Synthesis and Reactivity of Hydridotris(pyrazolyl) Borate Dihydrogen Ruthenium Complexes

Beatriz Moreno,[†] Sylviane Sabo-Etienne,[†] Bruno Chaudret,*[,†] Ana Rodriguez,[‡] Felix Jalon,[‡] and Swiatoslaw Trofimenko[§]

Contribution from the Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France, the Departamento de Quimica Inorganica, Universidad de Castilla−La Mancha, Campus Universitario, 13071 Ciudad Real, Spain, and the DuPont Company, Experimental Station 302/216, Wilmington, Delaware 19880-0302

Received March 10, 1995[®]

Abstract: The reaction of various hydridotris(pyrazolyl) borate salts with RuHCl(COD)(bpm) (**3**) (bpm = bispyrazolylmethane; COD = 1,5-cyclooctadiene) produces LRuH(COD) (L = hydridotris(3,5-dimethylpyrazolyl) borate, Tp*, **4a**; hydridotris(3-isopropyl-4-bromopyrazolyl) borate, Tp′,**4b**). Hydrogenation of **4a,b** under 3 bar of dihydrogen in pentane yields $LRuH(H_2)_2$ in high yield (L = Tp*, **5a**; L = Tp′, **5b**). **5a,b** were characterized by classical analytical and spectroscopic methods including T_1 measurements (**5a**, $T_{1\min}$ = 26 ms at 163 K, 400 MHz; **5b**, $T_{1\min}$ = 28 ms at 182 K, 300 MHz) and by partial deuteration leading to the sequential observation of the series of isotopomers $LRuH_{5-x}D_x$ ($x = 1-4$). The observed J_{H-D} coupling constant in these isotopomers of **5a** and **5b**, respectively 5.4 and 5.2 Hz, allows the calculation of J_{H-D} of coordinated hydrogen deuteride, namely 27 and 26 Hz, in agreement with two unstretched dihydrogen ligands. Hydrogenation of **4a** or **4b** in the presence of a ligand L′ or substitution of H_2 by L′ in **5a** or **5b** leads to the new hydrido dihydrogen complexes $LRuH(H_2)L'$ (L′ = PCy_3, L = Tp*, **6a**; L = Tp′, **6b**; L′ = THT, L = Tp*, **7a**; L = Tp′, **7b**; L′ = py, L = Tp*, **8a**; L = Tp′, **8b**; L′ = $NHEt_2$, L = Tp*, **9a**). Hydrogenation of **4a** in the presence of excess ligand L′ leads to the disubstituted complexes Tp*RuH-$(L')_2$ (L′ = py, **10a**; L′ = THT, **11a**). T_1 measurements for **10a** and **11a** allow the determination of the relaxation for a monohydride in these systems, and thus the calculation of the H−H distance of the coordinated dihydrogen molecules in **5a**−**9a** yields values in each case near 0.9 Å. Substitution of H_2 in **5a** occurred with CO to yield $Tp^*RuH(CO)_2$ (**12a**). Surprisingly, **5a** does not react with CH_3I, CH_3COOH, and CF_3COOH but does with $HBF_4{\cdot}Et_2O$ and CF_3SO_3H. The latter reaction leads in the presence of MeCN to $[Tp^*Ru(MeCN)_3](CF_3SO_3)$ (**14a**). Finally, both **5a** and **5b** readily undergo H/D exchange at room temperature between deuterated aromatic solvents (C_6D_6 or $C_6D_5CD_3$) and both the ruthenium bound hydrogens and the methyl and pyrazolyl groups of the ligands, thus demonstrating the high reactivity of these compounds for C−H activation.

Interest in the chemistry of transition metal "polyhydrides" has developed considerably during the past few years. Several reasons are at the origin of this development. First, these compounds can adopt a variety of structures (coordination of only hydrides or of one or two dihydrogen molecules) that greatly influence their reactivity.[1−6] Several techniques are now available besides X-ray or neutron diffraction to assign the mode of coordination of dihydrogen, namely spectroscopic methods (NMR in solution: measurement of the longitudinal relaxation time T_1, measure of J_{H-D}; solid state NMR; infrared spectroscopy)[1−4] as well as inelastic neutron scattering.[7] Furthermore, complexes displaying a classical ground state can exhibit anomalous spectroscopic properties assigned to quantum mechanical exchange of hydrogens in the coordination sphere of transition metals, possibly as a result of the existence of a thermally accessible dihydrogen state.[8,9] Finally, these compounds can lose H_2 thermally, photolytically, or upon protonation to give unsaturated species able, for example, to activate C−H bonds and perform hydrogen transfer reactions.[3]

In recent years, the chemistry of hydride and dihydrogen complexes containing nitrogen donor ancillary ligands instead of the usual phosphines has been particularly studied.[10] Thus, substituted hydridotris(pyrazolyl) borate ligands[11] were shown to stabilize polyhydride complexes of high coordination number,[12] to favor dihydrogen coordination as for $[TpIrH(H_2)$-

---

[†] CNRS.

[‡] Universidad de Castilla La−Mancha.

[§] DuPont Co.

[®] Abstract published in *Advance ACS Abstracts*, June 15, 1995.

(1) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(2) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 295. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (c) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

(3) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(4) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

(5) Burdett, J. K.; Eisenstein, O.; Jackson, S. A. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1991; p 149.

(6) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135/136*, 845.

(7) Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993**, *97*, 2378.

(8) For the quantum mechanical nature of exchange couplings, see: (a) Jones, D. H.; Labinger, J. A.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 3087. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G. *J. Am. Chem Soc.* **1989**, *111*, 3088. (c) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Neshyba, S. P.; Duchamp, J. C.; Szcyrba, J. *J. Am. Chem. Soc.* **1990**, *112*, 920.

(9) For the relation between exchange couplings and the existence of a dihydrogen state, see: (a) Barthelat, J. C.; Chaudret, B.; Daudey, J. P.; De Loth, P.; Poilblanc, R. *J. Am. Chem. Soc.* **1991**, *113*, 9896. (b) Limbach, H.-H.; Scherer, G.; Maurer, M.; Chaudret, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1369. (c) Limbach, H.-H.; Ullrich, S.; Buntkowsky, G.; Sabo-Etienne, S.; Chaudret, B. Submitted for publication.

(10) (a) Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guilard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654. (b) Harman, W. D.; Taube H. *J. Am. Chem. Soc.* **1990**, *112*, 2261. (c) Hasegawa, T.; Li, Z.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352.

(11) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. (c) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497. (d) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

0002-7863/95/1517-7441$09.00/0

$(PMe_3)]^+$[13] and Tp^*IrH_4,[14] or even to stabilize dihydrogen derivative complexes which would not exist otherwise, such as $Tp^*RhH_2(H_2)$.[15]

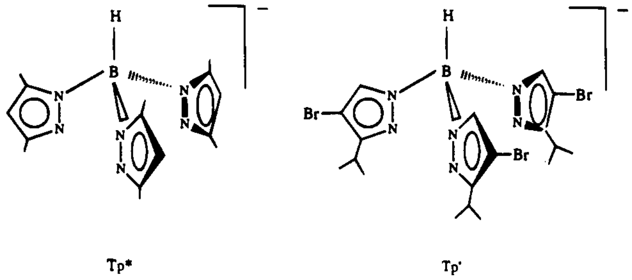
We have developed in our group for several years the chemistry of polyhydride complexes of ruthenium, which includes the synthesis and reactivity of a thermally stable bis(dihydrogen) complex,[16] the synthesis of 16-electron dihydrogen derivatives,[17] and the preparation of trihydrides displaying exchange couplings.[18] In an effort to introduce the Tp ligands into the ruthenium polyhydride chemistry, we have prepared the complexes $LRuH(H_2)(PCy_3)$ by reaction of KL (L = Tp, Tp*) with $RuHI(H_2)(PCy_3)$.[19] However, the yield of the reaction was low and the cumulative yield very low. Thus, although new ruthenium complexes containing Tp ligands have been synthesized in recent years,[20] these compounds contain coligands such as CO, PR_3, arene, or Cp groups which prevent a general access to complexes containing weakly coordinated ligands, to polyhydrides, or to unsaturated fragments similar to "Cp^*Ru^+".[21]

In search of a general entry into Tp[Ru] chemistry, we considered a pathway starting from the polymeric compound $[RuCl_2(COD)]_n$ (**1**). Thus, some of us showed that the reaction of **1** with bis(pyrazolyl)methane (bpm) led to $RuCl_2(COD)(bpm)$ (**2**). Although this compound was quite inert, the hydride derivative RuHCl(COD)(bpm) (**3**) formed upon reaction of **2** with $LiBHEt_3$ was a good starting material to prepare TpRuH(COD) (**4**) from KTp, thanks to the trans labilizing effect of the hydride ligand.[22] **4** was found to be totally inert toward hydrogenation, but this chemistry could be extended to the synthesis of similar complexes containing the hydridotris(3,5-dimethylpyrazolyl) borate (Tp*) or hydridotris(3-isopropyl-4-bromopyrazolyl) borate (Tp′) ligands (see Chart 1).

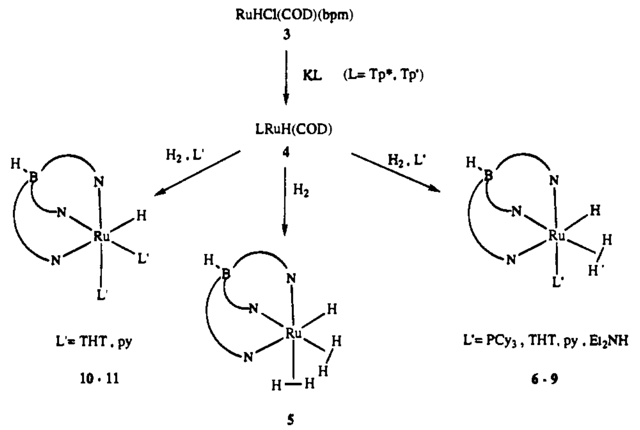
We present in this paper the preparation of novel ruthenium "polyhydrides", in particular hydridobis(dihydrogen) derivatives, their spectroscopic characterization, and their chemistry. A preliminary account of this chemistry has been published.[23]

Synthesis of New Hydride Complexes. The reaction of **3** with KTp* or TlTp′ in acetone leads to a yellow solution from which yellow solids analyzing for LRuH(COD) (L = Tp*, **4a**; L = Tp′, **4b**) were obtained in *ca.* 70% yield upon appropriate workup (see Scheme 1). The complexes were characterized by mass spectrometry using the DCI method in the case of **4a** and the FAB method in the case of **4b**. In both cases, satisfactory spectra were obtained showing M + 1 at *m/z* 509 for **4a** and M at *m/z* 786 (most intense peak corresponding to simulated spectrum) for **4b**. Full ^1H and ^{13}C NMR characterization of the new complexes is given under Experimental Section, whereas selected spectroscopic properties are listed on Table 1. The most salient feature of these spectra is the difference in the chemical shifts found for the hydride signals, respectively at −6.42 (**4a**) and −8.12 ppm (**4b**). The olefinic protons resonate, respectively, at 3.71 and 4.36 ppm (**4a**) and at 3.13 and 3.51 ppm (**4b**), whereas the corresponding carbons appear near 69 and 71.5 ppm in both cases. These data suggest a weaker trans effect of the Tp′ ligand compared to the Tp* one and hence a higher electron releasing property of the Tp* ligand. However, the spectroscopic properties of complexes containing either the Tp* or the Tp′ ligand have been found to be very similar in the rest of this study. The difference observed here could result from a difference in the mode of coordination of the ligand, which is classically linked by three pyrazolyl groups in the case of **4a** but could be linked by two pyrazolyl groups and the boron hydride in the case of **4b**, as deduced from the IR properties of both complexes (*vide infra*).

Chart 1. Structure of the Substituted Hydridotris(pyrazolyl) Borate Ligands (Tp* and Tp′) Used in This Study



Scheme 1. Synthesis of New Hydrido Ruthenium Derivatives Containing the Tp* or Tp′ Ligands



Whereas hydrogenation of **4** proved to be unsuccessful, **4a** and **4b** react smoothly with 3 bar of dihydrogen in pentane at room temperature overnight or at 90 °C for 2 h, respectively. In both cases, the solution changes from yellow to colorless and a white powder precipitates at room temperature. Washing the powder with pentane leads to analytically pure complexes of formulation $LRuH_5$ in excellent yield (L = Tp*, **5a**; L = Tp′, **5b**). Similar procedures, namely hydrogenation of a solution of **4a** in toluene or of **4b** in pentane under 3 bar of dihydrogen in a Fischer-Porter bottle at various temperatures

---

[12] Hamilton, D.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198.

[13] Heinekey, D. M.; Oldham, W. *J. Am. Chem. Soc.* **1994**, *116*, 3137.

[14] Paneque, M.; Poveda, M.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519.

[15] Bucher, U.; Lengweiler, T.; Nanz, D.; von Philipsborn, W.; Venanzi, L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 548.

[16] (a) Chaudret, B.; Poilblanc, R. *Organometallics* **1985**, *4*, 1722. (b) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598. (c) Christ, M. L.; Sabo-Etienne, S.; Chung, G.; Chaudret, B. *Inorg. Chem.* **1994**, *33*, 5316. (d) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082.

[17] (a) Chaudret, B.; Chung, G.; Eiseinstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314. (b) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800. (c) Burrow, T.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1995**, *34*, 2470.

[18] Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.

[19] Halcrow, M.; Chaudret, B.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1993**, *No. 5*, 465.

[20] (a) Hill, A. F. *J. Organomet. Chem.* **1990**, *395*, C35. (b) McNair, A. M.; Boyd, D. C.; Mann, K. R. *Organometallics* **1986**, *5*, 303. (c) Steyn, M. M. deV.; Singleton, E.; Hietkamp, S.; Liles, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 2991. (d) Alcock, N. W.; Hill, A. F.; Melling, R. P. *Organometallics* **1991**, *10*, 3898. (e) Alcock, N. W.; Burns, I. D.; Claire, K. S.; Hill, A. F. *Inorg. Chem.* **1992**, *31*, 2906. (f) Sun, N.-Y.; Simpson, S. J. *J. Organomet. Chem.* **1992**, *434*, 341.

[21] See for example: (a) Carreno, R.; Chaudret, B.; Labroue, D.; Sabo-Etienne, S. *Organometallics* **1993**, *12*, 13. (b) Urbanos, F.; Halcrow, M.; Fernandez-Baeza, J.; Dahan, F.; Labroue, D.; Chaudret, B. *J. Am. Chem. Soc.* **1993**, *115*, 3484.

[22] Fajardo, M.; de la Hoz, A.; Diaz, E.; Jalon, F.; Otero, A.; Rodriguez, A.; Tejeda, J.; Belletti, D.; Lanfranchi, M.; Pellinghelli, M.-A. *J. Chem. Soc., Dalton Trans.* **1993**, 1935.

[23] Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1994**, *116*, 2635.

Table 1. Selected Spectroscopic Properties for New Hydride Complexes

complex	$\nu_{\text{H-H}}$ (cm^{-1})	$\nu_{\text{Ru-H}}$ (cm^{-1})	$\nu_{\text{B-H}}$ (cm^{-1})	RMN ^{1}H δ_H (ppm)	$T_{1(\text{min})}$ (ms)	$J_{\text{HD(obs)}}$ Hz	$J_{\text{HD(calc)}}$ Hz	$r_{\text{HH(calc)}}$ (Å)
Tp*RuH(COD) (**4a**)		2053	2545	-6.42^a				
Tp*RuH(H_2)$_2$ (**5a**)	2361	1950	2510	-11.27^a	26^b (163 K)^f	5.4	27.0	0.90
Tp*RuH(H_2)(PCy_3) (**6a**)	*d*	2034	2520	-10.71^a	22^c (218 K)^g	7.0	21.0	0.92
Tp*RuH(H_2)(THT) (**7a**)	2250	1950	2503	-9.62^a	19^c (223 K)^g	8.1	24.3	0.89
Tp*RuH(H_2)(py) (**8a**)	*d*	1970	2498	-8.17^a	19^c (233 K)^g	8.9	26.7	0.90
Tp*RuH(H_2)($NHEt_2$) (**9a**)	*e*	*e*	*e*	-9.26^a	19^c (223 K)^g	7.9	23.7	0.90
Tp*RuH(py)$_2$ (**10a**)		1838	2502	-14.11^a	250^c (233 K)^g			
Tp*RuH(THT)$_2$ (**11a**)		1906	2517	-14.21^a	400^c (243 K)^g			
Tp*RuH(CO)$_2$ (**12a**)			2521	-9.25^a				
Tp′RuH(COD) (**4b**)		2084 1986	*d*	-8.12^a				
Tp′RuH(H_2)$_2$ (**5b**)	*d*	1973	2489	-11.82^a	28^c (182 K)^h	5.2	26	
Tp′RuH(H_2)(PCy)$_3$ (**6b**)	*d*	2041	2448	-11.47^a	30^c (208 K)^h			
Tp′RuH(H_2)(THT) (**7b**)	*d*	1955	2453	-10.5^a	21^c (228 K)^h			
Tp′RuH(H_2)(py) (**8b**)	*d*	1943	2449	-9.04^a	20^c (230 K)^h			

^{a} C_6D_6. ^{b} $C_6D_5CD_3$/THF-d_8. ^{c} $C_6D_5CD_3$. ^{d} Not seen. ^{e} Not measured. ^{f} Measured at 400 MHz. ^{g} Measured at 250 MHz. ^{h} Measured at 300 MHz.

(see Experimental Section) in the presence of a ligand L′, can be used to prepare the derivatives of general formulation $LRuH_3L'$ (L = Tp*, L′ = PCy_3,[17] **6a**; L = Tp′, L′ = PCy_3, **6b**; L = Tp*, L′ = THT, **7a**; L = Tp′, L′ = THT, **7b**; L = Tp′, L′ = py, **8b**; THT = tetrahydrothiophene, py = pyridine; see Scheme 1). In the case of the Tp* derivatives, the new complexes are obtained after reduction of the volume of the toluene solutions and addition of pentane, whereas in the case of the Tp′ derivatives, reduction of the volume of the pentane solutions leads to the precipitation of the new compounds. It is noteworthy that in all cases the presence of the extra ligand L′ in the solution facilitates the hydrogenation reactions. The hydrogenation reaction of **4a** in the presence of 1 equiv of pyridine did not produce Tp*RuH_3(py) (**8a**) but instead a mixture of **5a** and the new monohydride complex Tp*RuH(py)$_2$ (**10a**), which can be obtained pure when the hydrogenation reaction is carried out in the presence of excess pyridine. Similarly, it is possible to prepare the analogous complex Tp*RuH(THT)$_2$ (**11a**) by hydrogenating **4a** in the presence of excess THT. It is interesting to note that these reactions are very easy and complete within 1.5 h at room temperature. The preparation of Tp*RuH_3(py) (**8a**) was achieved by reacting **5a** with 1 equiv of pyridine in toluene at 60 °C for 1 h, whereas the biscarbonyl complex Tp*RuH(CO)$_2$ (**12a**) was obtained by reacting **5a** with 3 bar of CO in toluene at room temperature overnight and isolated after concentration and addition of pentane as an off-white solid in 92% yield.

All of these new compounds were isolated pure in high yield (see Experimental Section) and characterized by microanalysis together with IR and NMR spectroscopies and in some cases mass spectrometry. A mass spectrum of **5a** was obtained using the DCI method (stream of NH_3). The main peaks showing the isotopic pattern of ruthenium were observed at *m/z* 403 (M − H), 433 (M − H + $2NH_3$), and 450 (M − 5H + $3NH_3$) (all values given for the most intense peak corresponding to ^{102}Ru).

In addition to those isolated compounds, we found that the room temperature reaction of **4a** with excess Et_2NH in toluene under H_2 yields rapidly a mixture of **5a** and Tp*RuH_3(Et_2NH) (**9a**), which proved to be impossible to separate.

Spectroscopic Characterization of the New Complexes. ^{1}H and ^{13}C NMR. Selected data of the new complexes are presented in Table 1, and full characterization is given under Experimental Section.

(a) **$LRuH_5$ Complexes.** Both **5a** and **5b** show at all temperatures (down to 153 K in the case of **5a**) a single signal at high field near −11 ppm. Integrations using large repetition delays (30 s) indicate the presence of five metal-bound hydrogen atoms in both **5a** and **5b**. The minimum of the longitudinal relaxation time (T_1) was found to be 26 ms at 163 K (400 MHz) for **5a** and 28 ms at 182 K (300 MHz) for **5b**. In addition, both the ^{1}H and the ^{13}C NMR spectra indicate a symmetrical environment for the Tp ligands. (**5a**: ^{1}H NMR 2.31 and 2.32 (CH_3), 5.73 (C*H*) ppm; ^{13}C NMR 12.87 and 16.93 (CH_3), 106.24 (CH), 143.73 (CCH_3) ppm. **5b**: ^{1}H NMR 1.38 (CH_3), 3.66 (C*H*Me_2), 7.25 (C*H*) ppm; ^{13}C NMR 19.41 (CH_3), 30.6 ($CHMe_2$), 137.1 (CH), 157.03 ($CCHMe_2$) ppm.)

5a and **5b** undergo H−D exchange with the deuterated aromatic solvent, leading to the observation of a 1:1:1 triplet growing near the hydride singlet (J_{H-D} = 5.4 Hz for **5a** and J_{H-D} 5.2 Hz for **5b**; see Figure 1). Furthermore, bubbling D_2 through a C_6D_6 solution of **5a** allowed the observation of all isotopomers, namely Tp*RuH_4D (**5a-*d***), Tp*RuH_3D_2 (**5a-*d*$_2$**), Tp*RuH_2D_3 ((**5a-*d*$_3$**), Tp*$RuHD_4$ (**5a-*d*$_4$**), respectively, as nonbinomial triplet (1:1:1), quintet (1:2:3:2:1), septet (1:3:6:7:6:3:1), and nonet (1:4:10:16:19:16:10:4:1). In the case of **5b**, gentle warming of a C_6D_6 solution leads rapidly to the observation of a nonbinomial (1:4:10:16:19:16:10:4:1) nonet characterizing Tp′$RuHD_4$ (**5b-*d*$_4$**) (see Figure 2 and Reactivity).

To prepare as selectively as possible highly deuterated species, **4a** was reacted at 80 °C with 3 bar of D_2 in C_6D_6 for 3 days. In this case, little "hydride signal" was visible and mainly due to **5a-*d*$_4$** as well as to some **5a-*d*$_3$**. This was confirmed by a ^{2}D NMR study of the same sample showing the presence of **5a-*d*$_5$**, **5a-*d*$_4$**, and some **5a-*d*$_3$**, which were observed as, respectively, a

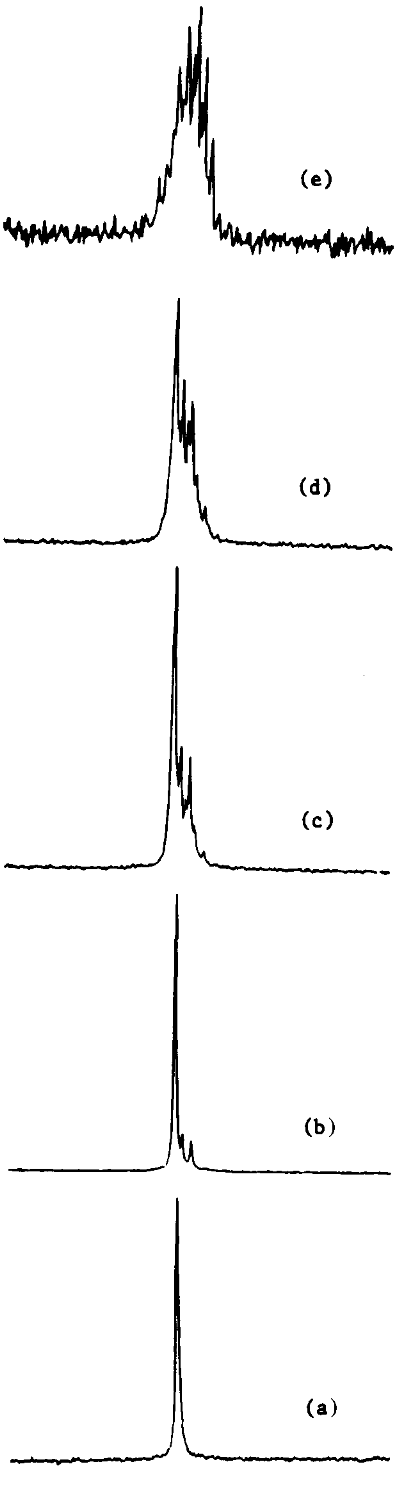


Figure 1. Modification of the high field ^1H NMR signal of **5a** as a function of time in C_6D_6 at room temperature (250 MHz): (a) initial signal; (b) after 30 s; (c) after 5 min; (d) after 10 min; (e) after 24 h.

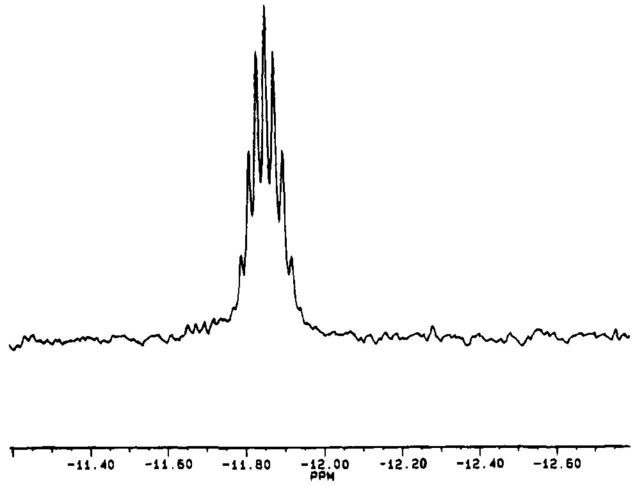


Figure 2. High field ^1H NMR signal of Tp'RuHD$_4$ (**5b-*d*$_4$**) showing the expected nonet pattern (250 MHz, C_6D_6).

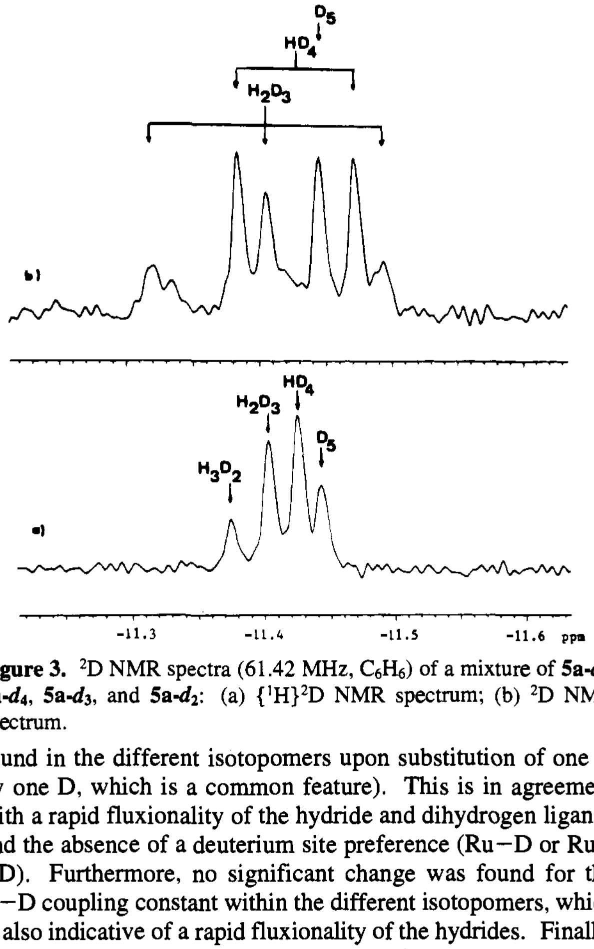


Figure 3. ^2D NMR spectra (61.42 MHz, C_6H_6) of a mixture of **5a-*d*$_5$**, **5a-*d*$_4$**, **5a-*d*$_3$**, and **5a-*d*$_2$**: (a) $\{^1H\}^2D$ NMR spectrum; (b) ^2D NMR spectrum.

singlet, a doublet, and a triplet upon coupling with the hydrides (see Figure 3). Interestingly, when running the NMR in C_6H_6 instead of C_6D_6, we could observe the inverse isotope exchange reaction and the formation of **5a-*d*$_2$**. These deuteration experiments, whether observed in ^1H or ^2D NMR, allow us to determine exactly the number of ruthenium-bound hydrogens, which was found to be five. In addition, in contrast to recently reported iridium polyhydrides containing the Tp* ligand, little isotopic shift is observed for the chemical shifts of the different isotopomers[13,14] (variations of 30−18 ppb to high field were found in the different isotopomers upon substitution of one H by one D, which is a common feature). This is in agreement with a rapid fluxionality of the hydride and dihydrogen ligands and the absence of a deuterium site preference (Ru−D or Ru−HD). Furthermore, no significant change was found for the H−D coupling constant within the different isotopomers, which is also indicative of a rapid fluxionality of the hydrides. Finally, we can note the extensive deuteration of the Tp* ligand during the preparation of **5a-*d*$_5$** and **5a-*d*$_4$** isotopomers. This result will be discussed under Reactivity, whereas the T_1 and J_{H-D} values found for **5a** and **5b** will be analyzed in the spectroscopy discussion together with the results obtained for other compounds.

(b) LRuH$_3$L' Complexes. Complexes **6a**−**9a** and **6b**−**8b** also show like **5a,b** a single resonance for the hydride signal at all accessible temperatures between −8.17 (**8a**) and −11.47 (**7b**) (see Table 1). The signals are all singlets except those for **6a** and **6b**, which show a doublet pattern (J_{P-H} = 18 and 17.5 Hz, respectively). The integration ratios toward the other ligands are in agreement with the presence of three metal-bound hydrogens in all complexes. The slight high field shift observed for all Tp′ dihydrogen complexes compared to the Tp* ones could result from a higher electron releasing effect of the Tp′ ligand, which would lead to a more important stretching of the coordinated H−H molecule and hence to a shortening of the Ru−H bond. A similar effect is found for a series of complexes containing the same Tp ligand; the chemical shifts vary from near −8 ppm when the *cis*-ancillary ligand is pyridine to −11 ppm when it is PCy_3, the ligand showing the larger electron releasing effect. The relaxation time T_1 minimum is found for all compounds near 19−20 ms with the exception of phosphine complexes (22 ms at 218 K for **6a**, 30 ms at 208 K for **6b**). H−D coupling constants were measured on partially deuterated compounds **6−9** which were prepared either by H−D exchange with D_2 or C_6D_6 or by addition of an L′ ligand to **5a-*d*₄** and observed either as a triplet or as a quintet corresponding to MH_2D and MHD_2 derivatives. Coupling constants between *ca.* 7 and 9 Hz were measured as a function of the complex (see Table 1) and will be discussed later in this paper together with the structures of these derivatives.

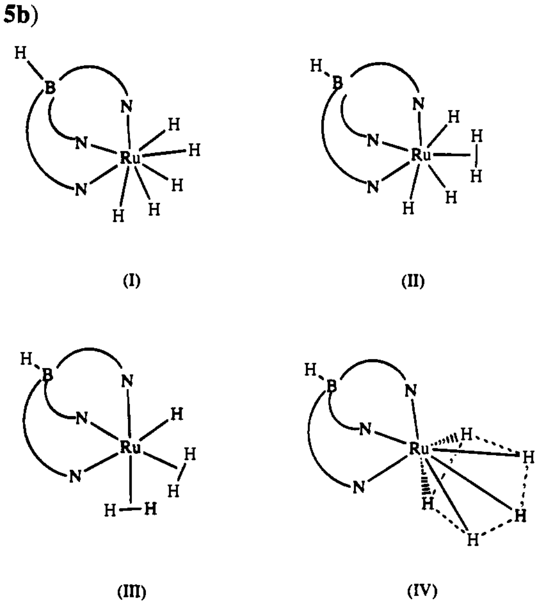
In addition, the NMR spectra show the presence of the L (Tp*, Tp′) and L′ (PCy_3, THT, py, or $NHEt_2$) ligands in correct integration ratios. As expected, the three pyrazol rings are no longer magnetically equivalent. For example, in the case of the Tp* derivatives, two hydrogens directly linked to the pyrazolyl rings resonate near 5.9 ppm, whereas the third one resonates at higher field depending upon L′ (5.56 and 5.64 ppm for **7a** and **8a**, respectively). In the case of **6a** a single broad signal is observed at *ca.* 5.8 ppm. The asymmetry is also visible when the methyl protons or the signals of the Tp′ group are observed. The ^{13}C NMR spectra are in agreement with the proposed sructures and do not show any significant features besides the asymmetry of the Tp ligands.

(c) **LRuH(L′)₂ Complexes.** In this case, only Tp* derivatives were prepared. They show a hydride signal at high field of intensity 1, at −14.11 (**10a**), −14.21 (**11a**), and −9.25 ppm (**12a**). The difference between these values could result from the better π-accepting properties of CO. In addition, both the ^1H and the ^{13}C NMR spectra indicate the presence of two L′ ligands and the asymmetry of the Tp* group. The relaxation time T_1 was measured for **10a** and **11a** to estimate the relaxation due to effects other than H−H dipole−dipole relaxation for the metal-bound hydrogens of **5a−9a** and to calculate the H−H distance within the coordinated dihydrogen molecule. Minima of 250 ms at 233 K (250 MHz) and 400 ms at 243 K (250 MHz) were found for **10a** and **11a**, respectively.

(d) **Calculations of $J_{\mathrm{H-D}}$ Values within Coordinated H−D Molecules.** The T_1 minima measured for all polyhydride complexes described in this paper are short (between 19 ms, 250 MHz, for **7a** and 30 ms, 300 MHz, for **6b**; see Table 1) and in agreement with the presence of at least one coordinated dihydrogen molecule per complex. The observed $J_{\mathrm{H-D}}$ values (5.4 and 5.2 Hz in **5a**,**b**, between 7 and 9 Hz in "trihydrides") are also in agreement with a rapid interconversion between ruthenium-bound hydride and dihydrogen groups. In this section, we will propose a formulation for all new polyhydrides using the H−D coupling constants calculated within the coordinated H−D molecule. This will be compared with the H−H distances within the coordinated dihydrogen molecules calculated from T_1 data.

For the trihydrides, assuming an $M(H)(H_2)$ formulation and a rapid fluxionality between hydride and dihydrogen, it is possible, considering that couplings between a hydride and coordinated H−D or between a deuteride and coordinated H_2 are zero, to calculate $J_{\mathrm{H-D}}$ nonclassically ($J_{\mathrm{H-D/NC}}$):

Chart 2. Possible Structures for $LRuH_5$ (L = Tp*, **5a**; L = Tp′, **5b**)


(I) (II) (III) (IV)

$$J_{\mathrm{H-D/NC}} = 3J_{\mathrm{H-D/obs}}$$

$J_{\mathrm{H-D/obs}}$ is the observed coupling constant in the fluxional molecule. The values found for **6a−9a** are, respectively, 21.0, 24.3, 26.7, and 23.7 Hz. These values are typical for dihydrogen molecules coordinated to a transition metal center. They reveal a moderate amount of stretching of the corresponding H−H bond.[1−6] This amount of stretching of the H−H bond increases from pyridine to PCy_3 as the $J_{\mathrm{H-D}}$ value decreases and the $T_{1\min}$ increases. This is in agreement with the increased electron density on the complex as a result of the good σ-donor properties of the phosphine ligand.

As stated above, the $J_{\mathrm{H-D/obs}}$ values for **5a** and **5b** are, respectively, 5.4 and 5.2 Hz. These values are too large for classical $^2J_{\mathrm{H-D}}$ couplings and, together with T_1 data, rule out a classical formulation for these compounds. It is, however, noteworthy that a value of 3.7 Hz has been found for $[CpIrH_3(AsPh_3)]^+$,[24] a complex shown to be classical by neutron diffraction, and a value of 3.3 Hz for the recently reported Tp^*IrHD_3.[14]

5a and **5b** could adopt three different structures (see Chart 2), namely a classical one ($LRuH_5$, I), a mono dihydrogen one ($LRuH_3(H_2)$, II) or a bis dihydrogen one ($LRuH(H_2)_2$, III). Structure I is ruled out as previously discussed. Given the same assumptions as for the trihydrides, it is possible to calculate for structure II by a statistical treatment the relationship between the observed H−D coupling constant and the H−D coupling constant within coordinated H−D ($J_{\mathrm{H-D/C}}$ is the classical $^2J_{\mathrm{H-D}}$ coupling constant between a hydride and a deuteride).

$$J_{\mathrm{H-D/obs}} = 1/10(3J_{\mathrm{H-D/C}} + J_{\mathrm{H-D/NC}})$$

$$J_{\mathrm{H-D/NC}} = 10J_{\mathrm{H-D/obs}} - 3J_{\mathrm{H-D/C}}$$

This gives for **5a**

$$J_{\mathrm{H-D/NC}} = 54 - 3J_{\mathrm{H-D/C}}\ (\mathrm{Hz})$$

Assuming a $J_{\mathrm{H-D/C}}$ value of at most 3 Hz, one finds $J_{\mathrm{H-D/NC}}$ = 45 Hz higher than $J_{\mathrm{H-D}}$ in free H−D (43.2 Hz). This is impossible and rules out structure II. In contrast, the calculations for structure III give

---

[24] Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 920.

$$J_{\mathrm{H-D/NC}} = 5(J_{\mathrm{H-D/obs}}) = 27\ \mathrm{Hz}\ (\mathbf{5a})\ \text{or}\ 26\ \mathrm{Hz}\ (\mathbf{5b})$$

These values are typical for complexes binding a moderately stretched dihydrogen ligand and are in agreement with the values found for the relaxation time T_1. It is, however, noteworthy that a final possibility would be a polyhydrogen structure (IV, Chart 2).[25] In such a case we find

$$J_{\mathrm{H-D/obs}} = 1/2({}^1J_{\mathrm{H-D}} + {}^2J_{\mathrm{H-D}})$$

where ${}^1J_{\mathrm{H-D}}$ is the coupling between two adjacent nuclei and ${}^2J_{\mathrm{H-D}}$ the coupling between two nonadjacent nuclei. This gives for **5a**

$${}^1J_{\mathrm{H-D}} + {}^2J_{\mathrm{H-D}} = 10.4\ \mathrm{Hz}$$

This value could be reasonable for the sum of a coupling corresponding to a very elongated H−H bond and one typical ${}^2J$ coupling.

In summary, stuctures I and II are ruled out, whereas structure IV cannot be ruled out using arguments due to H−D couplings but has no precedent. We therefore propose that **5a** and **5b** adopt structure III, *i.e.* a structure in which an octahedral ruthenium II center accommodates one hydride and two dihydrogen ligands. We have already pointed out the differences between the structures of $\mathrm{Cp^{\#}RuH_3(PR_3)}$ ($\mathrm{Cp^{\#}}$ = Cp, Cp*)[18] and those of $\mathrm{LRuH_3(PR_3)}$ (L = Tp, Tp*).[19] $\mathrm{Cp^{\#}}$ complexes are trihydrides displaying exchange couplings, whereas Tp ones are hydrido dihydrogen derivatives. The reasons for these differences could be both the octahedral geometry imposed by the Tp ligands and the poorer electron releasing ability of these ligands. Similar effects are also probably present to explain the bis dihydrogen structure of **5a** and **5b**.

(e) **Calculation of the H−H Distances.** Given structures **5**−**9** established in the preceding section, it is possible to calculate H−H distances within the coordinated dihydrogen molecules from the T_1 minimum values. Such calculations can be relatively ambiguous since it is usually difficult to estimate precisely the relaxation due to all effects (R_0) other than dipole−dipole relaxation ($R_{\mathrm{d-d}}$) within the dihydrogen molecule. In our case, the measurements for **10a** and **11a** give us an upper limit of relaxation R_0. Another problem is to determine whether it is appropriate to use approximations for rapid or slow rotation of $\mathrm{H_2}$. Again, in our case we can admit that the rapid rotation limit is operative since we observe a rapid fluxionality of hydride and dihydrogen ligands at all accessible temperatures. Hence, given the hydride contribution to the observed relaxation (R_{H}) and the dihydrogen contribution (R_{H2}) and following Halpern's approach,[26] the observed relaxation (R_{obs}) for **7a** is

$$3R_{\mathrm{obs}}(\mathbf{7a}) = R_{\mathrm{H}} + 2R_{\mathrm{H2}}$$

$$R_{\mathrm{H}} \le R_{\mathrm{obs}}(\mathbf{11a}) \qquad R_{\mathrm{H2}} = R_{\mathrm{d-d}} + R_{\mathrm{o}} \qquad R_{\mathrm{o}} \le R_{\mathrm{obs}}(\mathbf{11a})$$

$$\Rightarrow 3R_{\mathrm{obs}}(\mathbf{7a}) \le 2R_{\mathrm{d-d}} + 3R_{\mathrm{obs}}(\mathbf{11a})$$

$$R_{\mathrm{d-d}} \ge 3/2[R_{\mathrm{obs}}(\mathbf{7a}) - R_{\mathrm{obs}}(\mathbf{11a})];\ R_{\mathrm{d-d}} \ge 75.2\ \mathrm{s^{-1}}$$

Using the rapid rotation approximation and the equation developed by Morris,[27] we calculate the H−H distance ($r_{\mathrm{H-H}}$) as

$$r_{\mathrm{H-H}} = 4.611\sqrt[6]{[1/(B\ (\mathrm{MHz}) \times R_{\mathrm{d-d}}\ (\mathrm{s^{-1}}))]}$$

$$r_{\mathrm{H-H}}(\mathbf{7a}) \le 0.89\ \text{Å}$$

A similar calculation for **8a** using the relaxation found for **10a** gives

$$R_{\mathrm{d-d}} \ge 3/2[R_{\mathrm{obs}}(\mathbf{8a}) - R_{\mathrm{obs}}(\mathbf{10a})];\ R_{\mathrm{d-d}} \ge 72.95\ \mathrm{s^{-1}}$$

$$r_{\mathrm{H-H}}(\mathbf{8a}) \le 0.90\ \text{Å}$$

For **6a**, the relaxation due to interaction between the rotating dihydrogen molecule and phosphine protons is probably important but difficult to calculate with precision. We can take as a lower value the relaxation found for **9a**, which will lead to

$$r_{\mathrm{H-H}}(\mathbf{6a}) = ca.\ 0.92\ \text{Å}$$

In this case this is probably a lower limit of the H−H distance.

Finally, it remains to calculate the H−H distance within the dihydrogen molecules of **5a**. We can admit that the relaxation due to all other effects is at most equal to that found for **11a**. This includes the effect of the Tp* ligand, that of ruthenium, and that of the solvent. In addition, **11a** shows relaxation due to the THT ligand, which does not seem to be very important. Hence, if we conclude that **5a** adopts structure III, the relaxation equation is the following:

$$5R_{\mathrm{obs}}(\mathbf{5a}) = R_{\mathrm{H}} + 4R_{\mathrm{H2}}$$

$$R_{\mathrm{H}} \le R_{\mathrm{obs}}(\mathbf{11a}) \qquad R_{\mathrm{H2}} = R_{\mathrm{d-d}} + R_{\mathrm{o}} \qquad R_{\mathrm{o}} \le R_{\mathrm{obs}}(\mathbf{11a})$$

$$\Rightarrow R_{\mathrm{d-d}} \ge 5/4[R_{\mathrm{obs}}(\mathbf{5a}) - R_{\mathrm{obs}}(\mathbf{11a})]$$

$$r_{\mathrm{H-H}}(\mathbf{5a}) \le 0.90\ \text{Å}$$

These approximate calculations demonstrate that all dihydrogen complexes show similar H−H distances within their respective coordinated dihydrogen molecules in agreement with the similar $J_{\mathrm{H-D}}$ values observed. Furthermore, this shows that the most important effect for the stretching of coordinated dihydrogen is due in these systems to the Tp* ligand trans to all hydride and dihydrogen ligands. Only the presence of a phosphine ligand induces a significant lengthening of the H−H bond. It is finally interesting to compare these values with those found for a series of hydrido dihydrogen derivatives containing two $\mathrm{PCy_3}$ ligands for which distances near 1 Å were observed or calculated.[17] The results obtained in this study therefore demonstrate the poor electron releasing properties of the Tp ligands.

Infrared Spectroscopy. Besides matrix experiments, very few examples of infrared study on dihydrogen compounds have been reported.[28] This fact arises essentially from the difficulty to observe the characteristic stretches for dihydrogen ($\nu_{\mathrm{H-H}}$, $\nu_{\mathrm{M-H2}}$) which are usually weak and/or hidden by other absorptions ($\nu_{\mathrm{C-H}}$, for example). The homogeneous series of complexes reported in this study and the easy deuteration of the different species give us a rare opportunity to analyze in detail the IR spectra of complexes containing or not coordinated dihydrogen. Some characteristic vibrations are given in Table 1.

All complexes but **4b** show the $\nu_{\mathrm{B-H}}$ stretch near 2500 cm^{-1}. The exact values vary between 2448 cm^{-1} for **6b** and 2545 cm^{-1}

---

(25) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg.Chem.* **1987**, *26*, 3054.

(26) Desrosiers, P. J.; Cai, P.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

(27) Bautista, M. T.; Capellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 4876.

(28) (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (b) Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L.; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954.

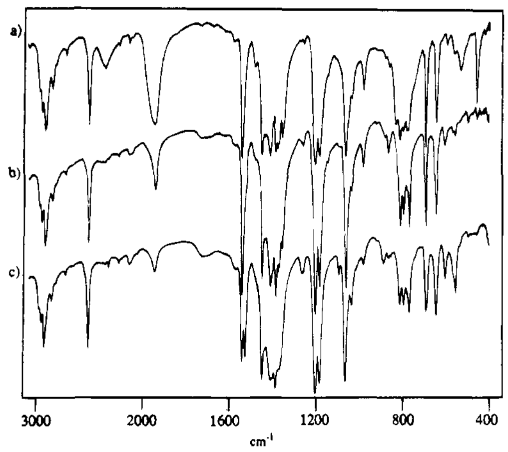


Figure 4. Infrared spectra (KBr disks) of **5a** at various deuteration levels: (a) not deuterated; (b) low deuteration level; (c) high deuteration level.

Table 2. Proposed Assignments for the Infrared Data (KBr Disks) of **5a** and **7a** and Their Isotopomers

ν (cm^{-1})	$Tp^*RuH(H_2)_2$ (**5a**)	$Tp^*RuH(H)_2(THT)$ (**7a**)
ν_{HH}	2361	2250
$\nu_{HD(calc)}$	2045	1948
$\nu_{HD(exp)}$		
$\nu_{DD(calc)}$	1670	1591
$\nu_{DD(exp)}$	1705	1620
ν_{RuH2} and ν_{RuH}	1950	1948
$\nu_{RuD2(calc)}$ and $\nu_{RuD(calc)}$	1379	1380
$\nu_{RuD2(exp)}$ and $\nu_{RuD(exp)}$	1380	
$\nu_{RuHD(calc)}$	1592	1590
$\nu_{RuHD(exp)}$	1530	1530

for **4a**. These values will depend both on the electronic density of the metal center and on steric effects which will modify the geometry of the Tp ligands and are therefore difficult to rationalize. However, the case of **4b** is atypical since we do not observe any band near 2500 cm^{-1}, but two bands near 2000 cm^{-1}(at 2084 and 1986 cm^{-1}). A similar case has been recently encountered by some of us on $Tp^*Ru(CH_3)(COD)$.[29] In this case, an X-ray crystal structure has demonstrated that the absence of absorption near 2500 cm^{-1} was related to a mode of coordination of Tp* involving only two pyrazol groups and an agostic Ru−H−B interaction. In the present case, it is likely that a similar situation is present. The band at 1986 cm^{-1} could arise from this agostic interaction. We have not been able to confirm this proposal by NMR probably because of the line width of the proton linked to boron.

The monohydride complexes all show a single intense band for the Ru−H stretch but quite variable in position (2053 cm^{-1} for **4a**, 1838 cm^{-1} for **10a**, and 1906 cm^{-1} for **11a**). In the case of **12a**, two bands are visible near 2000 cm^{-1} attributed to CO stretches, but a shoulder near 1900 cm^{-1} could be attributed to the Ru−H stretch or some coupled mode. The complexes containing coordinated dihydrogen also exhibit a strong absorption near 1900−2000 cm^{-1} together with broad bands at higher frequency (near 2300−2400 cm^{-1}). These observations led us to study in detail the infrared spectra of **5a** and **7a** at various deuteration levels (see Figure 4 and Table 2). Modifications occur in both the high frequency (2500−1300 cm^{-1}) and low frequency regions of the spectra (<1000 cm^{-1}).

In the high frequency region, the spectra of **5a** and **7a** exhibit a broad absorption that we attribute to ν_{H-H} at, respectively, *ca.* 2361 and 2250 cm^{-1}. Upon deuteration, these bands shift to *ca.* 1705 and 1620 cm^{-1} instead of the expected 1670 and 1591 cm^{-1} for a ν_{H-H} to ν_{D-D} shift. It is noteworthy that the H−H elongation mode has been very rarely observed and only for complexes containing unstretched dihydrogen molecules. In our case, since NMR data indicate that the H−H distance in coordinated dihydrogen is near 0.9 Å, we expect to find the H−H stretch at lower frequency than in Kubas compounds (r_{H-H} *ca.* 0.8 Å, ν_{H-H} *ca.* 2600 cm^{-1}) and, hence, the observation of $\nu_{s\text{-}Ru-H2}$ at higher frequency. Therefore, the ν_{H-H} , ν_{Ru-H}, and $\nu_{s\text{-}Ru-H2}$ modes may be coupled which will increase the complexity of the spectra and lead to some differences between calculated and observed isotopic shifts. It is, however, noteworthy that in Kubas dihydrogen derivatives small differences between calculated and observed isotopic shifts are also found.[28a]

Both **5a** and **7a** exhibit a strong absorption centered, respectively, at 1950 and 1948 cm^{-1}. In both compounds this band is unsymmetrical and displays shoulders, respectively, at *ca.* 1970 and 1995 cm^{-1} (**5a**) and *ca.* 1980 cm^{-1} (**7a**). Interestingly, in the case of **5a**, the shoulder at 1970 cm^{-1} disappears first at low deuteration level. At high deuteration level, a weak absorption remains visible at 1950 cm^{-1}. This band could correspond to a pure ν_{Ru-H} mode since then the probability to find a $Ru-H_2$ mode to explain this band or to couple with the Ru−H one is very low. If the deuteration were complete, the coupled $Ru-D/Ru-D_2$ modes should appear at $1/\sqrt{2}\nu_{Ru-H}$ or ν_{Ru-H2}, *i.e.* between 1380 and 1400 cm^{-1}. A new band is clearly present near 1380 cm^{-1} in the spectrum of **5a**, whereas in the case of **7a** it may be hidden by other strong absorptions. In addition, a new band is visible near 1530 cm^{-1} for both **5a** and **7a**. We propose that it could be due to $\nu_{s\text{-}Ru-HD}$; the pure $\nu_{s\text{-}Ru-H2}$ mode would be expected at 1875 cm^{-1}.

In the low frequency region, the situation is more complex. We can follow the disappearances of bands at 834, *ca.* 780, 532, and 458 cm^{-1} and the appearance of bands at 607 and 555 cm^{-1} corresponding to the first two. No new absorptions corresponding to the two bands at low frequency (532 and 458 cm^{-1}) were observed. The attribution of all these bands is doubtful; they appear in the region where Kubas observes the ν_{M-H2} vibrations,[28] but in our case the corresponding bands should probably appear at higher frequency. Other candidates are δ_{Ru-H2}, but we cannot make a definitive attribution.

In summary, this IR study allows us to observe a low frequency ν_{H-H} mode near 2300 cm^{-1} and complex absorptions due to ν_{Ru-H} and ν_{Ru-H2} near 1950 cm^{-1}. As far as we are aware, the only other low frequency H−H stretch observed for a dihydrogen complex is that at 2390 cm^{-1} for $FeH_2(H_2)(PPh_3)_3$ first reported by Aresta et al.[30] In the case of the other hydrido dihydrogen complexes containing the Tp* ligand and for all Tp′ dihydrogen derivatives, a single strong absorption was observed between 1900 and 2050 cm^{-1} but the band near 2300 cm^{-1} was probably too broad to be observed.

Reactivity. The unusual structure of **5a** and **5b** led us to undertake a survey of their reactivity. In a first step, we concentrated on **5a**, which is more readily accessible (see Scheme 2).

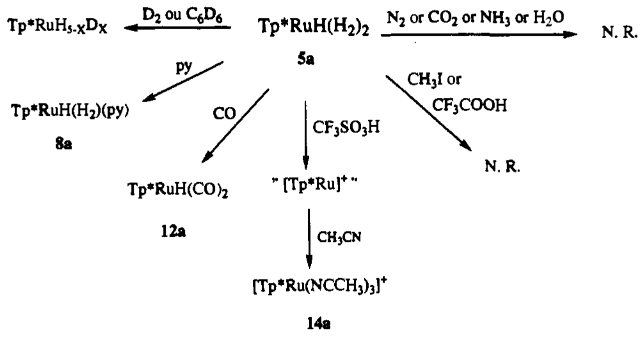
It is first important to mention that in the absence of dihydrogen **5a** transforms at 80 °C into a bright red, very little soluble complex (**13a**) showing a very distinct ^1H NMR spectrum. However, attempts to fully characterize or purify this compound have failed so far. It could perhaps be a dimer formed upon dissociation of H_2 like $[Cp^*RuH_2]_2$[31] or $Ru_2H_6(PCy_3)_4$.[16]

---

(29) Jalon, F. Unpublished results.

(30) Aresta, M.; Giannoccaro, P.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1971**, *5*, 115.

Scheme 2. Some Reactions of Tp*RuH(H_2)$_2$ (**5a**)



We have already indicated that **5a** reacts at room temperature with nucleophiles such as pyridine or CO to undergo a substitution reaction of H_2. In the case of CO, the disubstitution is immediate. NMR monitoring shows the presence of only **5a** and **12a** in variable proportions during the reaction but no hydrido dihydrogen intermediate. This can be related to the decrease in electron density when H_2 is substituted by CO which favors the immediate substitution of the second H_2 molecule. In the case of pyridine, a good σ donor and poor π acceptor ligand, it is possible to stop at the first substitution step. Other substitutions were attempted with H_2O, NH_3, CO_2, and N_2. The reaction conditions were either at room temperature in THF, toluene, or benzene-d_6 for 1–15 h, in which case no reaction was observed, or at 60 °C in toluene, in which case the decomposition product **13a** formed. These observations are quite surprising and demonstrate the stability of **5a**.

Even more surprising were the observations that no reaction occurred with CH_3COOH or CF_3COOH for 1–15 h in THF. Similarly, **5a** does not react with CH_3I at room temperature for 3 days and transforms into **13a** when the reaction mixture is heated at 50 °C. This suggests a strong electrophilic character of the hydrogen atoms coordinated to ruthenium. Cationic dihydrogen complexes have been previously shown to be electrophilic,[2-4] but this is the first such observation for a neutral dihydrogen derivative.

Only in the case of the reaction with $HBF_4{\cdot}Et_2O$ or CF_3SO_3H in THF did we observe a protonation leading to the evolution of dihydrogen. After the reaction mixture is evaporated to dryness, a residue is obtained which reacts with acetonitrile to give [Tp*Ru(MeCN)$_3$]CF_3SO_3 (**14a**). This complex was characterized by ^1H NMR and microanalysis. The ^1H NMR spectrum shows three singlets of equal intensity (9) for the three coordinated MeCN groups and the methyl groups of the Tp* ligand as well as one singlet of intensity 3 for the pyrazolyl protons. **14a** is analogous to [Cp*Ru(MeCN)$_3$](CF_3SO_3), used in particular by Fagan[32] for coordination to various classes of arenes, whereas the residue could be similar to the "Cp*Ru$^+$"[21] fragment that proved to be active for a large number of activation reactions including C–C bonds.

Finally, we carried out a study of the reactivity of **5a** and **5b** toward H–D exchange in a deuterated solvent (C_6D_6). The reactions were followed by ^1H NMR at five temperatures: 295, 305, 315, 325, and 335 K. We measured in each case the decrease in intensity of the hydride signal *vs* time by measuring the integration of the hydride signal and comparing with an internal standard, hexamethyldisiloxane. The purpose of this study was both to demonstrate the high activity of our complexes for C–H activation and to try to measure an energy of activation for this reaction in both cases and hence study the influence of the ligands on the reactivity. However, the reactions are complex and did not allow any reliable measure of the energy of activation using an Arrhenius plot. In fact, we observed an extensive deuteration of the ligands, both the alkyl (methyl for **5a**, isopropyl for **5b**) and the pyrazol protons were exchanged with deuterium. Figures 5 and 6 show the decrease in intensity for the hydride signals of **5a** and **5b** at 295 K *vs* time, whereas Figure 7 shows the same reaction for **5b** when carried out at 325 K. It is clear first that a stationary state is rapidly obtained in the case of the reaction carried out at 325 K, which corresponds to a rapid scrambling of all protons and deuterons present in solution. One can also notice the slight increase in activity of **5b** compared to **5a**, the origin of which has to be electronic since the Tp′ ligand is bulkier than the Tp* one.

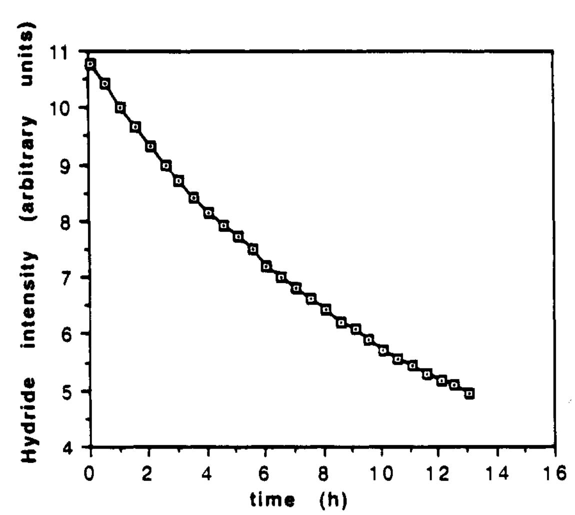


Figure 5. Variation of the intensity of the hydride signal of **5a** *vs* time measured at 295 K in C_6D_6.

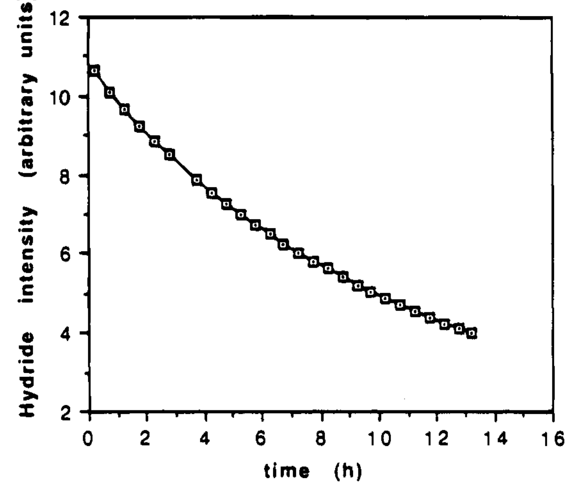


Figure 6. Variation of the intensity of the hydride signal of **5b** *vs* time measured at 295 K in C_6D_6.

Conclusion. In conclusion, we report in this paper a novel series of ruthenium dihydrogen complexes containing nitrogen donor ligands. Several unusual and/or interesting features were found in this series. First, the complexes LRuH(H_2)$_2$ (L = Tp*, Tp′) are the second examples of thermally stable coordination derivatives containing two dihydrogen molecules.

In these compounds both NMR (T_1 and J_{HD}) and infrared data indicate the presence of moderately stretched dihydrogen ligands. The comparison between the spectroscopic properties (ν_{Ru-H}, δ_{Ru-H}, T_1) of the complexes containing both hydride and dihydrogen ligands and those of similar monohydride

---

[31] Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-Oka, Y. *Organometallics* **1994**, *13*, 1129.

[32] Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

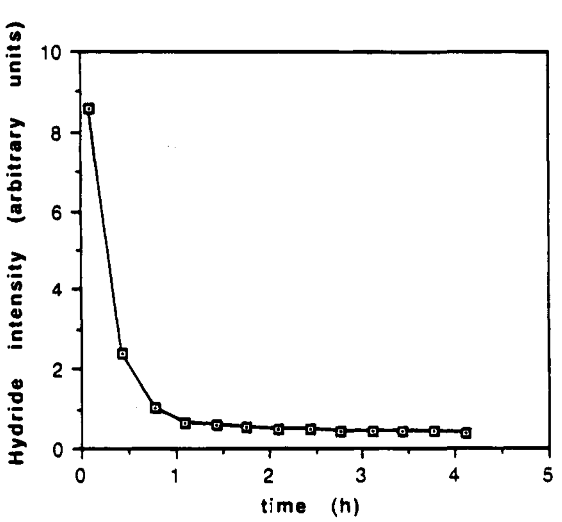


Figure 7. Variation of the intensity of the hydride signal of **5b** *vs* time measured at 325 K in C_6D_6.

derivatives ($Tp^*RuHL'_2$; L′ = py, THT) allows us to attribute vibration bands arising from the coordination of dihydrogen (ν_{H-H}, ν_{Ru-H_2}) as well as to calculate reasonable values of the H−H distances within the dihydrogen molecule (r_{H-H} = *ca.* 0.9 Å). Furthermore, the existence of the series of compounds $Tp^*RuH(H_2)L'$ (L′ = H_2, py, THT, PCy_3, $NHEt_2$) allows us to study the influence of the *cis*-ancillary ligand on dihydrogen coordination. Finally, the spectroscopic properties of both series of complexes, namely those containing the Tp* ligand and those containing the Tp′ one, are very similar, which suggests similar electronic properties for these two ligands. However, the small differences observed between the dihydrogen derivatives **5a**−**8a** and **5b**−**8b** suggest that the Tp′ ligand shows better electron releasing properties.

The order of H−H distances resulting from T_1 measurements (**7a** < **5a** ~ **8a** ~ **9a** < **6a**) and J_{HD} values (**8a** ~ **5a** > **7a** ~ **9a** > **6a**) shows that the electron donating properties of the dihydrogen molecule are probably near those of a sulfur donor and of a nitrogen ligand in these systems but less effective than a phosphorus donor ligand. This result demonstrates then the significant electron releasing properties of the H_2 ligand.

Reactivity studies demonstrate the relative inertness of the hydrido bis(dihydrogen) derivatives toward electrophiles such as CF_3COOH or CH_3I. This is consistent with an electrophilic character of the hydrogen coordinated to ruthenium whether as hydrides or as dihydrogen and suggests that the Tp ligand is relatively poorly donating compared to Cp or phosphine ligands. Nevertheless, an access was found to a new unsaturated cationic fragment "Tp^*Ru^+", probably more electrophilic than the Cp^*Ru^+ fragment, the reactivity of which will be explored in the future. Finally, the bis(dihydrogen) derivatives **5a** and **5b** undergo substitution of H_2 with nucleophiles and more importantly rapid H−D exchange reactions involving multiple C−H bond activations.

Experimental Section

All manipulations were carried out in an argon atmosphere by use of Schlenk techniques. The solvents were dried and distilled under nitrogen and thoroughly degassed under argon before use. Microanalyses were performed at the laboratory's service. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 1725 FT-IR spectrometer. NMR spectra were recorded on Bruker AC200 (200.1 MHz for ^1H), AM250 (250.13 MHz for ^1H), and AMX 400 (400 MHz for ^1H) spectrometers as well as on a Varian FT300 (300 MHZ for ^1H) spectrometer operating on the Fourier transform mode. Integration ratios were measured with long repetition times (30−60 s) to avoid relaxation problems. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey Ltd., and the other reagents were from Aldrich. RuHCl(COD)(bpm) was synthesized according to a published method.[22]

Tp*RuH(COD) (4a). To a suspension of RuHCl(COD)(bpm) (2 g; 5 mmol) in 40 mL of acetone was added KTp* (1.76 g; 5 mmol). The reaction mixture was stirred for 1 h at room temperature. The resulting yellow solution was filtered and evaporated to dryness. The bpm ligand was eliminated by sublimation. The residue was extracted with pentane and filtered. Removal of pentane under reduced pressure provided a yellow solid. Yield: 75%.

^1H NMR (C_6D_6, 200 MHz) δ −6.42 (s, 1H), 1.90 (m, 4H, CH_2), 2.19 (s, 6H, $2CH_3$), 2.37 (s, 3H, CH_3), 2.49 (s, 6H, $2CH_3$), 2.54 (br, 2H, CH_2), 2.65 (m, 2H, CH_2), 2.78 (s, 3H, CH_3), 3.71 (m, 2H, CH), 4.36 (m, 2H, CH), 5.59 (s, 2H, Tp*CH), 6.08 (s, 1H, Tp*CH); ^{13}C NMR (C_6D_6, 50.3 MHz) δ 13.47, 13.67, 15.44, 16.72 (all q, CH_3, J = 127 Hz), 31.87 (t, J = 127.6 Hz, CH_2), 33.03 (t, J = 127.6 Hz, CH_2), 67.88 (d, J = 156.0 Hz, CH), 69.66 (d, J = 158.6 Hz, CH), 108.55 (d, J = 173.0 Hz, Tp**C*H), 110.21 (d, J = 170.1 Hz, Tp**C*H), 144.05, 145.96, 152.06, 153.40 (all s, Tp**C*CH$_3$); IR (KBr) ν_{BH} = 2545, ν_{RuH} = 2053 cm^{-1}; DCI, MS (carrier gas NH_3) M = 508, Ru^{102}, found *m/z* 509 (M + H). Anal. Calcd for $C_{23}H_{35}BN_6Ru$: C, 54.44; H, 6.95; N, 16.56. Found: C, 54.27; H, 6.95; N, 16.77.

Tp*RuH(H$_2$)$_2$ (5a). A suspension of Tp*RuH(COD) (1 g; 1.98 mmol) in 10 mL of pentane was introduced into a Fischer-Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 15 h at room temperature, over which time a white precipitate separated. It was filtered off, washed with pentane, and dried *in vacuo*. Yield: 93%.

^1H NMR (C_6D_6, 200 MHz) δ −11.27 (s, 5H), 2.31 (s, 9H, $3CH_3$), 2.32 (s, 9H, $3CH_3$), 5.73 (s, 3H, Tp*CH); ^{13}C NMR (C_6D_6, 61.9 MHz) δ 12.87 (q, J = 128 Hz, CH_3), 16.93 (q, J = 128 Hz, CH_3), 106.24 (d, J = 172.3 Hz, Tp**C*H), 143.73 (s, Tp**C*CH$_3$); T_{1min} at 163 K (δ −11.26, 400 MHz, THF-d_8/$C_6D_5CD_3$ 1:4) 26 ms; IR (KBr) ν_{BH} = 2510, ν_{HH} = 2361, ν_{RuH} = 1950 cm^{-1}; DCI, MS (carrier gas NH_3) M = 404, Ru^{102}, found *m/z* 403 (M − H), 433 (M − 5H + $2NH_3$), 450 (M − 5H + $3NH_3$). Anal. Calcd for $C_{15}H_{27}BN_6Ru$: C, 44.67; H, 6.74; N, 20.83. Found: C, 44.49; H, 6.51; N, 20.06.

Tp*RuH(H$_2$)(PCy$_3$) (6a). A Fischer-Porter bottle was charged with Tp*RuH(COD) (80 mg; 0.16 mmol), 8 mL of toluene, and PCy_3 (44.2 mg; 0.16 mmol). The bottle was pressurized to 3 bar of H_2. The reaction mixture was stirred for 2 h at 80 °C. The resulting solution was concentrated to 1 mL, and 5 mL of pentane was added. A white solid precipitated. It was filtered off, washed with 2 mL of pentane, and dried *in vacuo*. Yield: 87%.

^1H NMR (C_6D_6, 250 MHz) δ −10.71 (d, J_{PH} = 18 Hz, 3H), 1−2 (m, 33H, PCy_3), 2.14 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.54 (s, 6H, $2CH_3$), 2.60 (s, 6H, $2CH_3$), 5.8 (br s, 3H, Tp*CH); $^{31}P\{^1H\}$ NMR (C_6D_6, 101.2 MHz) δ 63.05 (s); T_{1min} at 218 K (δ −10.71, 250 MHz, C_7D_8) 22 ms; IR (KBr) ν_{BH} = 2520, ν_{Ru-H} = 2034 cm^{-1}. Anal. Calcd for $C_{33}H_{58}BN_6PRu$: C, 58.14; H, 8.58; N, 12.33. Found: C, 58.07; H, 9.10; N, 12.07.

Tp*RuH(H$_2$)(THT) (7a). A Fischer-Porter bottle was charged with Tp*RuH(COD) (206 mg; 0.41 mmol), 10 mL of toluene and THT (72 μL; 0.82 mmol). The bottle was pressurized to 3 bar of H_2. The reaction mixture was stirred for 2 h at 50 °C. The resulting solution was concentrated to 1 mL, and 5 mL of pentane was added. A cream solid precipitated. It was filtered off, washed with 2 mL of pentane, and dried *in vacuo*. Yield: 52%.

^1H NMR (C_6D_6, 200 MHz) δ −9.62 (s, 3H), 1.42 (m, 4H, $2CH_2$), 2.39 (m, 4H, $2CH_2$), 2.46 (s, 6H, $2CH_3$), 2.71 (s, 12H, $4CH_3$), 5.56 (s, 1H, Tp*CH), 5.98 (s, 2H, Tp*CH); ^{13}C NMR (C_6D_6, 50.3 MHz) δ 13.18 (q, J = 128 Hz, CH_3), 13.58, 15.26, 16.85 (q, J = 126.8 Hz, CH_3), 29.72 (t, J = 129.6 Hz, CH_2), 42.68 (t, J = 145.5 Hz, CH_2), 105.96 (d, J = 172.8 Hz, Tp**C*H), 106.77 (d, J = 171.5 Hz, Tp**C*H), 142.91, 144.17, 150.59, 151.70 (all s, Tp**C*CH$_3$); T_{1min} at 223 K (δ −9.62, 250 MHz) 19 ms; IR (KBr) ν_{BH} = 2503, ν_{HH} = 2250, ν_{RuH} = 1950 cm^{-1}. Anal. Calcd for $C_{19}H_{33}BN_6RuS$: C, 46.62; H, 6.81; N, 17.17; S, 6.55. Found: C, 47.06; H, 6.82; N, 16.16; S, 6.11.

Tp*RuH(H$_2$)(py) (8a). To a solution of Tp*RuH(H$_2$)$_2$ (93 mg; 0.23 mmol) in 5 mL of toluene was added pyridine (18 μL; 0.23 mmol). The reaction mixture was heated to 60 °C for 1 h. The resulting red solution was evaporated to dryness, and the red solid was washed with 5 mL of pentane and dried *in vacuo*. Yield: 88%.

^{1}H NMR (C_6D_6, 200 MHz) δ −8.17 (s, 3H), 2.05 (s, 6H, 2CH_3), 2.36 (s, 3H, Tp*CH_3), 2.44 (s, 3H, CH_3), 2.52 (s, 6H, 2CH_3), 5.64 (s, 1H, Tp*CH), 5.96 (s, 2H, Tp*CH), 6.26 (br, 2H), 6.56 (m, 1H), 6.76 (t, J = 7,5 Hz, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz) δ 13.00, 13.23, 14.77, 16.98 (CH_3), 106.01, 106.52 (Tp*CH), 147.72, 150.94 (Tp*$C$$CH_3$), 122−124 (CH); $T_{1\min}$ at 233 K (δ −8.17, 250 MHz, C_7D_8) 19 ms; IR (KBr) ν_{BH} = 2498, ν_{RuH} = 1970 cm^{-1}. DCI, MS (carrier gas NH_3) M = 481, Ru^{102}, found *m/z* 480 (M − H), 495 (M − 3H + NH_3), 512 (M − 3H + 2NH_3). Anal. Calcd for $C_{20}H_{30}BN_7Ru$: C, 49.99; H, 6.31; N, 20.41. Found: C, 50.48; H, 6.31; N, 19.35.

Tp*RuH(H_2)($NHEt_2$) (9a). A Fischer-Porter bottle was charged with Tp*RuH(COD) (80 mg; 0.16 mmol), 8 mL of toluene, and Et_2NH (1 mL). The bottle was pressurized to 3 bar of H_2. The reaction mixture was stirred for 2 h at room temperature. The resulting solution was concentrated to 0.5 mL, and 3 mL of pentane was added. A cream solid precipitated. It was filtered off, washed with 2 mL of pentane, and dried *in vacuo*. This compound was contaminated with Tp*RuH(H_2)$_2$.

^{1}H NMR (C_6D_6, 200 MHz) δ −9.26 (s, 3H), 5.52 (s, 1H, Tp*CH), 6.01 (s, 2H, Tp*CH); $T_{1\min}$ at 223 K (δ −9.26, 250 MHz, $C_6D_5CD_3$) 19 ms.

Tp*RuH(py)$_2$ (10a). A Fischer-Porter bottle was charged with Tp*RuH(COD) (226 mg; 0.45 mmol), 8 mL of toluene, and pyridine (143 μL; 1.80 mmol). The bottle was pressurized to 3 bar of H_2. The reaction mixture was stirred for 1.5 h at room temperature. The resulting red solution was evaporated to dryness, and the red solid was washed with 2 mL of pentane and dried *in vacuo*. Yield: 94%.

^{1}H NMR (C_6D_6, 200 MHz) δ −14.11 (s, 1H), 1.47 (s, 3H, CH_3), 2.05 (s, 6H, 2CH_3), 2.54 (s, 6H, 2CH_3), 2.66 (s, 3H, CH_3), 5.87 (s, 2H, Tp*CH), 6.09 (s, 1H, Tp*CH), 6.26 (br, 6H, CH), 6.76 (t, 4H, J = 8.5 Hz, CH); ^{13}C NMR (C_6D_6, 50.3 MHz) δ 13.03 (q, J = 127.9 Hz, CH_3), 13.43 (q, J = 127.6 Hz, CH_3), 14.62 (m, CH_3), 14.76 (q, J = 126.8 Hz, CH_3), 106.59 (d, J = 172 Hz, Tp*CH), 106.77 (d, J = 172 Hz, Tp*CH), 122.62 (d, J = 162.3 Hz, CH), 130 (br, CH), 143.45, 143.68, 149.56, 152.86 (all s, Tp*$C$$CH_3$), 158.52 (d, J = 180.8 Hz, CH); $T_{1\min}$ at 233 K (δ −14.11, 250 MHz, C_7D8) 250 ms; IR (KBr) ν_{BH} = 2502, ν_{RuH} = 1838 cm^{-1}. Anal. Calcd for $C_{25}H_{33}BN_8Ru$ + (0.5 C_5H_{12}): C, 55.64; H, 6.64; N, 18.88. Found: C, 55.76; H, 6.30; N, 18.69. The 0.5 equiv of pentane was detected and integrated by ^{1}H NMR.

Tp*RuH(THT)$_2$ (11a). A Fischer-Porter bottle was charged with Tp*RuH(COD) (265 mg; 0.52 mmol), 10 mL of toluene, and THT (184 μL; 2.08 mmol). The bottle was pressurized to 3 bar of H_2. The reaction mixture was stirred for 1.5 h at room temperature. The resulting solution was concentrated to 1 mL, and 4 mL of pentane was added. A yellow solid precipitated. It was filtered off, washed with 2 mL of pentane, and dried *in vacuo*. Yield: 90%.

^{1}H NMR (C_6D_6, 50.3 MHz) δ −14.21 (s, 1H), 1.64 (m, 8H, CH_2), 2.40 (s, 6H, 2CH_3), 2.58 (s, 3H, CH_3), 2.62 (m, 8H, CH_2), 2.72 (s, 3H, CH_3), 2.73 (s, 6H, 2CH_3), 5.84 (s, 2H, Tp*CH), 6.11 (s, 1H, Tp*CH);^{13}C NMR (C_6D_6, 50.3 MHz) δ 13.32 (q, J = 127.4 Hz, CH_3), 13.58 (q, J = 127.3 Hz, CH_3), 15.25 (q, J = 126.1 Hz, CH_3), 16.93 (q, J = 130.8 Hz, CH_3), 29.91 (d, J = 130.8 Hz, CH_2), 39.70 (d, J = 142.3 Hz, CH_2), 106.43 (d, J = 170.6 Hz, Tp*CH), 106.89 (d, J = 169.3 Hz, Tp*CH), 143.67, 143.84, 151.58, 151.98 (all s, Tp*$C$$CH_3$); $T_{1\min}$ at 243 K (250 MHz) 400 ms; IR (KBr) ν_{BH} = 2517, ν_{RuH} = 1906 cm^{-1}. Anal. Calcd for $C_{23}H_{39}BN_6RuS_2$: C, 47.98; H, 6.84; N, 14.60; S, 11.14. Found: C, 48.41; H, 6.85; N, 14.93; S, 10.25.

Tp*RuH(CO)$_2$ (12a). A Fischer-Porter bottle was charged with Tp*RuH(H_2)$_2$ (68 mg; 0.17 mmol) and 5 mL of toluene. The bottle was pressurized to 3 bar of CO. The reaction mixture was stirred for 15 h at room temperature. The resulting solution was concentrated to 0.5 mL, and 2 mL of pentane was added. A white solid precipitated. It was filtered off and dried *in vacuo*. Yield: 92%.

^{1}H NMR (C_6D_6, 200 MHz) δ −9.25 (s, 1H), 2.18 (s, 6H, 2CH_3), 2.29 (s, 3H, Tp*CH_3), 2.44 (s, 9H, 3CH_3), 5.55 (s, 2H, Tp*CH), 5.70 (s, 1H, Tp*CH); ^{13}C NMR (C_6D_6, 50.3 MHz) δ 12.55 (q, J = 128.3 Hz, CH_3), 12.83 (q, J = 127.8 Hz, CH_3), 15.15 (q, J = 128.4 Hz, CH_3), 16.08 (q, J = 127.8 Hz, CH_3), 106.67 (d, J = 173.5 Hz, Tp*CH), 143.97, 144.40, 151.10, 151.68 (all s, Tp*$C$$CH_3$), 202 (s, CO); IR (KBr) ν_{BH} = 2521, ν_{RuH} = *ca.* 2000 (shoulder), ν_{CO} = 1947, 2027 cm^{-1}. Anal. Calcd for $C_{17}H_{23}BN_6O_2Ru$: C, 44.84; H, 5.11; N, 18.46. Found: C, 44.41; H, 5.36; N, 17.71.

[Tp*Ru($NCCH_3$)$_3$]$^+$[CF_3SO_3]$^-$ (14a). To a solution of Tp*RuH(H_2)$_2$ (83 mg; 0.21 mmol) in 4 mL of THF at −80 °C was added CF_3SO_3H (19 μL; 0.21 mmol). The reaction mixture was stirred at −80 °C for 1 h and then warmed to room temperature and kept at this temperature for 1 h. The resulting red solution was evaporated, and the solid was dissolved in 4 mL of CH_3CN and stirred for 1 h. The solution was evaporated to dryness and the solid recrystallized from acetone/pentane and isolated as a pink powder. Yield: 72%.

^{1}H NMR ((CD_3)$_2$CO, 200 MHz) δ 2.47 (s, 9H, 3CH_3), 2.53 (s, 9H, 3CH_3), 2.82 (s, 9H, 3CH_3), 5.99 (s, 3H, Tp*CH). Anal. Calcd for $C_{22}H_{31}N_9BRuF_3SO_3$ + (0.5(CH_3)$_2$CO): C, 40.50; H, 4.78; N, 18.08; S, 4.59. Found: C, 40.69; H, 4.94; N, 17.39; S, 4.79. The 0.5 equiv of acetone was also detected and integrated by ^{1}H NMR.

Tp′RuH(COD) (4b). TlTp′ (200 mg; 0.25 mmol) was added to a suspension of RuHCl(COD)(bpm) (100 mg; 0.25 mmol) in acetone (5 mL). This mixture was stirred for 2 h at room temperature. The solution was removed by filtration, and the yellow solid residue was extracted with 40 mL of Et_2O. Removal of the solvent under reduced pressure provided a yellow solid. Yield: 68%.

^{1}H NMR (C_6D_6, 300 MHz) δ −8.12 (s, 1H), 1.19 (d, J = 7.3 Hz, 6H, 2CH_3), 1.24 (d, J = 7.1 Hz, 6H, 2CH_3), 1.37 (d, J = 6.9 Hz, 6H, 2CH_3), 1.52 (d, J = 8.0 Hz, 2H, 1CH_2), 1.66 (d, J = 8.1 Hz, 2H, 1CH_2), 2.10 (br, 4H, 2CH_2), 3.13 (br, 2H, 2CH), 3.21 (sept, 1H, H^{iPr}), 3.33 (sept, 2H, H^{iPr}), 3.51 (br, 2H, 2CH), 7.62 (s, 2H, Tp′CH), 7.64 (s, 1H, Tp′CH); ^{13}C NMR (C_6D_6, 75.45 MHz) δ 20.09 (q, J = 126.9 Hz, 2CH_3), 20.27 (q, J = 126.9 Hz, 2CH_3), 21.31 (q, J = 126.9 Hz, 2CH_3), 26.71 (d, J = 127.4 Hz, C^{iPr}), 28.68 (d, J = 127.9 Hz, C^{iPr}), 29.93 (t, J = 128.9 Hz, CH_2), 31.84 (t, J = 128.4 Hz, CH_2), 71.49 (d, J = 156.6 Hz, CH), 71.96 (d, J = 156.6 Hz, CH), 89.66, 93.42 (Tp′CBr), 134.7 (d, J = 187.3 Hz, Tp′CH), 135.24 (d, J = 193.9 Hz, Tp′CH), 155.32, 158.04 (Tp′CCH(CH_3)$_2$); IR (KBr) ν_{RuH} = 2084, 1986 cm^{-1}; MS (FAB, nitrobenzyl alcohol matrix) M = 786, Ru^{102}, found *m/z* 786 (M). Anal. Calcd for $C_{26}H_{38}BBr_3N_6Ru$: C, 39.74; H, 4.84; N, 10.69. Found: C, 40.14; H, 4.86; N, 10.44.

Tp′RuH(H_2)$_2$ (5b). PtO_2 (8 mg; 0.08 mmol) was added to a solution of Tp′RuH(COD) (150 mg; 0.19 mmol) in pentane (25 mL). This mixture was stirred for 2 h at 90 °C under 3 bar of dihydrogen in a Fischer-Porter bottle. The solution changed from yellow to white. After cooling to room temperature, the solvent was removed by an N_2 stream. A white powder was obtained in a quantitative yield.

^{1}H NMR (C_6D_6, 200 MHz) δ −11.82 (s, 5H), 1.38 (d, J = 7.08 Hz, 18H, 6CH_3), 3.66 (sept, 3H, H^{iPr}), 7.25 (s, 3H, Tp′CH); ^{13}C NMR (C_6D_6, 75.45 MHz) δ 19.41 (q, J = 126.4 Hz, CH_3), 30.6 (d, J = 127.9 Hz, C^{iPr}), 90.4 (Tp′CBr), 137.1 (d, J = 192.9 Hz, Tp′CH), 157.03 (Tp′CCH(CH_3)$_2$); $T_{1\min}$ ($C_6D_5CD_3$, 300 MHz at 182 K) 28 ms; IR (KBr) ν_{BH}= 2489, ν_{RuH}= 1973 cm^{-1}; MS (FAB, nitrobenzyl alcohol matrix) M = 682, Ru^{102}, found *m/z* 676 (M − 6H). Anal. Calcd for $C_{18}H_{30}BBr_3N_6Ru$: C, 31.70; H, 4.43; N, 12.32. Found: C, 31.97; H, 4.19; N, 11.83.

Tp′RuH(H_2)(PCy_3) (6b). PCy_3 (30 mg, 0.13 mmol) was added to a solution of Tp′RuH(COD) (100 mg; 0.13 mmol) in pentane (25 mL). This mixture was pressurized under 3.5 bar of dihydrogen in a Fischer-Porter bottle, heated at 110 °C, and stirred for 12 h. After cooling to room temperature, the solvent was concentrated to 2 mL by an N_2 stream, and a white powder was isolated by filtration. Yield: 74%.

^{1}H NMR (C_6D_6, 300 MHz) δ −11.47 (d, J = 17.5 Hz, 3H), 1−2 (m, 51H), 3.93 (br, 3H, H^{iPr}), 7.32 (br, 3H, Tp′CH); $T_{1\min}$ ($C_6D_5CD_3$, 300 MHz at 208 K) 30 ms; IR (KBr) ν_{BH}= 2448, ν_{RuH} = 2041 cm^{-1}. One equivalent of toluene was also detected and integrated by ^{1}H NMR. Anal. Calcd for $C_{36}H_{61}BBr_3N_6PRu$ + ($C_6H_5CH_3$): C, 49.07; H, 6.55; N, 8.02. Found: C, 49.13; H, 6.43; N, 8.44.

Tp′RuH(H_2)(THT) (7b). This complex was synthesized from Tp′RuH(COD) (100 mg; 0.13 mmol) and THT (11.22 μL; 0.13 mmol) as described above for **6b** but at 50 °C. A white powder was obtained in a quantitative yield.

^{1}H NMR (C_6D_6, 300 MHz) δ −10.5 (s, 3H,), 1.21 (m, 4H, 2CH_2), 1.31 (d, J = 7.0 Hz, 6H, 2CH_3), 1.38 (d, J = 7.0 Hz, 6H, 2CH_3), 1.48 (d, J = 7.4 Hz, 6H, 2CH_3), 2.04 (m, 4H, 2CH_2), 3.73 (sept, 1H, H^{iPr}), 3.97 (sept, 2H, H^{iPr}), 7.00 (s, 1H, Tp′CH), 7.40 (s, 2H, Tp′CH); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.45 MHz) δ 19.42, 20.08, 20.43 (CH_3), 28.50 (CH_2), 29.27, 30.35, (C^{iPr}), 41.11 (CH_2), 90.30 (Tp′CBr), 136.88, 137.67

(Tp'CH), 157.37 (Tp'CCH(CH$_3$)$_2$); $T_{1\text{min}}$ (C$_6$D$_5$CD$_3$, 300 MHz at 228 K) 21 ms; IR (KBr) ν_{BH} = 2453, ν_{RuH} = 1955 cm^{-1}. Anal. Calcd for $C_{22}H_{36}BBr_3N_6RuS$: C, 34.40; H, 4.69; N, 10.94. Found: C, 34.65; H, 4.69; N, 10.58.

Tp'RuH(H$_2$)(py) (8b). This complex was synthesized from Tp'RuH(COD) (100 mg; 0.13 mmol) and py (10.24 μL, 0.13 mmol) as described above for **6b** but at 30 °C for 30 min. The complex was found to be impossible to separate from small amounts of **5b**. Yield: 52%.

^{1}H NMR (C$_6$D$_6$, 300 MHz) δ −9.04 (s, 3H), 0.85 (d, J = 7.4 Hz, 6H, 2CH$_3$), 1.29 (d, J = 7.1 Hz, 6H, 2CH$_3$), 1.39 (d, J = 7.4 Hz, 6H, CH$_3$), 3.07 (sept, 2H, H^{iPr}), 3.91 (sept, 1H, H^{iPr}), 5.69 (br, 1H), 6.38 (t, J = 7.6 Hz, 1H), 6.60 (br, 1H), 7.14 (s, 1H, Tp'CH), 7.25 (br, 1H), 7.46 (s, 2H, Tp'CH), 8.28 (br, 1H); ^{13}C NMR (C$_6$D$_6$, 75.45 MHz) δ 19.0 (q, J = 126.4 Hz, 2CH$_3$), 19.47 (q, J = 126.4 Hz, 2CH$_3$), 20.06 (q, J = 126.9 Hz, 2CH$_3$), 28.75 (d, J = 128.9 Hz, C^{iPr}), 30.21 (d, J = 130.8 Hz, C^{iPr}), 88.65, 90.25 (Tp'CBr), 122.05 (d, J = 163.7 Hz, CH), 122.97 (d, J = 166.2 Hz, CH), 132.09 (d, J = 164.7 Hz, CH), 136.84 (J =191.3 Hz, Tp'CH), 137.09 (d, J = 192.4 Hz, Tp'CH), 155.19 (d, J = 177.4 Hz, CH), 156.82, 156.99 (Tp'CCH(CH$_3$)$_2$), 158.41 (d, J = 190.4 Hz, CH); $T_{1\text{min}}$ (C$_6$D$_5$CD$_3$, 300 MHz at 230 K) 20 ms; IR (KBr) ν_{BH} = 2449, ν_{RuH} = 1943 cm^{-1}.

Acknowledgment. B.M. gratefully acknowledges INTEVEP S.A. and CONICIT for a grant; B.M., S.S.E., and B.C. thank PICS France-Vénézuéla and CNRS for support.

JA9507978