Synthesis, Characterization, and Acidity of Ruthenium Dihydrogen Complexes with 1,4,7-Triazacyclononane, 1,4,7-Trimethyl-1,4,7-triazacyclononane, and Hydrotris(pyrazolyl)borato Ligands

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Received November 24, 1997

Protonation of $[^{R}CnRuH(L)(L')]^{+}$ (^{R}Cn = 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane; L,L′ = $(PPh_3)_2$, dppe, and CO,PPh_3) produced the corresponding dicationic dihydrogen complexes $[^{R}CnRu(H_2)(L)(L')]^{2+}$. Protonation of TpRuH(dppe) (Tp = hydrotris(pyrazolyl)borato) yielded the new monocationic dihydrogen complex $[TpRu(H_2)(dppe)]^{+}$. The acidity of the dihydrogen complexes $[^{R}CnRu(H_2)(L)(L')]^{2+}$ and monocationic dihydrogen complexes $[TpRu(H_2)(L)(L')]^{+}$ (L,L′ = dppe, $(PPh_3)_2$, CH_3CN,PPh_3, and CO,PPh_3) has been studied. It was found that the dicationic complexes are more acidic than their monocationic Tp and Cp counterparts. $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ was found to be more acidic than $[^{H}CnRu(H_2)(CO)(PPh_3)]^{2+}$, probably due to the stronger H−H interaction in the latter complex. It is also noted that triazacyclononane and hydrotris(pyrazolyl)borato dihydrogen complexes with pseudo aqueous pK_a values well above that of H_3O^{+} can be deprotonated by H_2O to form the corresponding monohydride complexes in organic/aqueous mixed solvents. It is believed that deprotonation of the dihydrogen ligands in these complexes is assisted by strong solvation of H^{+} by H_2O.

Introduction

Knowledge about the acidity of dihydrogen complexes may help to understand mechanisms of stoichiometric and/or catalytic reactions involving heterolytic cleavage of dihydrogen bond[1] and to design new catalytic processes. The most interesting examples involving heterolytic cleavage of dihydrogen reported recently include intramolecular protonation of alkyl ligands by dihydrogen ligands in the hydrogenation reactions,[2] intramolecular protonation of vinylidene ligands by dihydrogen ligands to form carbyne complexes,[3] and transition metal catalyzed H/D exchange reactions.[4]

During the past few years, there have been numerous efforts in defining the factors affecting the acidity of dihydrogen complexes, especially dihydrogen complexes of the types $[Cp'Ru(H_2)(PP)]^{+}$ (Cp′ = Cp, Cp*; PP = diphosphines),[5,6] $[MH(H_2)(PP)_2]^{+}$ (M = Fe, Ru, Os; PP = diphosphines),[7,8] $[MCl(H_2)(PP)_2]^{+}$ (M = Fe, Ru, Os; PP = diphosphines),[8,9] and $[M(L)(H_2)(PP)_2]^{2+}$ (M = Fe, Ru, Os; PP = diphosphines; L = CO, CH_3CN).[8,10] Deprotonation of dihydrogen ligands with various bases

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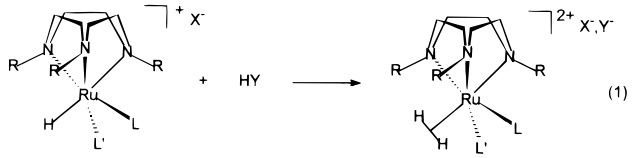
S0276-7333(97)01037-6 CCC: $15.00
Publication on Web 04/17/1998

have been reported for other complexes,[11] for example, $[IrH(H_2)(bq)(PPh_3)_2]^+$ (bq = 7,8-benzoquinolinate) by BuLi, $[Os(H_2)(NH_3)_5]^{2+}$ by NaOMe, and $[Os(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ by Et_2O. These studies show that acidity of dihydrogen complexes can vary widely depending on ligands and metals.

Cyclopentadienyls,[12] hydrotris(pyrazolyl)borates,[13,14] and 1,4,7-triazacyclononane derivatives (^{R}Cn)[15,16] are very useful ligands in organometallic chemistry and homogeneous catalysis. The three ligands are similar in that they all coordinate to metals in a facial geometry and are formally 6e donors on ionic model. They are different in their π-accepting ability, with cyclopentadienyls being the strongest and 1,4,7-triazacyclononane derivatives the weakest. It is therefore expected that the three ligands should show differences in stabilizing dihydrogen ligands and in affecting the acidity of the resulting dihydrogen and hydride complexes. However, such comparison has not been made yet. Despite that numerous complexes of the formula $[(C_5R_5)RuH_2(L)(L')]^+$ (L,L′ = neutral ligands such as monophosphines, diphosphines, CO, solvent molecules) are known,[5,6,17] only a few $[TpRu(H_2)(L)(L')]^+$ complexes have been reported,[14a,b,i] and the isostructural complexes $[^RCnRu(H_2)(L)(L')]^{2+}$ are virtually unknown. While pK_a values of complexes of the type $[(C_5R_5)Ru(H_2)(L)(L')]^+$ have been reported,[5,6] that of the isostructural Tp and ^{R}Cn complexes have not been well studied. We report here the synthesis and properties of some ruthenium complexes supported by 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane ligands and the acidity of $[^RCnRu(H_2)(L)(L')]^{2+}$ and $[TpRu(H_2)(L)(L')]^+$.

Results and Discussion

Synthesis and Characterization of $[^RCn(H_2)(L)(L')]^{2+}$ Complexes. The dihydrogen complexes $[^RCnRu(H_2)(L)(L')]^{2+}$ (**5**−**8**) were synthesized by protonation of the corresponding monohydride complexes **1**−**4** with $HBF_4{\cdot}Et_2O$ or CF_3SO_3H (eq 1).



1, R = H, (L)(L') = $(PPh_3)_2$ **5**, R = H, (L)(L') = $(PPh_3)_2$ X^- = Y^- = BF_4^-
2, R = H, (L)(L') = $(CO)(PPh_3)$ **6**, R = H, (L)(L') = $(CO)(PPh_3)$ X^- = Y^- = BF_4^-
3, R = Me, (L)(L') = dppe **7**, R = Me, (L)(L') = dppe X^- = Y^- = $CF_3SO_3^-$
4, R = Me, (L)(L') = $(CO)(PPh_3)$ **8**, R = Me, (L)(L') = $(CO)(PPh_3)$ X^- = PF_6^-, Y^- = $CF_3SO_3^-$

The starting monohydride complexes $[^{Me}CnRuH(dppe)]CF_3SO_3$ (**3**)[16d] and $[^{Me}CnRuH(CO)(PPh_3)]PF_6$ (**4**)[16d] are known compounds. The monohydride complex $[^HCnRuH(PPh_3)_2]BF_4$ (**1**) was prepared by reacting ^{H}Cn with $RuHCl(PPh_3)_3$ in the presence of $NaBF_4$. We have attempted to prepare the analogous complex $[^{Me}CnRuH(PPh_3)_2]BF_4$ by using ^{Me}Cn in place of ^{H}Cn. However, the preparation was not successful and some intractable materials were obtained. Failure of the reaction is probably due to large steric interaction between triphenylphosphine and the sterically more demanding ^{Me}Cn ligand. The complex $[^HCnRuH(CO)(PPh_3)]BF_4$ (**2**) was prepared by refluxing a mixture of ^{H}Cn and $RuHCl(CO)(PPh_3)_3$ in 2-methoxyethanol, followed by precipitation with $NaBF_4$. A similar procedure has been used previously for the preparation of $[^{Me}CnRuH(CO)(PPh_3)]PF_6$ (**4**).[16d]

The new monohydride complexes can be readily characterized by their NMR, IR, and elemental analysis. The structure of complex **1** has also been confirmed by X-ray diffraction. The molecular structure of the cation $[^HCnRuH(PPh_3)_2]^+$ is shown in Figure 1. Crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

The structure could be described as a distorted octahedron with the hydride trans to N(2). The distortion can be attributed to the coordination geometry of

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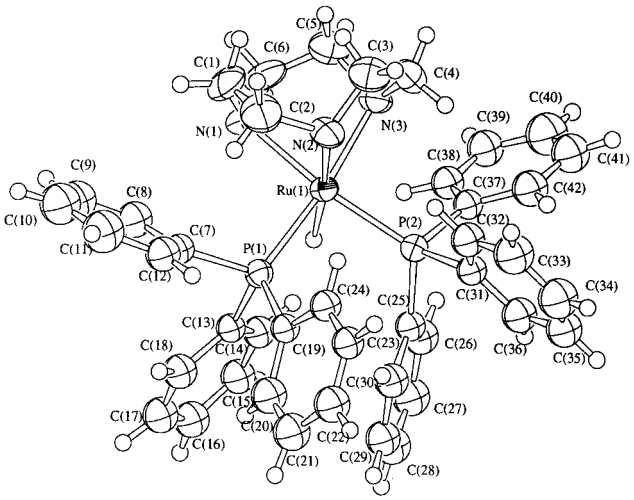

Figure 1. Molecular structure of the cation $[^{H}CnRuH(PPh_3)_2]^+$.

Table 1. Crystal Data and Refinement Details for $[^{H}CnRuH(PPh_3)_2]BF_4 \cdot 2CH_2Cl_2$

formula	$C_{44}H_{47}BCl_4F_4N_3P_2Ru$
fw	1009.51
color and habit	red blcok
cryst dimens (mm)	0.22 × 0.23 × 0.29
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	10.598(1)
b, Å	20.046(1)
c, Å	21.973(1)
V, Å^3	4668.1(4)
Z	4
d_{calcd}, g cm^{-3}	1.436
F(000)	2060.00
radiation	Mo Kα (λ = 0.710 73 Å)
μ(Mo Kα), cm^{-1}	6.83
T, °C	25.0
diffractometer	Marresearch image plate scanner
$2\theta_{max}$, deg	3.0−50.0
scan type	ω
exposure (min)	5
no. of reflns collcd	28 766
no. of unique reflns	4741
no. of obsd reflns	3178 ($F > 3.0\sigma(F)$)
abs corr	interimage scaling
no. of params refined	328
final *R* indices (obsd data), %	R = 7.2, R_w = 9.9
goodness of fit	3.41
data-to-param ratio	9.69
largest diff peak, e Å^{-3}	0.63
largest diff hole, e Å^{-3}	−0.52

the ^{H}Cn ligand. The N−Ru−N angles and Ru−N bond distances in complex **1** are very similar to those observed for related complexes such as $[^{Me}CnR(PMe_3)(P(OMe)_3(C{\equiv}CPh)]PF_6$,[16a] $[^{Me}CnRu(PMe_3)(\eta^3\text{-}PhC_3CHPh)]PF_6$,[16a] $[^{Me}CnRuH(\eta^4\text{-}COD)]PF_6$,[16e] and $[^{Me}CnRu(\eta^5\text{-}C_8H_{11})]PF_6$.[16e] The bond Ru−N(2) (2.30(1) Å) is slightly longer than Ru−N(1) (2.20(1) Å) and Ru−N(3) (2.19(1) Å), presumably due to the trans influence of the hydride ligand. The P(1)−Ru−P(2) angle (96.4°) is smaller than that observed for $CpRuH(PPh_3)_2$ (101.4°)[18a] and comparable to that observed for $CpRuH(PMe_3)_2$.[18b,c]

Protonation of the monohydride complexes **1**−**4** with $HBF_4 \cdot Et_2O$ or CF_3SO_3H produced the dihydrogen complexes **5**−**8** (eq 1). The dihydrogen complex $[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$ (**5**), isolated as yellow solid by addition of Et_2O to a CH_2Cl_2 solution of $[^{H}CnRuH(PPh_3)_2]BF_4$ acidified with slightly excess $HBF_4 \cdot Et_2O$, was contaminated by small amount of aquo complex $[^{H}CnRu(H_2O)(PPh_3)_2](BF_4)_2$. Apparently, the aquo complex was formed by displacement of η^2-H_2 in **5** by adventitious water in the solvents. Similar contamination problem was encountered in the preparation of the dihydrogen complex $[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)_2$ (**7**). But it will be seen (vide infra) that, in the absence of acid, water acts as a base to deprotonate the η^2-H_2 in **5** or **7**. The dihydrogen complexes **5** and **7** are stable in the solid state at room temperature, but in solution, the η^2-H_2 ligand is displaced by strongly coordinating solvent such as acetonitrile. The very acidic CO-containing dihydrogen complexes **6** and **8** are unstable with respect to loss of H_2, both in the solid state and in solution, at room temperature. These complexes were prepared by acidification at −30 °C with excess $HBF_4 \cdot Et_2O$ and were characterized in situ with NMR spectroscopy.

The existence of the η^2-H_2 moieties in complexes **5**−**8** was confirmed by variable-temperature T_1 measurements and the observation of large ^1J(HD) coupling constants for the corresponding isotopomers which were prepared by acidification of **1**−**4** with DBF_4 or CF_3SO_3D. In particular, the ^1J(HD) coupling constants for the isotopomers were observed in the range of 29.4−31.8 Hz, and T_1(min) values, in the range of 12−24 ms at 400 MHz. The changes in the ^1J(HD) and T_1(min) are rather small especially in view of the fact that the electronic properties of the ligands have been changed drastically. It is also interesting to note that the ^1J(HD) for $[^{H}CnRu(HD)(CO)(PPh_3)]^{2+}$ (31.8 Hz) is slightly large than that of $[^{Me}CnRu(HD)(CO)(PPh_3)]^{2+}$ (30.0 Hz), but the T_1(min) for $[^{H}CnRu(H_2)(CO)(PPh_3)]^{2+}$ (14 ms) is slightly longer than that of $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ (12 ms). The shorter T_1(min) for $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ is undoubtedly caused by the extra relaxation due to the methyl groups.[19]

Complexes **5**−**8** provide additional examples of *dicationic* dihydrogen complexes. In contrast to the abundance of isolable monocationic dihydrogen complexes, well characterized dicationic dihydrogen complexes are still very limited in numbers. Reported dicationic dihydrogen complexes were mainly those of the osmium complexes such as $[Os(H_2)(NH_3)_5]^{2+}$,[20a] $[Os(H_2)(en)_2(L)]^{2+}$,[20b] *trans*-$[Os(H_2)(dppe)_2(CH_3CN)]^{2+}$,[10] $[Os(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ (bpy = 2,2′-dipyridyl),[11k] $[Os(H_2)(CO)(bpy)_2]^{2+}$,[11k] and $[Os(H_2)(CO)(dppp)_2]^{2+}$.[8] Dicationic dihydrogen complexes of other metals are limited to *trans*-$[Fe(H_2)(L)(dppe)_2]^{2+}$ (L = CO, CNH)[21] and $[Ru(H_2)(CO)(dppp)_2]^{2+}$.[8]

Synthesis and Characterization of $[TpRu(H_2)(L)(L')]^+$ Complexes. The dihydrogen complexes $[TpRu(H_2)(PPh_3)_2]BF_4$ (**14**) and $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$ (**15**) were recently synthesized by us from protonation reactions of the corresponding monohydride complexes with $HBF_4 \cdot Et_2O$.[14b] With similar strategy, the new

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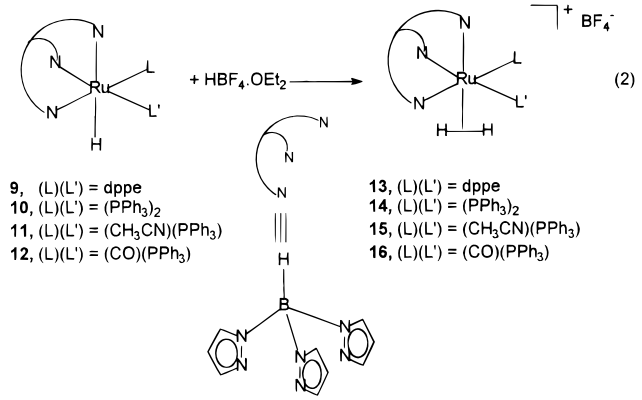
Table 2. Selected Bond Distances (Å) and Angles (deg) for $[^{H}CnRuH(PPh_3)_2]BF_4 \cdot 2CH_2Cl_2$

		Interatomic Distance			
Ru−P(1)	2.286(4)	Ru−P(2)	2.270(4)	Ru−N(1)	2.20(1)
Ru−N(2)	2.30(1)	Ru−N(3)	2.19(1)	Ru−H	1.8(2)
		Intramolecular Angles			
P(1)−Ru−P(2)	96.4(1)	P(1)−Ru−N(1)	93.8(4)	P(1)−Ru−N(2)	102.2(4)
P(1)−Ru−N(3)	172.8(4)	P(1)−Ru−H	95(5)	P(2)−Ru−N(1)	164.5(4)
P(2)−Ru−N(2)	110.8(4)	P(2)−Ru−N(3)	90.6(3)	P(2)−Ru−H	85(6)
N(1)−Ru−N(2)	78.2(6)	N(1)−Ru−N(3)	79.0(5)	N(1)−Ru−H	82(6)
N(2)−Ru−N(3)	76.9(5)	N(2)−Ru−H	154(6)	N(3)−Ru−H	83(6)

dihydrogen complexes $[TpRu(H_2)(dppe)]BF_4$ (**13**) and $[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**16**) were prepared (eq 2).



Like **5** and **7**, the isolated **13** was contaminated by a small amount of aquo complex $[TpRu(H_2O)(dppe)]BF_4$. It should be mentioned that the CO-containing dihydrogen complex **16** is unstable with respect to loss of H_2 at room temperature; therefore, the acidification had to be carried out at −30 °C and **16** was not isolated but was studied in situ.

The existence of the η^2-H_2 moiety in $[TpRu(H_2)(dppe)]BF_4$ **(13)** was confirmed by observation of a T_1(min) value of 14 ms for **13** and a large ^1J(HD) coupling constant of 32.5 Hz for the corresponding isotopomer $[TpRu(HD)(dppe)]BF_4$, which was prepared by acidification of **9** with DBF_4. Similarly, the existence of the η^2-H_2 moiety in **16** is evidenced by short T_1(min) of this complex and large ^1J(HD) coupling constant (33.3 Hz) of the corresponding isotopomer $[TpRu(HD)(CO)(PPh_3)]BF_4$.

Comparison of the Abilities of Cp^-, Tp^-, and ^{R}Cn in Stabilizing Dihydrogen Complexes. Although Cp^-, Tp^-, and ^{R}Cn are isoelectronic and all adopt facial geometry, their abilities to stabilize dihydrogen ligands are different. For example, while $[CpRuH_2(PPh_3)_2]^+$ is a classical dihydride complex, both $[TpRu(H_2)(PPh_3)_2]^+$ and $[^{H}CnRu(H_2)(PPh_3)_2]^{2+}$ are molecular dihydrogen complexes. Subtle differences in the Tp and ^{R}Cn complexes are also noted. Although the ^{R}Cn dihydrogen complexes **5**−**8** are dicationic and the Tp dihydrogen complexes **13**−**16** are monocationic,^1J(HD) couplings of the isotopomers of the ^{R}Cn complexes are consistently smaller than those of the Tp counterparts. This is probably the result of ^{R}Cn being better σ-donors than Tp and the latter being able to act as π-accepting ligand. In consonance with the trends in ^1J(HD) couplings, we have observed that the η^2-H_2 ligands in the Tp complexes **13**−**16** are much more readily displaced by water in the absence of H_2 pressure than those in **5**−**8**. Reactions of these complexes with water warrant further discussion later.

Acidity of the Dihydrogen Complexes. We have attempted to rank the relative acidity of the dihydrogen complexes. A useful approach to do so is to measure the pseudo aqueous pK_a values.[6−10] In this approach, equilibrium constants for the reactions of L_nMH (precursors to dihydrogen complexes) and an acid with known aqueous pK_a value are determined in nonaqueous solutions. The pseudo aqueous pK_a of the dihydrogen complexes are then calculated in reference to the aqueous pK_a of the acid. The pseudo aqueous pK_a values of **5**, **7**, **13**, **14**, and **15** were estimated by studying the equilibrium shown in eq 3 with ^{1}H NMR in CD_2Cl_2, using the hydride complexes $RuHCl(dppe)_2$, $CpRuH(PPh_3)_2$, and CpRuH(dppm) as the bases. The pseudo aqueous pK_a values of $[RuCl(H_2)(dppe)_2]^+$,[9b] $[CpRuH_2(PPh_3)_2]^+$,[6b] and $[CpRu(H_2)(dppm)]^+$ [6b] have been determined previously in CD_2Cl_2 using a similar method. The equilibrium mixture could be conveniently obtained by protonation

$$[L_nRu(H_2)]^{n+} + L'_nMH \leftrightarrow [L_nRuH]^{(n-1)+} + L'_nMH_2^+ \quad (3)$$

with a limited amount of $HBF_4 \cdot Et_2O$ of a mixture of $[L_nRuH]^{(n-1)+}$ and L'_nMH. All the equilibria were obtained at room temperature, except in the case of $[TpRu(H_2)(CH_3CN)(PPh_3)]^+$, which was carried out at −30 °C. The relative concentrations of the dihydrogen complexes and the metal hydrides in equilibrium were estimated from integrations of the upfield hydride signals in the ^{1}H NMR spectra, and therefore, the equilibrium constants can be estimated on the basis of the known pK_a values of $L'_nMH_2^+$. The pseudo aqueous pK_a value of the Tp carbonyl dihydrogen complex $[TpRu(H_2)(CO)(PPh_3)]BF_4$ (**16**) was determined in a similar manner at −80 °C, using $[^{H}CnRu(H)(CO)(PPh_3)]BF_4$ (**2**) as the base.

The pK_a values of the ^{R}Cn carbonyl dihydrogen complexes **6** and **8** could not be estimated by use of eq 3 because they are much more acidic than the $L'_nMH_2^+$ complexes. The pK_a values of **6** and **8** were estimated by studying the protonation reactions of **2** and **4** with $HBF_4 \cdot Et_2O$ (eq 4) using ^{1}H NMR at −80 °C. The

$$[^{R}CnRuH(CO)(PPh_3)]PF_6 + HBF_4 \cdot Et_2O \leftrightarrow [^{R}CnRu(H_2)(CO)(PPh_3)](PF_6)(BF_4) + Et_2O \quad (4)$$

relative molar concentrations of $HBF_4 \cdot Et_2O$, Et_2O, the ruthenium carbonyl hydrides and the carbonyl dihydrogen complexes were estimated on the basis of the ^{1}H NMR integrations. The pK_a values of **6** and **8** were estimated to be −1.3 and −2.6, respectively, taking the pK_a of $HBF_4 \cdot Et_2O$ as −2.4.[22] Details on the acidity measurements are summarized in Table 3.

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Table 3. Acidity Measurements of Dihydrogen Complexes in CD_2Cl_2[a]

M(H_2)	B	K_{eq}	pK_a(M(H_2))
[^{H}CnRu(H_2)(PPh_3)$_2$](BF_4)$_2$ (**5**)	RuHCl(dppe)$_2$	31.6	4.5
[^{H}CnRu(H_2)(CO)(PPh_3)](BF_4)$_2$ (**6**)	Et_2O	0.07[b]	−1.3
[^{Me}CnRu(H_2)(dppe)$_2$](CF_3SO_3)$_2$ (**7**)	RuHCl(dppe)$_2$	166	3.8
[^{Me}CnRu(H_2)(CO)(PPh_3)](PF_6)(CF_3SO_3) (**8**)	Et_2O	1.56[b]	−2.6
[TpRu(H_2)(PPh_3)$_2$]BF_4 (**13**)	CpRuH(dppm)	0.303	7.6
[TpRu(H_2)(dppe)]BF_4 (**14**)	CpRuH(dppm)	0.179	7.9
[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4 (**15**)	CpRuH(PPh_3)$_2$	0.277[c]	8.9
[TpRu(H_2)(CO)(PPh_3)]BF_4 (**16**)	[^{H}CnRuH(CO)(PPh_3)]$^+$	0.498[b]	−0.6

[a] pK_a values (on the pseudo aqueous scale) of the dihydrogen complexes are estimated by means of the equation pK_a(M(H_2)) = pK_{eq} + pK_a(HB^+); K_{eq} is the equilibrium constant of eq 3 or the reciprocal of the equilibrium constant of eq 4. [b] At −80 °C. [c] -30 °C.

Table 4. Spectroscopic Properties and Acidities of Hydride Complexes

complexes	T_1(min), ms[a] (temp)	^1J(HD), Hz	d(HH), Å[b]	pK_a[c]	ref
[^{H}CnRu(H_2)(PPh_3)$_2$](BF_4)$_2$ (**5**)	20 (250 K)	29.4	0.93	4.5	this work
[^{H}CnRu(H_2)(CO)(PPh_3)](BF_4)$_2$ (**6**)	14 (248 K)	31.8	0.89	−1.3[d]	this work
[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)$_2$ (**7**)	24 (266 K)	29.4	0.93	3.8	this work
[^{Me}CnRu(H_2)(CO)(PPh_3)(PF_6)(CF_3SO_3) (**8**)	12 (224 K)	31.0	0.92	−2.6[d]	this work
[TpRu(H_2)(dppe)]BF_4 (**13**)	14 (230 K)	32.5	0.88	7.9	this work
[TpRu(H_2)(PPh_3)$_2$]BF_4 (**14**)	21 (240 K)	32.0	0.89	7.6	this work
[TpRu(H_2)(CH_3CN)(PPh_3]BF_4 (**15**)	16 (231 K)	33.0	0.87	8.9[e]	this work
[TpRu(H_2)(CO)(PPh_3)]BF_4 (**16**)	12 (224 K)	33.3[d]	0.86	−0.6[d]	this work
[CpRuH_2(PPh_3)$_2$]$^+$				8.3	6b
[CpRu(H_2)(dppm)]$^+$		21.9	1.05	7.1	6b
[Cp*Ru(H_2)(dppm)]$^+$	18 (220 K)	20.9	1.07	9.2[f]	6b
[CpRu(H_2)(dppe)]$^+$		24.9	1.00	7.0	6b

[a] At 400 MHz. [b] Calculated on the basis of ^1J(HD) values as described in ref 9a. [c] pK_a values were determined in CD_2Cl_2 but reported on the pseudo aqueous scale. [d] Determined at −80 °C. [e] Determined at −30 °C. [f] Determined in THF.

Comments on the Acidity. It should be stressed that the pseudo aqueous pK_a values of complexes **5**−**8** and **13**−**16** are obtained on the basis of the assumption that the differences in the pK_a values of the dihydrogen complexes and the reference acids are the same in water and CD_2Cl_2. Since the assumption has not been confirmed yet, the pseudo aqueous pK_a values of the complexes may be different from the true aqueous pK_a values and should not be treated too seriously. However, the pseudo aqueous pK_a values can still provide valuable information in the trend of the acidity of the complexes. For comparison, the pseudo aqueous pK_a values of the new dihydrogen complexes and related [(η^5-C_5R_5)RuH_2(L)(L′)]$^+$ complexes are listed in Table 4. To see the effect of H−H bonding on the acidity, the T_1(min) and r(HH) for the dihydrogen complexes and ^1J(HD) for the HD isotopomers are also listed if available. The hydrogen−hydrogen separations, r(HH), were calculated according to an empirical equation (eq 5)[9a]

$$r(\mathrm{HH}) = 1.42 - 0.0167J(\mathrm{HD}) \qquad (5)$$

that shows a linear relationship between J(HD) and r(HH) in a wide variety of η^2-H_2 complexes whose J(HD) values fall in the range 7−35 Hz. An essentially identical linear relationship is also predicted by quantum chemical calculation for complexes of the type [Os(NH_3)$_4$L(H_2)]$^{2+}$ for a wide range of trans ligands L.[23]

It can be seen from Table 4 that isostructural and monocationic Tp and Cp ruthenium dihydrogen complexes have similar acidity. The dicationic ^{R}Cn dihydrogen complexes **5** and **7** are significantly more acidic than their Tp and Cp analogues (by 3−4 pK_a units difference). The carbonyl-containing ^{R}Cn dihydrogen complexes [^{Me}CnRu(H_2)(CO)(PPh_3)]$^{2+}$ (pK_a = −2.6) and [^{H}CnRu(H_2)(CO)(PPh_3)]$^{2+}$ (pK_a = −1.3) are also more acidic than the analogous monocationic Tp complex [TpRu(H_2)(CO)(PPh_3)]$^+$ (pK_a = −0.6) but to a smaller extent. Several highly acidic dicationic dihydrogen complexes have been reported; for example, the dicationic dihydrogen complex *trans*-[Os(H_2)(dppe)(CH_3CN)]$^{2+}$ has a pseudo aqueous pK_a value close to −2.[10] The complex [Os(H_2)(CO)(bpy)(PPh_3)$_2$]$^{2+}$ can be deprotonated by diethyl ether.[11k] The dicationic dihydrogen complexes [M(H_2)(CO)(dppp)$_2$]$^{2+}$ (M = Ru, Os) were reported to have pK_a values close to −6.[8] It should be mentioned that dicationic dihydrogen complexes are not necessarily stronger acids than monocationic complexes; for example, [Os(H_2)(NH_3)$_5$]$^{2+}$ was reported to be a weak acid and is stable to moderately strong base such as NaOMe. The high pK_a value of this complex is probably due to the strong electron-donating effect of the NH_3 ligands.[20a]

Within the ^{H}Cn, ^{Me}Cn, and the Tp dihydrogen complex series, substitution of phosphine group for CO leads to a 5−8 unit decrease in the pK_a value. The observation is very similar to that observed for [RuCl(H_2)(L)(PMP)]$^+$ (L = CO, PPh_3).[24] The same trend has also been observed for classical hydride complexes. For example, $MnH(CO)_5$ has a pK_a(CH_3CN) of 15.1[25] vs 20.4 for MnH(CO)(PPh_3),[26] $CpCrH(CO)_3$ has a pK_a(CH_3CN) of 13.3[27] vs 21.8 for $CpCrH(CO)_2(PPh_3)$,[28] and $HCo(CO)_4$ has a pK_a of 8.3[25] vs 15.4 for $HCo(CO)_3(PPh_3)$.[25] These observations may indicate that the inductive effect of the ligands is very important in determining the acidity of the dihydrogen complexes.

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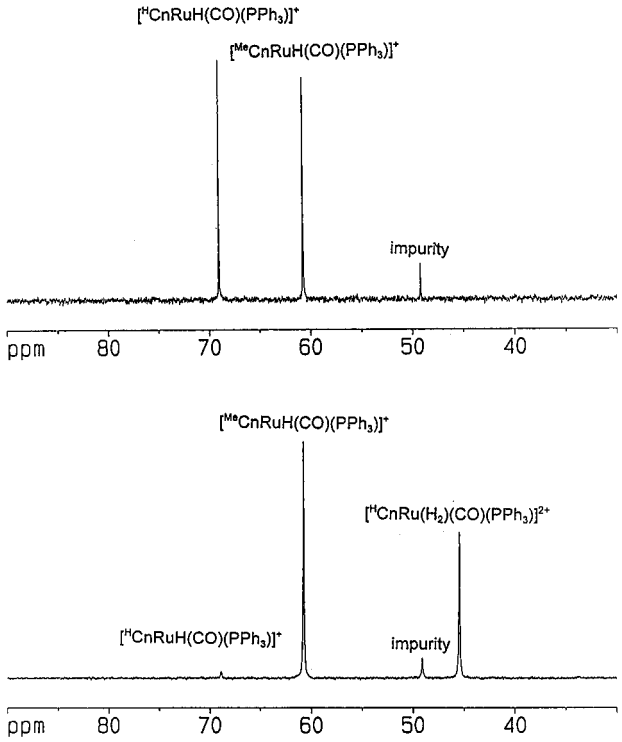

Figure 2. ^{31}P NMR spectra of $[^{Me}CnRuH(CO)(PPh_3)]^+$ and $[^{H}CnRuH(CO)(PPh_3)]^+$ in CD_2Cl_2 at −35 °C (top) and ($[^{Me}CnRuH(CO)(PPh_3)]^+$ and $[^{H}CnRuH(CO)(PPh_3)]^+$) + $HBF_4{\cdot}Et_2O$ in CD_2Cl_2 at −80 °C (bottom).

It is well established that the acidity of hydride complexes are strongly influenced by the metals as well as auxiliary ligands.[29,30] With a few exceptions, the acidity of isostructural classic hydride complexes decreases as ligands become more electron-donating and as the metal is replaced successively by heavier metals in the same group. The relative acidities of most of the complexes studied in this work are consistent with the trend. However, exception is observed for complexes **6** and **8**. It might be expected that complex **8** should be less acidic than complex **6** because ^{Me}Cn is more electron-donating than ^{H}Cn, as reflected from the ^1J(HD) coupling constants of the corresponding isotopomers of complexes **6** and **8**. In fact, complex **8** was found to be more acidic than complex **6** on the basis of the equilibrium study as described before. The more acidic nature of complex **8** compared to complex **6** is further supported by the fact that the complex $[^{H}CnRuH(CO)(PPh_3)]^+$ is preferentially protonated when a mixture of $[^{H}CnRuH(CO)(PPh_3)]^+$ and $[^{Me}CnRuH(CO)(PPh_3)]^+$ was treated with a limited amount of $HBF_4{\cdot}OEt_2$ (see Figure 2).

It is not apparent why the ^{Me}Cn complex **8** is more acidic than the ^{H}Cn complex **6**. It is possible that the H−H bond strength in **6** and **8** may play some role in determining the relative acidity. The more electron-donating ^{Me}Cn ligand in **8** renders the H−H interacton weaker than that in complex **6** which contains the less donating ^{H}Cn ligand, and the weaker H−H interaction may make a dihydrogen complex more acidic than may be suggested by the general trend in the acidity of classic hydride complexes. Morris et al. has recently proposed that the dramatic reduction of the pK_a value of *trans*-$[RuCl(H_2)(dppe)_2]^+$ vs that of *trans*-$[RuH(H_2)(dppe)_2]^+$ could be attributed to a lower H−H bond strength in the former. The high acidity of the trihydride complex $[RuH_3(dppf)_2]^+$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) compared to that of $[RuH(H_2)(dppe)_2]^+$ is also in accord with this idea.[9b]

Reactions of Dihydrogen Complexes with Water. We have recently discussed the roles of the dihydrogen complexes $[TpRu(H_2)(PPh_3)_2]^+$ (**14**) and $[TpRu(H_2)(CH_3CN)(PPh_3)]^+$ (**15**) in olefin hydrogenation reactions.[14b] It was noted that their catalytic activities are greatly enhanced when the reactions were performed in THF/H_2O mixed solvents instead of anhydrous THF. The enhancement effect is attributed to deprotonation of η^2-H_2 by H_2O to generate the active metal hydride species. The deprotonation reaction with water has been demonstrated with NMR study with complex **14**. It is somewhat surprising to find out in the present study that the pseudo aqueous pK_a values of complexes **14** (7.6) and **15** (8.9) are significantly higher than that of H_3O^+ (−1.74).[31] As H_2O is a very weak base, it is not expected that H_2O should be basic enough to deprotonate the dihydrogen complexes.

To see if deprotonation by water would also occur on other dihydrogen complexes with pseudo aqueous pK_a values significantly higher than that of H_3O^+, we have tested the reactivities of complexes $[TpRu(H_2)(dppe)]^+$ (**13**, pK_a = 7.9), $[^{H}CnRu(H_2)(PPh_3)_2]^{2+}$ (**5**, pK_a = 4.5), and $[^{Me}CnRu(H_2)(dppe)]^{2+}$ (**7**, pK_a = 3.8) toward water.

In the absence of H_2 pressure, like complex **14**, H_2O displaced the η^2-H_2 ligand in **13** to give $[TpRu(H_2O)(dppe)]^+$. The reaction took a different route under H_2 pressure in CD_2Cl_2/H_2O biphasic medium. When 50−100 μL of H_2O was added to a 0.4 mL CD_2Cl_2 solution of **13** in a Wilmad pressure-valved NMR tube, phase separation occurred. The ^{1}H NMR spectrum of the CD_2Cl_2 phase showed that some of the η^2-H_2 was displaced by H_2O via simple ligand substitution reaction. But after the tube was pressurized with 15 atm of H_2, most of the dihydrogen complex was re-formed; partial deprotonation of η^2-H_2 by H_2O took place, as evidenced by the appearance of the ruthenium hydride signal in the ^{1}H NMR spectrum.

The dihydrogen complexes **5** and **7** are more stable with respect to loss of H_2 at room temperature; thus, deprotonation studies with H_2O can be carried out in the absence of H_2 atmosphere in CD_2Cl_2. It was shown that the dihydrogen complexes were deprotonated completely to form the monohydride complexes. The observation is probably not surprising, as complexes **5** and **7** are more acidic than their Tp analogues.

Deprotonation of η^2-H_2 in complexes **5**, **7**, **13**, and **14**, which have pseudo aqueous pK_a values above 3, in biphasic conditions, is probably due to the strong solvation of H^+ by H_2O. It is also likely that the difference in the pK_a values of the dihydrogen complexes in aqueous solution may not be as large as the pseudo aqueous pK_a values may imply.

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Conclusion

We have synthesized and characterized the first dihydrogen complexes supported by triazacyclononane ligands. These complexes are also new members of the still very small family of dicationic dihydrogen complexes. Triazacyclononane ligands seem to have similar properties as the hydrotris(pyrazolyl)borates in stabilizing dihydrogen ligands. The dicationic ^{R}Cn dihydrogen complexes are more, and in some cases significantly more, acidic than their hydrotris(pyrazolyl)borato and cyclopentadienyl analogues, which are monocationic. Water can deprotonate ^{R}Cn and Tp dihydrogen complexes with pseudo aqueous pK_a values significantly larger than that of H_3O^+, probably due to strong solvation of H^+ by H_2O.

Experimental Section

All reactions were carried out under a dry N_2 atmosphere using Schlenk techniques. All solvents were distilled and degassed prior to use. Dichloromethane and acetonitrile were distilled from calcium hydride; tetrahydrofuran, diethyl ether, and hexane were distilled from sodium benzophenone ketyl. 1,4,7-Triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane were prepared as reported.[32] The complexes $RuHCl(CO)(PPh_3)_3$,[33] $^{Me}CnRuCl_3$,[34] $[^{Me}CnRuH(dppe)]CF_3SO_3$,[16d] $[^{Me}CnRuH(CO)(PPh_3)]PF_6$,[16d] $TpRuH(PPh_3)_2$,[14b] $[TpRu(H_2)(PPh_3)_2]BF_4$,[14b] $TpRuH(CH_3CN)(PPh_3)$,[14b] $[TpRu(H_2)(CH_3CN)(PPh_3)]BF_4$,[14b] and $TpRuH(CO)(PPh_3)$[14a] were synthesized according to literature methods. $HBF_4\cdot Et_2O$ was purchased from Fluka and was used as received.

Infrared spectra were obtained from a Nicolet Magna 750 FT IR spectrophotometer. ^{1}H NMR spectra were taken on a Bruker DPX 400 spectrometer. Chemical shifts were referenced to the residue peaks of the deuterated solvents. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 MHz. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4. T_1 relaxation measurements were carried out in CD_2Cl_2 at 400 MHz by the inversion−recovery method using a standard 180−τ−90 pulse sequence. FAB MS was carried out with a Finnigan MAT 95S mass spectrometer using 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

$[^{H}CnRuH(PPh_3)_2]BF_4$ (1). A mixture of $RuHCl(PPh_3)_3$ (0.50 g, 0.54 mmol), 1,4,7-triazacyclononane (0.20 g, 1.55 mmol), and $NaBF_4$ (0.10 g, 0.91 mmol) in 100 mL of THF was stirred under nitrogen for 2 h. The mixture was filtered through Celite, and the filtrate was concentrated to about 5 mL. Diethyl ether (10 mL) was added to precipitate out a yellow solid which was filtered out. The solid was washed with diethyl ether and vacuum-dried at room temperature. Yield: 0.36 g (79%). Anal. Calcd for $C_{42}H_{46}BN_3F_4P_2Ru$: C, 59.86; H, 5.50; N, 4.99. Found: C, 59.10; H, 5.73; N, 5.03. IR (KBr, cm^{-1}): ν(Ru−H) 1958 (w). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −15.98 (t, 1H, ^2J(HP) = 38.3 Hz, Ru−*H*), 2.29−3.44 (m, 2H, N−*H* and 12H, NCH_2), 5.24 (s, 1H, N−*H*), 7.19−7.43 (m, 30 H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 67.4 (s). FAB MS (*m*/*z*): 756, $[M - BF_4]^+$; 494, $[M - BF_4 - PPh_3]^+$.

$[^{H}CnRuH(CO)(PPh_3)]BF_4$ (2). A mixture of $RuHCl(CO)(PPh_3)_3$ (2.50 g, 2.69 mmol) and 1,4,7-triazacyclononane (0.50 g, 3.87 mmol) in 250 mL of 2-methoxyethanol was refluxed under nitrogen for 18 h. The mixture was filtered, and the filtrate was concentrated to about 40 mL. Sodium tetrafluoroborate (0.66 g, 6 mmol) was added, and the resulting mixture was filtered to afford the crude product which was washed with ethanol and diethyl ether. It was then extracted with 20 mL of dichloromethane, and the solvent of the extract was removed to yield a white solid. Yield: 0.44 g (27%). Anal. Calcd for $C_{25}H_{31}BN_3OF_4PRu$: C, 49.36; H, 5.14; N, 6.91. Found: C, 49.10; H, 5.23; N, 6.78. IR (KBr, cm^{-1}): ν(CO) 1920 (vs), ν(Ru−H) 1997 (w). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −12.83 (d, 1H, ^2J(HP) = 28.8 Hz, Ru−*H*), 2.81 (s, 1H, N−*H*), 2.45−3.40 (m, 12H, NCH_2), 3.90 (s, 1H, N−*H*), 5.12 (s, 1H, N−*H*), 7.34−7.58 (m, 15H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 68.1 (s). FAB MS (*m*/*z*): 522, $[M]^+$.

TpRuH(dppe) (12). A 1,4-dioxane solution (100 mL) of $TpRuH(PPh_3)_2$ (0.50 g, 0.60 mmol) and dppe (0.30 g, 0.75 mmol) was stirred under nitrogen at 100 °C for 16 h. The solution was cooled and concentrated to about 5 mL. Diethyl ether (10 mL) was added to give a yellow solid, which was filtered out. The solid was washed with diethyl ether and then dried under vacuum. Yield: 0.35 g (82%). Anal. Calcd for $C_{35}H_{35}BN_6P_2Ru$: C, 58.89; H, 4.94; N, 11.78. Found: C, 58.88; H, 5.10; N, 11.54. IR (KBr, cm^{-1}): ν(Ru−H) 1909 (w), ν(B−H) 2470 (br). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −14.23 (t, 1H, ^2J(HP) = 28.0 Hz, Ru−*H*), 2.09−2.49 (m, 4H, CH_2CH_2), 5.34 [t, 1H, H(pz)], 5.58 (d, 1H, H(pz)], 5.90 [t, 2H, H(pz′)], 7.03 [d, 2H, H(pz′)], 7.47 [d, 1H, H(pz)], 7.61 [d, 2H, H(pz′)] (pz = pyrazolyl group trans to hydride, pz′ = pyrazolyl groups trans to dppe; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 6.86, 6.98, 7.13, 7.35, 7.89 (m, 20 H of dppe phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 90.0 (s). FAB MS (*m*/*z*): 714, $[M]^+$.

Dihydrogen Complexes and Their Isotopomers. The carbonyl dihydrogen complexes **6**, **8**, and **16** are unstable with respect to loss of H_2 at room temperature. It is also difficult to obtain dihydrogen complexes **5**, **7**, and **13** in pure form because they are usually contaminated by their corresponding aquo complexes. The dihydrogen complexes were therefore only characterized in situ.

The complexes $[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$ (**5**), $[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)_2$ (**7**), and $[TpRu(H_2)(dppe)]BF_4$ (**13**) were prepared as follows. In a typical experiment, a sample (10 mg) of a metal hydride was loaded into a 5 mm NMR tube, which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Dichloromethane-d_2 (0.4 mL) was added to dissolve the sample, followed by addition of 5 μL of $HBF_4\cdot Et_2O$ or CF_3SO_3H. The solution was immediately analyzed by NMR spectroscopy.

$[^{H}CnRu(H_2)(PPh_3)_2](BF_4)_2$ (5). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.04 [br, 2H, Ru−(H_2)], 2.35−4.29 (m, 2H, N−*H* and 12H NCH_2), 5.84 (s, 1H, N-*H*), 7.26−7.44 (m, 30H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 39.5 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 22 (273 K), 21 (263 K), 20 (253 K), 20 (243 K), 21 (233 K), 23 (223 K), 27 (213 K), 34 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 20 ms at 250 K.

$[^{Me}CnRu(H_2)(dppe)](CF_3SO_3)_2$ (7). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.79 [br, 2H, Ru−(H_2)], 1.93 (m, 2H, NCH_2), 2.56−2.69 (m, 4H, PCH_2), 2.79−2.81 (m, 6H, NCH_2), 7.48−7.62 (m, 20H of PPh_3). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 7.4 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 29 (313 K), 27 (303 K), 26 (293 K), 25 (283 K), 25 (273 K), 24 (263 K), 25 (253 K), 26 (243 K), 28 (233 K), 31 (223 K), 37 (213 K), 47 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 24 ms at 266 K.

$[TpRu(H_2)(dppe)]BF_4$ (13). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.28 [br, 2H, Ru−(H_2)], 2.82−2.96 (m, 4H, PCH_2), 5.25 [t, 1H, H(pz)], 5.52 [d, 1H, H(pz)], 6.09 [t, 2H, H(pz′)], 6.82 [d, 2H, H(pz′)], 7.51 [d, 1H, H(pz)], 7.79 [d, 2H, H(pz′)] (pz = pyrazolyl group trans to H_2, pz′ = pyrazolyl groups trans to dppe; all coupling constants for pyrazolyl proton resonances were about 2 Hz); 6.63, 7.06, 7.30, 7.53 (m, 20H of dppe phenyl groups). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ 45.7 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 22 (293 K), 20 (283 K), 18 (273 K), 17 (263 K), 15 (253 K), 14 (243 K), 14 (233 K), 13

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(228 K), 15 (218 K), 16 (213 K). A T_1 vs 1000/T plot gave a T_1(min) of 14 ms at 230 K.

The corresponding HD isotopomers were prepared analogously except that DBF_4, which was prepared by mixing HBF_4·Et_2O with D_2O in a volume ratio of 3:1, was used instead of HBF_4·Et_2O or CF_3SO_3H. The η^2-HD signals were observed after nulling the η^2-H_2 peaks by the inversion−recovery method.

[^{H}CnRu(HD)(PPh_3)$_2$]$^{2+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.06 [tt, ^1J(HD) = 29.4 Hz, ^2J(HP) = 6.3 Hz, R−(*H*D)].

[^{Me}CnRu(HD)(dppe)]$^{2+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.85 [tt, ^1J(HD) = 29.4 Hz, ^2J(HP) = 8.0 Hz, Ru−(*H*D)].

[TpRu(HD)(dppe)]$^{+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.34 [t, ^1J(HD) = 32.5 Hz), Ru−(*H*D)].

The CO-containing dihydrogen complexes **6**, **8**, and **16** were prepared as follows. In a typical experiment, a sample (10 mg) of the metal hydride was loaded into a 5 mm NMR tube, which was then capped with a rubber septum. The tube was evacuated and filled with nitrogen for three cycles. Dichloromethane-d_2 (0.4 mL) was added to dissolve the sample. The solution was cooled to −78 °C, and 5 μL of HBF_4 or CF_3SO_3H was added through a microsyringe. The tube was loaded into the NMR probe precooled to −30 °C (**6** and **8**) or −80 °C (**16**), and the sample was immediately analyzed by NMR spectroscopy.

[^{H}CnRu(H_2)(CO)(PPh_3)][BF_4)$_2$ (6). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −7.25 [br, 2H, Ru−(*H*$_2$)], 1.26−5.58 (m, 3H, N−*H* and 12H, NC*H*$_2$), 7.48−7.61 (m, 15H of PPh_3). ^{31}P{^{1}H} NMR (161.70 MHz, CD_2Cl_2): δ 45.7 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 15 (263 K), 13 (253 K), 14 (243 K), 18 (233 K), 19 (223 K), 20 (213 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 14 ms at 248 K.

[^{Me}CnRu(H_2)(CO)(PPh_3)][PF_6)(CF_3SO_3) (8). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −7.63 [br, 2H, Ru−(*H*$_2$)], 1.26−4.52 (m, 9H, NC*H*$_3$ and 12H, NC*H*$_2$), 7.41−7.66 (m, 15H of PPh_3). ^{31}P{^{1}H} NMR (161.70 MHz, CD_2Cl_2): δ 32.2 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 41 (258 K), 28 (253 K), 17 (248 K), 15 (243 K), 14 (238 K), 15 (223 K), 17 (215 K), 20 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 12 ms at 224 K.

[TpRu(H_2)(CO)(PPh_3)]BF_4 (16). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −6.84 [br, 2H, Ru−(*H*$_2$)], 5.89 [br, 1H, H(pz)], 6.05 [br, 1H, H(pz)], 6.31 [br, 1H, H(pz)], 6.40 [br, 1H, H(pz)], 6.66 [br, 1H, H(pz)], 7.76 [br, 2H, H(pz)], 7.85 1H, H(pz)], 7.94 [br, 1H, H(pz)]. ^{31}P{^{1}H} NMR (161.70 MHz, CD_2Cl_2): δ 45.7 (s). T_1 (400 MHz, CD_2Cl_2), ms (temperature): 13 (243 K), 12 (238 K), 11 (233 K), 11 (223 K), 12 (218 K), 13 (213 K), 14 (208), 47 (203 K). A ln T_1 vs 1000/T plot gave a T_1(min) of 12 ms at 224 K.

The corresponding HD isotopomers were prepared analogously except that DBF_4 was used in place of HBF_4·Et_2O. The η^2-HD signals were observed after nulling the η^2-H_2 peaks by the inversion−recovery method.

[^{H}CnRu(HD)(CO)(PPh_3)]$^{2+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −7.29 [t, ^1J(HD) = 31.8 Hz, Ru−(*H*D)].

[^{Me}CnRu(HD)(CO)(PPh_3)]$^{2+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −7.65 [t, ^1J(HD) = 31.0 Hz, Ru−(*H*D)].

[TpRu(HD)(CO)(PPh_3)]$^{+}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −6.87 [t, ^1J(HD) = 33.3 Hz, Ru−(*H*D)].

Acidity Measurement. pK_a values of **5**, **7**, and **13**−**16** were estimated by studying the equilibrium shown in eq 3. All measurements were carried out at room temperature except that of **15** (−30 °C) and **16** (−80 °C). In a typical experiment, appropriate amounts of [L_nRuH]$^{(n-1)+}$ and L′$_n$RuH were dissolved in CD_2Cl_2 in an NMR tube, and then a limited amount of HBF_4·Et_2O was added. ^{31}P and ^{1}H NMR spectra were taken. Relative molar concentrations of the equilibrated species were estimated from the ^{1}H NMR integrations of the hydride signals.

The pK_a values of the two ^{R}Cn carbonyl dihydrogen complexes **6** and **8** were estimated by use of the equilibrium depicted in eq 4. In a typical experiment, an appropriate amount of HBF_4·Et_2O was added to a CD_2Cl_2 solution of the metal hydride in an NMR tube. NMR spectra were recorded at −80 °C, and the relative molar concentrations of HBF_4·Et_2O, Et_2O, the metal hydride, and the dihydrogen complex were estimated on the basis of the ^{1}H NMR integrations.

Crystallographic Analysis for [^{H}CnRuH(PPh_3)$_2$]BF_4·$2CH_2Cl_2$. Suitable crystals for X-ray diffraction study were obtained by layering of hexane on a dichloromethane solution of [^{H}CnRuH(PPh_3)$_2$]BF_4. A red block crystal of dimension 0.22 × 0.23 × 0.29 mm was mounted in a glass capillary and used for X-ray structure determination. All measurements were made on a Marresearch image plate scanner with graphite monochromated Mo Kα radiation. The crystal system is orthorhombic, and the space group is $P2_12_12_1$ (No. 19). The data were collected at 25 °C using the ω scan technique to a maximum 2θ value of 51.2°. A total of 4741 intensity measurements were made using the ω scan technique. The linear coefficient, μ, for Mo Kα radiation is 6.8 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques using the TEXSAN program package. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The final cycle of full-matrix least-squares refinements was based on 3178 observed reflection ($I > 3.00\sigma(I)$) and 328 variable parameters and converged with unweighted and weighted agreement factors R = 7.2%, and R_w = 9.9% with GOF = 3.41. The data:parameter ratio was 9.69:1 and residual electron density/hole 0.63/-0.52 e Å^{-3}. Further crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

Acknowledgment. The authors acknowledge the financial support from the Hong Kong Research Grant Council (Earmarked Grant HKP91/94P). We thank Dr. Hon Man Lee for measuring the acidity of complex **14**.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, complete bond lengths and bond angles, anisotropic displacement coefficients, and isotropic displacement coefficients for [^{H}CnRuH(PPh_3)$_2$]BF_4·$2CH_2Cl_2$ (15 pages). Ordering information is given on any current masthead page.

OM9710374