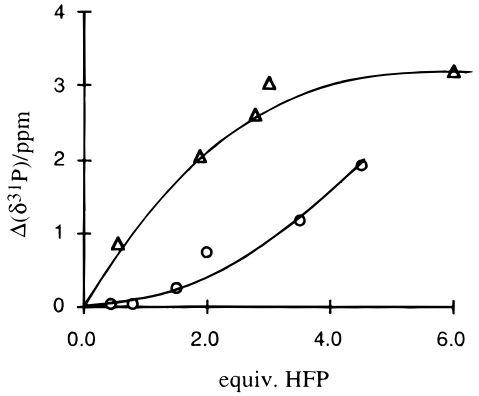

Figure 4. Plot of the ^{31}P NMR chemical shift variations for **2** (△) and **3** (○) versus HFP concentration.

To gain more insight into this phenomenon, a study of the chemical shift variation of the hydride signal of **2** and **3** was carried out at room temperature as a function of the concentration in hydrogen bond donor. For this purpose, we have chosen HFP which is the best hydrogen bond donor used in this study. The results are reported in Tables1 and 2 and Figures1−4. In the case of **2**, the chemical shift of the hydride signal appears to be very sensitive to a low concentration of HFP whereas at high HFP concentration a saturation is observed, a behavior typical of equilibria involving hydrogen bonds (see Figures 1 and 3).[5] At all steps of HFP addition, this signal remains a triplet. Broadening was observed upon measuring the ^{1}H NMR spectrum at lower temperature, but no evidence for a decoalescence process was obtained down to 183 K. The behavior of **3** contrasts with that of **2** since no significant chemical shift variation occurs upon addition of up to 1.5 equiv of HFP. However, upon increase of HFP concentration a broadening of the hydride signal occurs and finally at high HFP concentration a new broad triplet signal is observed which displays a reduced J_{H-P} coupling constant of 13 Hz (see Figures 2 and 3). The broad hydride signal resulting from the addition of 4.5 equiv HFP to **3** is due to a fast exchange between two interconvertible

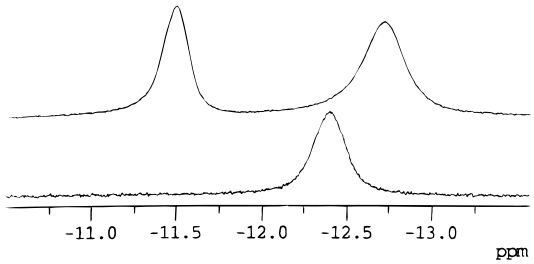

Figure 5. ^{1}H NMR spectrum in the hydride region for a mixture of **3** + 4.5 equiv of HFP: (top) at 213 K; (bottom) at 293 K.

species as evidenced by NMR spectroscopy recorded at 213 K (see Figure 5). At this temperature, again in contrast with the behavior of **2**, 2 peaks are clearly visible at −11.5 and −12.7 ppm on the high field ^{1}H NMR spectrum and at 53.2 and 50.2 ppm on the ^{31}P{^{1}H} NMR spectrum which coalesce upon warming the solution up to room temperature. The low-field ^{1}H NMR spectrum is also demonstrative of the decoalescence process between two similar complexes. The main difference is the splitting of a broad peak near 5.7 ppm at room temperature into three signals at 9.6, 5.45, and 4.05 ppm attributed respectively to the OH proton of the alcohol, to an NH_2 group,

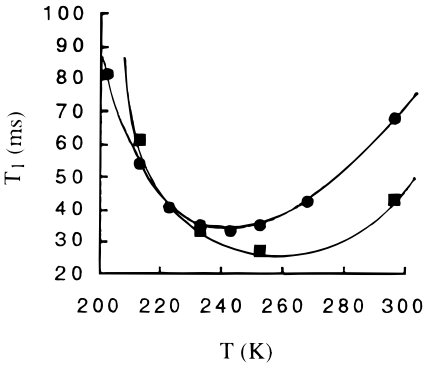

Figure 6. Plot of the T_1 values for **2** (●) and **2** + 3 equiv of 4-iodophenol (■) versus temperature (K).

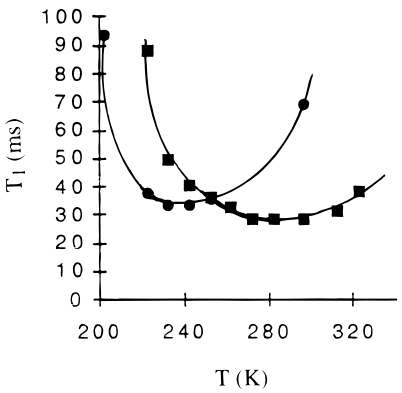

Figure 7. Plot of the T_1 values for **3** (●) and **4** (■) versus temperature (K).

and to the NH proton of **3**. These data suggest the presence of an equilibrium involving protonation of the coordinated amino group and therefore that hydrogen bonding in the case of **3** concerns the nitrogen lone pair rather than the hydride. The ^{31}P chemical shift variations observed for **2** and **3** as a function of the HFP concentration are reported in Figure 4. The resulting curves are comparable to the ones reported in Figure 3 for the ^{1}H chemical shifts.

To confirm the preceding hypothesis, we have investigated the protonation of **3** by $(HNMe_2Ph)[B(C_6F_5)_4]$, which was found to be the best agent. Addition of the salt to **3** at room temperature in toluene leads instantaneously to $[RuH(H_2)(py-NH_2)(PCy_3)_2][B(C_6F_5)_4]$ (**4**), which can be isolated after evaporation of the solvent and washing with pentane (see Scheme 1). The ^{1}H NMR spectrum recorded in toluene-d_8 shows the pyridine hydrogen located on the carbon α to nitrogen at 8.1 ppm, the amino protons at 4.55 ppm, and the hydride signal at −13.19 ppm. Integration of these three signals using a long repetition delay (20 s) in order to avoid relaxation problems confirmed the presence of respectively 1, 2, and 3 protons and hence the exclusive protonation on the amido ligand to give a coordinated amino group. The charge of the complex is then formally located on ruthenium. Interestingly, under the same conditions, the protonation reaction of **2** resulted in the loss of the hydride and dihydrogen ligands and formation of an oily unidentified compound.

Influence of Hydrogen Bonding and of Protonation on Hydride/Dihydrogen Relaxation. We have proposed on the basis of relaxation data and of measurements of J_{H-D} in partially deuterated isotopomers that complexes **2** and **3** contain a stretched dihydrogen ligand (ca. 1.3 Å). This system offers an unique opportunity to study the influence of hydrogen bonding and of a charge on dihydrogen coordination. However, we could only obtain T_1 data on **2**, **2**·HOR, **3** and **4** since protonation of **2** did not lead to a new dihydrogen complex and since the addition of HFP to **3** led to a dynamic equilibrium between **3** and **4**. In the latter case the relaxation data could result from T_1 averaging.

Figure 6 shows the relaxation curves of **2** and **2**·HOC_6H_4I (3 equiv). 4-Iodophenol was chosen for the study since, according to Table 1, it shows a large effect on the variation of chemical shift of the hydride signal of **2** and since it seems the best for measurements in toluene at various temperatures. The result is a slight decrease of the T_1 minimum value for **2**·HOC_6H_4I as compared to **2** (27 ms as compared to 33 ms) and a slight increase in the temperature of the minimum (253 K as compared to 243 K). The latter effect reveals the presence of a correlation time longer in the case of the adduct **2**·HOC_6H_4I than in pure **2** and is therefore in agreement with an association of the complex with the added phenol, likely through hydrogen bonding. The decrease in the relaxation time is small and could result from two factors, namely (i) excess relaxation due to a short distance between the phenol proton and the hydride and (ii) shortening of the H−H bond because of a decrease in the electronic density on the metal. The increase in relaxation is comparable to previous results obtained on a tungsten monohydride[4] or a ruthenium trihydride[5] and are therefore likely due to the proton/hydride interaction.

The relaxation curves for the "hydride" signals of **3** and **4** are shown in Figure 7. The difference in the relaxation time of the two signals (36 ms for **3**; 27 ms for **4**) is comparable to that observed for **2** and **2**·HOC_6H_4I. A larger influence of the presence of the cationic charge was expected as a result of the decrease of the electron density on the metal. However, precedent studies have shown that this effect can be small, such as for example for $[Re(H_2)(CO)_3(PCy_3)_2]^+$ compared to the isoelectronic $W(H_2)(CO)_3(PCy_3)_2$.[8a,13] However, the minimum temperatures were shown to be very different, namely 233 K for **3** and 270−280 K for **4**, in agreement with the longer correlation time expected for an ionic species containing a bulky counteranion and probably surrounded by strongly interacting solvent molecules.

In summary, the presence of hydrogen bonding has little or no influence, as previously observed, on the relaxation of the hydride ligands. In addition, it was unexpected to observe that the presence of a charge has also little influence on the relaxation of the hydride. However, the temperature of the T_1 minimum clearly reveals the protonation and suggests hydrogen bonding.

Influence of Hydrogen Bonding on the Reactivity of Hydrido Dihydrogen Complexes. We have recently reported that, in an aprotic solvent such as toluene, the reactivity of **2** and **3** was identical and furthermore that both complexes were little reactive. The only clear reaction was found with triethylvinylsilane which led to the hydrido vinylidene complexes $RuH(C{=}C(H)SiEt_3)(L-X)(PCy_3)_2$ (L−X = py−O, **5**; L−X = py−NH, **6**).[7] Since **2** and **3** behave differently in the presence of a hydrogen bond donor, it was of interest to study the reactivity of both compounds with vinylsilane in the presence of a hydrogen bond donor. The reaction was carried out in toluene as previously described except that 3 equiv of HFP was added to both reaction mixtures. The reactions were found very different. Thus after 72 h at room temperature most of **2** was recovered unchanged whereas **3** reacted rapidly to give after complete hydride loss a mixture of unidentified compounds.

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This demonstrates that the presence of hydrogen bonding to a hydride has an inhibiting effect on the reactivity of the cis hydrido dihydrogen complex **2**. We favor a steric explanation for this effect; i.e., the presence of hydrogen bonding impedes the access to the reactive site. On the contrary, when hydrogen bonding and/or proton transfer occurs on a ligand, the electronic effect of the charge leads to an enhancement and a modification of the reactivity, even if little changes in the spectroscopic properties of the complex are visible.

Conclusion

This study demonstrates that two complexes displaying exactly the same spectroscopic properties and the same reactivity in an aprotic solvent can behave very differently when hydrogen bonding is present. The presence of noncovalent interactions is well-known for directing the course of organic or bioorganic reactions. We report here an example of such an effect in organometallic chemistry.

Experimental Section

All reactions were carried out under argon by using Schlenk glassware and vacuum line techniques. All solvents were freshly distilled from standard drying agents and thoroughly degassed under argon before use. Microanalyses were performed by the Laboratoire de Chimie de Coordination Microanalytical Service. NMR spectra were recorded on a Bruker AC200 (at 200.13 MHz for ^{1}H, at 188 MHz for ^{19}F, and at 81.015 MHz for ^{31}P) and on a Bruker AMX400 (at 100.62 MHz for ^{13}C), while variable-temperature proton spectra were obtained by using a Bruker AM 250 (at 250.134 MHz), all these spectrometers operating on the Fourier transform mode. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey Ltd. $RuH_2(H_2)_2(PCy_3)_2$ **(1)** was made according to the procedure described in ref 14.

Preparation of $RuH(H_2)(pyO)(PCy_3)_2$ (2). To a suspension of $RuH_2(H_2)_2(PCy_3)_2$ **(1)** (244 mg; 0.37 mmol) in 20 mL of pentane was added 2-hydroxypyridine (35 mg; 0.37 mmol) at room temperature. The reaction was allowed to react for 1 h, during which a white solid precipitated. The white precipitate was then filtered off, washed with 5 mL of pentane, and dried in vacuo. Yield: ca. 93%. Anal. Calcd for $RuC_{41}H_{73}P_2ON$: C, 64.88; H, 9.69; N, 1.85. Found: C, 64.40; H, 10.03; N, 2.39. IR (cm^{-1}, Nujol): 2019, 2031 (m, ν_{Ru-H}). ^{1}H NMR (200.13 MHz, C_6D_6, 296 K; δ): 8.16 (d), 7.16 (pt), 6.38 (pt), 6.34 (d) (4H, all for py); 1.2−2.2 (m, 66H, PCy_3); −12.64 (t, 3H, $^{2}J_{PH}$ = 14.3 Hz, $RuH(H_2)$). $T_{1(min)}$ (250.13 MHz, 243 K): 33 ms. ^{31}P{^{1}H(PCy_3)} NMR (81.01 MHz, C_6D_6, 296 K; δ): 49.1 (q, J_{PH} = 14 Hz). ^{13}C NMR (50.32 MHz, C_6D_6, 296 K; δ): 108.8 (d, J_{CH} = 164 Hz), 110.9 (d, J_{CH} = 163 Hz), 136.4 (d, J_{CH} = 157 Hz), 149.9 (d, J_{CH} = 170 Hz) (all for py).

Preparation of $RuH(H_2)(pyNH)(PCy_3)_2$ (3). Synthesis was as above, but using **1** (258 mg; 0.39 mmol) and 2-aminopyridine (37 mg; 0.39 mmol). A pale green precipitate was obtained in 91% yield. Anal. Calcd for $RuC_{41}H_{74}P_2N_2$: C, 64.96; H, 9.84; N, 3.69. Found: C, 64.75; H, 9.95; N, 3.57. IR (cm^{-1}, Nujol): 2015 (m, ν_{Ru-H}). ^{1}H NMR (200.13 MHz, C_6D_6, 296 K; δ): 8.11 (d), 7.04 (pt) 6.09 (pt), 5,72 (d) (4H, all for py); 3.85 (s, 1H, NH); 1.3−2.3 (m, 66H, PCy_3); −11.90 (t, 3H, $^{2}J_{PH}$ = 14.6 Hz, $RuH(H_2)$). $T_{1(min)}$ (250.13 MHz, 233 K): 36 ms. ^{31}P-{^{1}H} NMR (81.01 MHz, C_6D_6, 296 K; δ): 49.5 (s). ^{13}C (50.32 MHz, C_6D_6, 296 K; δ): 104.0 (d, J_{CH} = 163 Hz), 108.0 (d, J_{CH} = 157 Hz); 134.1 (d, J_{CH} = 157 Hz), 151.5 (d, J_{CH} = 172 Hz), 169.9 (s) (all for py).

Preparation of $[RuH(H_2)(pyNH_2)(PCy_3)_2][B(C_6F_5)_4]$ (4). To a solution of $RuH(H_2)(pyNH)(PCy_3)_2$ (85 mg; 0.11 mmol) in 15 mL of toluene was added $[PhNMe_2H][B(C_6F_5)_4]$ (90 mg; 0.11 mmol) at room temperature. The reaction was allowed to react for 1 h, during which the solution became yellow. The solvent was evaporated under vacuum and the resulting yellow solid was washed with 10 mL of pentane and dried in vacuo. Yield: ca. 88%. Anal. Calcd for $RuC_{65}H_{75}P_2N_2BF_{20}$: C, 54.29; H, 5.26; N, 1.95. Found: C, 54.11; H, 6.15; N, 1.77. ^{1}H NMR (200.13 MHz, C_7D_8, 296 K; δ): 8.09 (d), 7.46 (m), 6.89 (m) (4H, py); 4.55 (br, 2H, NH_2); 1.09−1.95 (m, 66H, PCy_3); −13.19 (br, 3H, $RuH(H_2)$). ^{31}P{^{1}H} NMR (81.01 MHz, C_7D_8, 296 K; δ): 49.7. ^{13}C NMR (100.62 MHz, C_7D_8, 296 K; δ): 149.4 (d, J_{CF} = 242 Hz), 140.5 (br), 137.3 (d, J_{CF} = 137.3 Hz) (all for $B(C_6F_5)_4$); 155.2, 152.2, 126.1, 121.0 (all for py). ^{19}F NMR (188 MHz, C_7D_8, 296 K; δ): −55.5 (br), −86.5 (t, J_{FF} = 17.5 Hz.), −90.2 (br) (all for $B(C_6F_5)_4$). $T_{1(min)}$ (250.13 MHz, 283 K): 28 ms.

NMR Experiments. NMR experiments were carried out in screw-thread cap NMR tubes with a septum allowing addition of reactants via a syringe. In a typical experiment, the NMR spectrum of a solution of **2** in benzene was recorded. Then, 0.55 equiv, 1.31 equiv (leading to a total amount of 1.86 equiv), 1.14 equiv (leading to a total amount of 3.0 equiv), 3.0 equiv (leading to a total amount of 6.0 equiv), and finally an excess of HFP (>10 equiv) were successively added to the same NMR tube. Successive NMR spectra were recorded after shaking the tube.

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