Neutron Diffraction Studies of $[Cp(PMe_3)_2RuH]$ and $[Cp(PMe_3)_2RuH_2]BF_4$ at 20 K

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The crystal and molecular structures of $[Cp(PMe_3)_2RuH]$ (**1**) and $[Cp(PMe_3)_2RuH_2]BF_4$ (**2**) have been determined from neutron diffraction measurements at 20 K. The Ru−H bond lengths in **1** (1.630(4) Å) and **2** (1.599(8), 1.604(9) Å) are the first terminal Ru−H distances to be determined by single-crystal neutron diffraction. The “$Cp'L_2Ru$” system is now the first to have neutron diffraction studies of the monohydride, dihydride, and dihydrogen species. This is of particular importance in understanding the activation of H_2 by this metal−ligand fragment. Thus detailed comparisons with the recent structure determination by neutron diffraction of the dihydrogen complex $[Cp^*(dppm)Ru(\eta^2\text{-}H_2)]BF_4$ (dppm = bis(diphenylphosphino)methane) [Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677−7681] are presented. A network of $C-H\cdots F-BF_3$ hydrogen bonds links the anion and cation moieties in **2**. The C(2)−H(2)···F(4) interaction has an H···F separation of only 2.078(8) Å, the shortest such interaction characterized to date by neutron diffraction. Ru−H stretching frequencies determined from the diffraction data are in good agreement with those from IR measurements.

Introduction

Considerable attention has been paid to the activation of dihydrogen by the “$Cp'L_2Ru$” moiety (Cp′ = C_5H_5 (Cp), C_5Me_5 (Cp*), C_5H_4Me (Cp‡); L = CO, PR_3, PAr_3; L_2 = diphosphines) primarily because it has been shown that the electronic demands of this species can be “tuned” substantially by changing the nature of the Cp′ or L_2 ligands. For example, studies focusing on the protonation of $Cp'L_2RuH$ have been shown to yield cationic ruthenium(II) dihydrogen complexes $[Cp'L_2Ru(\eta^2\text{-}H_2)]^+$ and/or cationic ruthenium(IV) dihydride complexes $[Cp'L_2RuH_2]^+$.[1−3] At present, structural information on complexes pertinent to this chemistry is still relatively sparse. Prior to our work in this area, crystal structures of the monohydride species $Cp(PPh_3)_2RuH$,[4] Cp(dppp)RuH (dppp = 1,2-bis(diphenylphosphino)propane),[5] and Cp(dppFc)RuH[6] (dppFc = $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$) had been reported, together with those of the dihydride compounds $[Cp^‡(dppe)RuH_2]PF_6$ (dppm = 1,2-bis(diphenylphosphino)ethane),[5b] $[Cp^‡(PPh_3)_2RuH_2]PF_6\cdot CH_2Cl_2$,[5b] and $Cp^*(SiHClMes)(PPr^i_3)RuH_2$ (Mes = mesityl)[7] and the dihydrogen complexes $[Cp^*(dppm)Ru(\eta^2\text{-}H_2)]BF_4$[2] (dppm = bis(diphenylphosphino)methane) and $Cp^‡(dppm)Ru(\eta^2\text{-}H_2)]PF_6$.[5b] Of all these structures, only that of $[Cp^*(dppm)Ru(\eta^2\text{-}H_2)]BF_4$ was determined by neutron diffraction, facilitating accurate location of the hydrogen ligands.

In the previously reported X-ray diffraction study of $[Cp(PMe_3)_2RuH]$ (**1**) the hydride ligand was located, but refinement yielded a substantially foreshortened bond length (Ru−H 1.36(8) Å).[3] The X-ray crystal structure of $[Cp(PMe_3)_2RuH_2]BF_4$ (**2**) did not yield the positions of the hydride ligands. However, their *trans* geometry was inferred from comparison of the non-hydrogen framework of the molecule with related structures.[3] Indeed a detailed analysis of all structural information available for d^6 $Cp'L_2MH$, d^6 $Cp'L_2M(\eta^2\text{-}H_2)$, and d^4 $Cp'L_2MH_2$ complexes led to the identification of distinct structural characteristics of each class of compounds.[3] Furthermore, we were able to demonstrate that, although hydride ligand positions determined from X-ray diffraction studies are presumed to be unreliable, interligand angles involving hydrides are often accurate to within a few degrees. However, M−H distances are typically much more inaccurate, often by as much as 0.2−0.3 Å. Thus, determination of the structures of **1** and **2** by neutron diffraction was undertaken and is reported herein, providing a unique opportunity to compare the geometries of these compounds with the

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dihydrogen complex of similar framework, [Cp*(dppm)-Ru(η^2-H_2)]BF_4 (**3**), which has also been characterized recently by neutron diffraction,[2] as was noted above. Furthermore, **1** and **2** are the first compounds for which terminal Ru−H distances have been determined by single-crystal neutron diffraction.

Experimental Section

Compounds **1** and **2** were prepared as previously described.[3] Crystals were obtained by slow sublimation at 50 °C under a vacuum in a sealed tube for **1** and by vapor diffusion of Et_2O into a CH_2Cl_2 solution at room temperature for **2**. The former are very air-sensitive, whereas the latter are stable for long periods (days) in air. The following experimental description applies to the neutron diffraction of both compounds. Unless otherwise indicated, where the numerical values differ for the two experiments, those for **1** precede those of **2**, the latter being given in parentheses.

A single crystal of volume 5.0 mm^3 (1.4 mm^3) was mounted on an aluminum pin with halocarbon grease and sealed under a helium atmosphere inside an aluminum container. This container was placed in a closed-cycle helium refrigerator[8] and mounted on the four-circle diffractometer at port H6S of the High Flux Beam Reactor at Brookhaven National Laboratory. The neutron beam, monochromated by Ge (220) planes in transmission geometry, was of wavelength 1.16395(10) Å as calibrated against a KBr crystal ($a_0 = 6.6000$ Å at 295 K). The sample temperature was maintained at 20.0(5) K during the experiment, and unit cell dimensions were determined by a least-squares fit of $\sin^2\theta$ values for 32 reflections in the range $47 < 2\theta < 58°$ ($52 < 2\theta < 60°$).

Intensity data were obtained over one quadrant of reciprocal space by means of $\omega/2\theta$ scans of variable step size and variable number of steps per scan. The intensities of two reflections were monitored during the data collection and showed no systematic variations throughout. Integrated intensities and variances were derived from the scan profiles. Lorentz factors were applied, as well as an absorption correction in the case of [Cp(PMe_3)$_2$RuH_2]BF_4 yielding transmission factors in the range 0.628−0.811. Averaging over 222 (85) symmetry-related pairs of reflections resulted in a weighted internal agreement factor $wR_{int}(F^2) = 0.039$ (0.024) and yielded 4008 (2311) independent observations. Further details are given in Table 1.

Initial coordinates were obtained from the X-ray crystal structures.[3] All hydrogen atoms were found by means of difference Fourier synthesis. Least-squares refinements were carried out by a full-matrix procedure,[9] minimizing $\sum w(F_o^2 - (k^2F_c^2)^2$ using all independent reflections other than 2 (7) excluded due to contamination by Al-powder scattering from the sample holder. The final model included positional and anisotropic displacement parameters for all atoms, the scale factor, k, and an isotropic type I extinction parameter[10] for a total of 344 (396) variable parameters. The refinement converged with fit indices $R(F^2) = 0.131$ (0.104), $R_w(F^2) = 0.109$ (0.096), and $S(F^2) = 1.03$ (1.09), based on 4006 (2304) reflections.

Results and Discussion

Molecular Structures. The neutron diffraction studies clearly establish that **1** and the cation of **2** exhibit three- and four-legged piano stool geometries, respectively, in which the hydride and phosphine ligands serve as the "legs". Each deviates slightly, but significantly, from the idealized C_s molecular symmetry. The molecular geometries of **1** and the cation of **2** are depicted in Figure 1. Atomic coordinates are given in Tables 2 and 3, and interatomic distances and angles are listed in Table 4.

These studies allow for the first time a detailed structural comparison to be made between monohydride, dihydride, and dihydrogen complexes in the same system, i.e. in this case with these ligands bound to the "Cp′P_2Ru" moiety. Thus, the structures of **1** and **2** will be discussed in the context of the recent neutron diffraction study of the "stretched" dihydrogen complex **3**.[2] A tabulation of this comparison of geometries is

Table 1. Neutron Data Collection and Refinement Parameters for 1 and 2

	[Cp(PMe_3)$_2$RuH] (**1**)	[Cp(PMe_3)$_2$RuH_2]BF_4 (**2**)
	Crystal Data	
space group, *Z*	$P2_1/n$, 4	*Cc*, 4
a (Å)	9.318(2)	14.284(3)
b (Å)	14.641(3)	10.135(2)
c (Å)	10.927(3)	11.517(2)
β (deg)	107.49(2)	99.36(2)
V (Å^3)	1422(1)	1645(1)
D_c (g·cm^{-3})	1.492	1.644
μ (cm^{-1})	2.998	3.747
extinction	1.1(1) × 10^3	0.4(2) × 10^3
max ext corr	1.26 for refln (002)	1.06 for refln ($20\bar{2}$)
	Diffraction Measurements	
T (K)	20.0(5)	20.0(5)
$(\sin\theta)/\lambda$ limit (Å^{-1})	0.70	0.70
no. of observns		
tot	4398	2493
indepdt (wR_{int})	4008 (0.039)	2311 (0.024)
used in refinement (*n*)	4006	2304
	Refinement[a]	
no. of variables (*v*)	344	396
$R(F^2)$, $R_w(F^2)$	0.131, 0.109	0.104, 0.096
$S(F^2)$	1.030	1.094

[a] $R(F^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$. $R_w(F^2) = [\sum w|F_o^2 - F_c^2|^2/\sum w(F_o^2)^2]^{1/2}$. $S(F^2) = [\sum w|F_o^2 - F_c^2|^2/(n - m)]^{1/2}$.

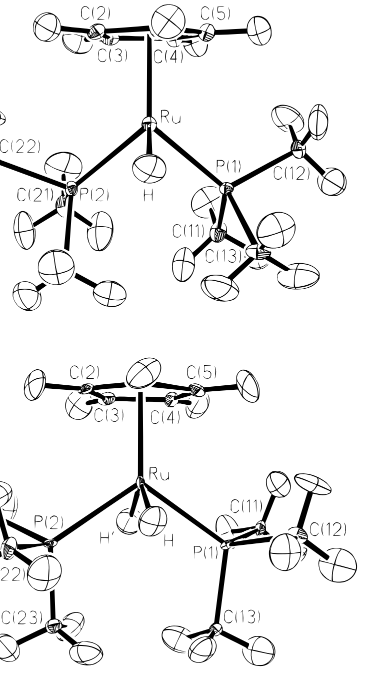

Figure 1. (a) Top: Molecular structure of **1** shown with 70% probability ellipsoids. (b) Bottom: Molecular structure of **2** (cation) shown with 70% probability ellipsoids.

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Table 2. Fractional Coordinates for 1

atom	*x*	*y*	*z*
Ru	0.0224(2)	0.2063(1)	0.2744(2)
H	0.1166(5)	0.2507(3)	0.4120(4)
P1	−0.0906(3)	0.3445(2)	0.2433(2)
P2	0.2273(3)	0.2500(2)	0.2220(2)
C1	−0.0432(2)	0.0845(1)	0.3700(2)
H1	−0.0192(5)	0.0795(3)	0.4734(4)
C2	0.0541(2)	0.0551(1)	0.2982(2)
H2	0.1618(5)	0.0211(3)	0.3368(5)
C3	−0.0208(2)	0.0740(1)	0.1647(2)
H3	0.0212(5)	0.0579(3)	0.0849(4)
C4	−0.1634(2)	0.1147(1)	0.1547(2)
H4	−0.2467(5)	0.1367(3)	0.0668(4)
C5	−0.1760(2)	0.1214(1)	0.2825(2)
H5	−0.2718(5)	0.1487(3)	0.3071(4)
C11	−0.0887(2)	0.4206(1)	0.1095(2)
H11a	−0.1570(6)	0.4811(3)	0.1088(5)
H11b	0.0263(6)	0.4430(4)	0.1191(5)
H11c	−0.1340(6)	0.3840(4)	0.0191(4)
C12	−0.2955(2)	0.3394(1)	0.2145(2)
H12a	−0.3419(5)	0.4082(3)	0.2058(5)
H12b	−0.3479(5)	0.3009(4)	0.1264(5)
H12c	−0.3185(5)	0.3044(3)	0.2947(5)
C13	−0.0390(2)	0.4265(1)	0.3760(2)
H13a	−0.1081(6)	0.4878(3)	0.3536(5)
H13b	−0.0531(6)	0.3937(4)	0.4615(5)
H13c	0.0789(6)	0.4464(4)	0.3972(5)
C21	0.2131(2)	0.2867(1)	0.0575(2)
H21a	0.3240(5)	0.2963(4)	0.0453(5)
H21b	0.1526(7)	0.2347(4)	−0.0105(5)
H21c	0.1511(6)	0.3502(4)	0.0350(5)
C22	0.3686(2)	0.1589(1)	0.2367(2)
H22a	0.4654(5)	0.1844(3)	0.2092(5)
H22b	0.4080(6)	0.1334(4)	0.3348(5)
H22c	0.3175(6)	0.1023(3)	0.1746(5)
C23	0.3449(2)	0.3413(1)	0.3165(2)
H23a	0.4397(5)	0.3589(3)	0.2823(5)
H23b	0.2770(6)	0.4018(3)	0.3135(5)
H23c	0.3861(6)	0.3192(3)	0.4177(4)

Table 3. Fractional Coordinates for 2

atom	*x*	*y*	*z*
Ru[a]	0.0000	0.1956(3)	0.0000
H	0.0860(6)	0.2189(7)	−0.0715(7)
H′	0.0232(6)	0.1806(8)	0.1399(7)
P1	0.1011(3)	0.0197(4)	0.0392(4)
P2	0.0713(3)	0.3877(4)	0.0727(4)
C1	−0.1044(3)	0.2190(3)	−0.1716(4)
H1	−0.0843(6)	0.2500(8)	−0.2537(7)
C2	−0.1326(3)	0.3046(3)	−0.0852(4)
H2	−0.1374(6)	0.4117(7)	−0.0931(8)
C3	−0.1542(3)	0.2257(3)	0.0104(4)
H3	−0.1774(6)	0.2599(8)	0.0911(8)
C4	−0.1386(3)	0.0905(3)	−0.0180(4)
H4	−0.1504(6)	0.0050(8)	0.0350(8)
C5	−0.1076(3)	0.0865(3)	−0.1304(4)
H5	−0.0934(6)	−0.0015(7)	−0.1769(8)
C11	0.0548(3)	−0.1130(3)	0.1200(4)
H11a	0.1086(6)	−0.1875(8)	0.1456(9)
H11b	−0.0076(7)	−0.1554(8)	0.0673(8)
H11c	0.0350(7)	−0.0758(8)	0.2014(7)
C12	0.1274(3)	−0.0674(3)	−0.0906(4)
H12a	0.1722(7)	−0.1535(9)	−0.0635(8)
H12b	0.1650(6)	−0.0010(9)	−0.1413(8)
H12c	0.0620(6)	−0.1006(8)	−0.1433(7)
C13	0.2197(3)	0.0510(3)	0.1205(4)
H13a	0.2574(7)	−0.0424(8)	0.1373(8)
H13b	0.2150(6)	0.1000(9)	0.2039(8)
H13c	0.2579(6)	0.1145(8)	0.0687(8)
C21	−0.0073(3)	0.4890(3)	0.1471(4)
H21a	0.0329(7)	0.5731(8)	0.1895(8)
H21b	−0.0346(7)	0.4303(8)	0.2143(8)
H21c	−0.0664(6)	0.5242(9)	0.0830(8)
C22	0.1047(3)	0.5013(3)	−0.0351(4)
H22a	0.1372(7)	0.5912(9)	0.0075(8)
H22b	0.0419(6)	0.5304(9)	−0.0970(8)
H22c	0.1564(6)	0.4553(8)	−0.0815(8)
C23	0.1799(3)	0.3792(3)	0.1814(4)
H23a	0.2023(6)	0.4788(8)	0.2097(8)
H23b	0.2346(6)	0.3336(8)	0.1385(8)
H23c	0.1682(6)	0.3211(8)	0.2559(8)
B	−0.1681(3)	0.7396(4)	−0.1387(4)
F1	−0.0771(4)	0.7686(4)	−0.1605(5)
F2	−0.1787(4)	0.7870(5)	−0.0273(5)
F3	−0.2359(4)	0.7979(4)	−0.2248(5)
F4	−0.1814(3)	0.6023(4)	−0.1411(4)

[a] *x* and *z* coordinates were held constant in order to define the crystallographic origin.

given in Table 5. The Ru−H bond lengths in **1** (1.630(4) Å) and **2** (1.599(8), 1.604(9) Å) are the first terminal Ru−H distances to be determined by single-crystal neutron diffraction. They exhibit the trend of shortening with increasing oxidation state of the metal, as predicted by Halpern and co-workers[11] on the basis of extrapolation across the periodic table from known structures, although they are 0.02−0.04 Å longer than the actual values predicted (Ru(II)−H 1.593 Å; Ru(IV)−H 1.583 Å).[11a] An earlier report of the neutron powder diffraction study of Sr_2RuD_6 gave an average Ru−D bond length of 1.69(4) Å.[12] The Ru−H separations in the dihydrogen complex **3** (1.66(2), 1.67(2) Å) are slightly longer than those in **1** and **2**, though this is barely significant considering the esd's. The trend of terminal hydride distances being shorter than the corresponding metal−dihydrogen separations has been observed in two iron complexes that contain both hydride and dihydrogen ligands[13] and is supported by ab initio calculations in which classical and nonclassical isomers of polyhydride complexes are compared.[14] However, it has been pointed out by Morris, Koetzle, and co-workers[2] that in cases of substantially "stretched" η^2-H_2 ligands (H−H > 1.1 Å), where $M \rightarrow H_2(\sigma^*)$ back-donation is strong, the M−H distances are either comparable to[15] or can be shorter than[16] the corresponding M−H(hydride) bond lengths.

The terminal hydride bond lengths are 0.1−0.2 Å shorter than those of μ_2-hydrides, Ru−H−Ru, derived from neutron diffraction studies,[17] which lie in the range 1.753−1.823 Å. The magnitude of this difference is typical of transition metals in the middle of the d-block.[18]

Figure 2a indicates that on protonation of $Cp'(PR_3)_2$-RuH to give either the cationic dihydride or dihydrogen

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Table 4. Selected Interatomic Distances (Å) and Angles (deg) for 1 and 2

	$[Cp(PMe_3)_2RuH]$ (**1**)	$[Cp(PMe_3)_2RuH_2]BF_4$ (**2**)
Ru−H	1.630(4)	1.604(9)
Ru−H′		1.599(8)
Ru−P1	2.259(3)	2.293(5)
Ru−P2	2.245(3)	2.292(5)
Ru−C1	2.242(3)	2.286(4)
Ru−C2	2.239(3)	2.273(4)
Ru−C3	2.250(3)	2.246(5)
Ru−C4	2.268(2)	2.228(4)
Ru−C5	2.252(3)	2.256(4)
P1−C11	1.842(3)	1.820(6)
P1−C12	1.842(3)	1.825(6)
P1−C13	1.832(3)	1.827(7)
P2−C21	1.842(3)	1.834(7)
P2−C22	1.846(3)	1.813(7)
P2−C23	1.837(3)	1.830(6)
C1−C2	1.432(3)	1.426(6)
C2−C3	1.443(3)	1.436(7)
C3−C4	1.430(3)	1.434(5)
C4−C5	1.440(3)	1.435(6)
C1−C5	1.423(3)	1.428(5)
H−Ru−H′		118.8(4)
H−Ru−P1	83.1(2)	72.8(3)
H−Ru−P2	81.9(2)	74.3(3)
H′−Ru−P1		73.0(3)
H′−Ru−P2		72.9(3)
P1−Ru−P2	95.8(1)	111.1(2)

Table 5. Comparison of Geometries of 1−3

dist (Å)/angle (deg)[a]	**1**	**2**	**3**[b]
Ru−H	1.630(4)	1.599(8), 1.604(9)	1.66(2), 1.67(2) [1.57]
H−Ru−H		118.8(4)	38(1)
X_c−Ru−H	124.6	120.1, 121.1	118.6, 119.4 [120.9]
RuH−RuP_2[c]	11.3	30.0, 31.3	18.8, 19.3 [−1.4]
X_cRuH−RuP_2[d]	89.1	89.4, 89.5	71.5, 71.8 [89.9]
Cp′−RuP_2[e]	67.3	87.4	57.7
P1−Ru−P2	95.8(1)	111.1(2)	71.4(3)

[a] Esd's in parentheses were directly determined from least-squares refinement. [b] Corresponding values calculated for the H−H midpoint (X_h) are given in brackets. [c] Angle between Ru−H vector and normal to RuP_2 plane; negative values indicate the vector is oriented away from the phosphorus atoms and toward the Cp′ ring. [d] Angle between the X_cRuH plane (X_c = Cp centroid) and RuP_2 plane. [e] Angle between the C_5 ring plane and the RuP_2 plane.

complex the X_c−Ru−H angle (X_c = Cp′ centroid, H = hydride ligand or H_2 midpoint, X_h) remains approximately constant at 120−125° while the phosphine ligand(s) move to accommodate an additional proton. Addition of a proton on the same side as the original hydride yields the dihydrogen ligand, whereas on the opposite side the *trans* dihydride species is produced.[19] Thus, the angle X_c−Ru−X_p (X_p = midpoint of two phosphorus atoms) *decreases* from 157.6° in the monohydride (**1**) to 147.7° in the dihydrogen complex (**3**) but is *increased* to 178.8° in the dihydride. This change in geometry reflects a pivoting of the RuP_2 plane about the metal center to accommodate the additional proton.[3]

The question of the importance of the L−Ru−L′ angle (here P−Ru−P′) versus the electron donor capability of the ligands in determining the relative stability of dihydrogen vs dihydride complex remains an interesting one. In **1** and **2**, not only are the phosphine ligands very electron-rich, thus promoting sufficient π-back-donation from the metal to convert any incipient dihydrogen complex into the dihydride isomer, but the P−Ru−P′ angle is unconstrained allowing it to increase from 95.8(1)° in **1** to 111.1(2)° in **2** in order to accommodate the second (*trans*) hydride ligand.

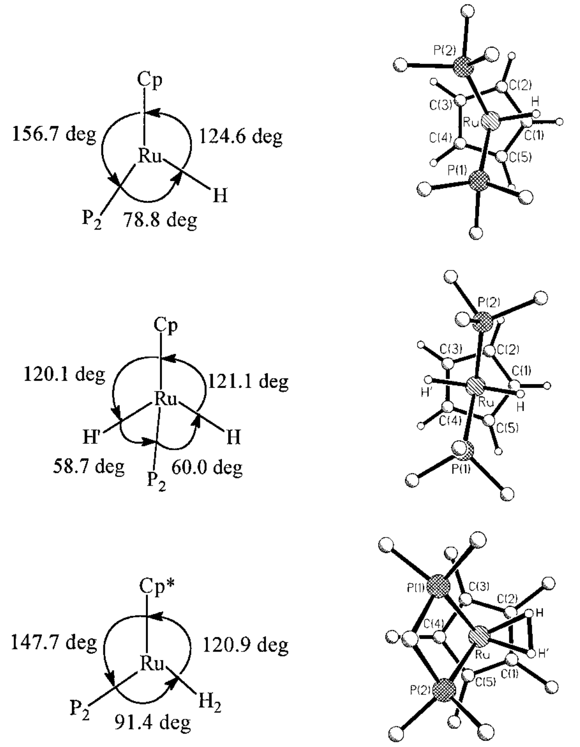

Figure 2. Comparison of the geometries of **1**−**3** (top to bottom) viewed (a, left) (schematically) perpendicular to the Ru−X_c vector (labels P2 and H2 refer to the projection of the atoms P1, P2, and their midpoint, X_p, and H, H′, and their midpoint, X_h, respectively) and (b, right) along the Ru−X_c vector. (Atom labels H and H′ for **3** correspond to the original labels[2] HRu1 and HRu2.)

Let us first consider the donor/acceptor capabilities of the ligands, L. Heinekey and co-workers have proposed that complexes of the form $[CpLL'RuH_2]^+$ (L = L′ = CO; L = CO, L′ = PR_3) exist as nonclassical dihydrogen complexes in solution,[1c,e] whereas for L = L′ = PR_3 the thermodynamically more stable isomer is the *trans*-dihydride.[1f] Ab initio MP2 calculations by Lin and Hall[20] also show that in $CpL_2RuH_2^+$ complexes the nonclassical isomer is stabilized when L is a π-acceptor ligand. However, these calculations suggest that even when L = CO the π-acceptor capability does not compensate sufficiently for the σ- and π-donor ability of the Cp ligand, thus still leaving the *trans*-dihydride complex as the most stable isomer.

Now let us consider the ring strain and steric effects of the dppm ligand. The apparent importance of the ring strain of the dppm ligand in destabilizing the *trans*-dihydride tautomer relative to the dihydrogen tautomer is emphasized by the fact that protonation of Cp′(dppm)RuH (Cp′ = Cp, Cp‡) yields exclusively dihydrogen complexes,[5b] whereas protonation of either Cp‡(dppe)RuH or Cp‡$(PPh_3)_2$RuH yields the corresponding dihydride species as the thermodynamic product, after rearrangement from the kinetic dihydrogen product.[1c] NMR evidence indicates[1c,2] that **3** exists in solution as an equilibrium mixture of the dihydrogen and *trans*-dihydride tautomers in approximately a 2:1 ratio. This

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[19] The observed structures reflect the thermodynamic products and are not indicative of the mechanism of protonation, which is believed in most cases to proceed via the dihydrogen tautomer.[1f]

[20] Lin, Z.; Hall, M. B. *Organometallics* **1992**, *11*, 3801−3804.

Table 6. C−H···F Hydrogen Bond Geometries for 2

interaction	C−H transform[a]	F···C (Å)	F···H (Å)	C−H (Å)	F···H−C (deg)	B−F···H (deg)
F1···H5−C5	II	3.277(6)	2.346(9)	1.077(9)	143.8(7)	98.1(4)
F1···H12c−C12	II	3.343(6)	2.370(10)	1.082(9)	148.9(7)	153.7(4)
F2···H4−C4	II	3.128(6)	2.338(9)	1.089(10)	128.0(7)	124.5(4)
F2···H13c−C13	III	3.395(7)	2.329(10)	1.083(10)	167.6(7)	106.6(4)
F2···H23b−C23	III	3.508(8)	2.484(12)	1.093(10)	155.6(7)	155.6(4)
F3···H3−C3	IV	3.446(8)	2.473(11)	1.093(11)	147.7(7)	102.5(4)
F3···H23a−C23	V	3.592(6)	2.500(9)	1.093(9)	176.4(7)	140.0(4)
F4···H2−C2	I	3.140(5)	2.078(8)	1.091(7)	163.6(7)	151.9(4)
F4···H12b−C12	III	3.358(7)	2.431(11)	1.088(10)	142.2(6)	123.1(4)

[a] Transformation applied to the original coordinates to generate those of the interacting C−H group: I = x, y, z; II = $x, 1.0 + y, z$; III = $-0.5 + x, 0.5 + y, z$; IV = $x, 1.0 - y, 0.5 + z$; V = $-0.5 + x, 1.5 - y, -0.5 + z$.

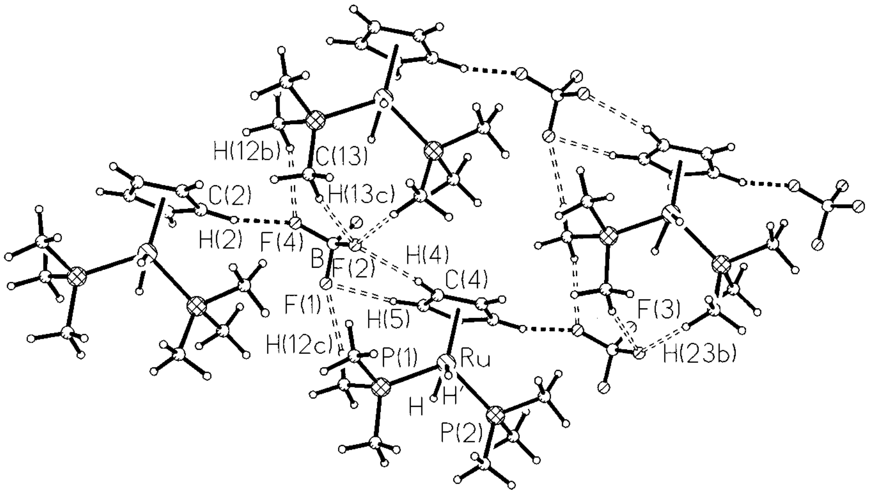

Figure 3. View of four units of [$Cp(PMe_3)_2RuH_2$]BF_4 from structure of **2**, showing the C−H···F hydrogen-bonding network. Dashed open bonds indicate H···F separations in the range 2.3−2.5 Å. The short C(2)−H(2)···F(4) hydrogen bonds (H···F 2.078(8) Å) are shown with dashed solid lines. Hydrogen bonds involving F(3) are omitted to aid clarity.

suggests that in **3** electronic effects, notably increased electron donation of the Cp* ligand relative to that of the Cp and Cp‡ analogs, are competing against ring strain effects to increase the relative stability of the *trans*-dihydride tautomer. Calculations using the crystallographic geometry of **3** (using PH_3 ligands instead of dppm) suggest that the *cis*-dihydride species should be more stable than the dihydrogen isomer by ca. 5.4 kcal/mol. However, in these calculations the *trans*-dihydride was assumed to be inaccessible. The implication is that, in addition to solvation effects, the steric effects of the phenyl substituents, which persist in solution,[2] may play an important role in determining the geometry of **3** and perhaps contribute to stabilization of the nonclassical isomer relative to the *trans*-dihydride. To our knowledge there is no experimental evidence to support the presence of a *cis*-dihydride species in any of the [CpL_2RuH_2]$^+$ systems studied to date.

Clearly further investigation is required to fully disentangle the effects of the geometry and the donor ability of ligands, i.e. steric effects and metal orbital hybridization effects *versus* the effects of raising or lowering metal orbital energies.

The orientation (about its approximate local C_5 axis) of the Cp′ ring relative to the other ligands is depicted in Figure 2b for **1**−**3**. In **1** and **2**, the Ru−H bond nearly eclipses the Cp C(1)−H(1) bond (torsion angle H−Ru−C(1)−H(1) = 7.1° for **1** and −8.0° for **2**). This conformation presumably arises from the need of the phosphine ligands to be staggered with respect to extra-annular Cp′ C−H or C−C bonds. In **3**, this requirement results in the M−X_h vector being staggered with respect to the C(1)−H(1) and C(2)−H(2) bonds and, therefore, the H−H′ bond lying parallel to the C(1)−C(2) bond (dihedral angle H−H′−C(1)−C(2) = 1.7°). That steric factors may play a major role in determining the orientation of the Cp′ ring relative to the other ligands in a piano-stool geometry structure has been demonstrated previously in the Cp′$Mo(CO)_3X$ system.[21]

Intermolecular Hydrogen Bonding. No unusual intermolecular contacts are observed for **1**. However, the fluorine atoms in **2** all make C−H···F contacts that are shorter than the sum of van der Waals radii (2.55 Å) of F and H (Table 6). The shortest of these interactions involves the Cp ligand rather than the methyl groups of the PMe_3 ligands, which is consistent with the relative C−H bond polarity anticipated for these ligands. Presumably this weak hydrogen-bonding network is the principal attractive interaction involved in defining the packing arrangement for this structure. The H···F separations exceed 2.3 Å with the exception of the very short C(2)−H(2)···F(4) interaction [C(2)−H(2) 1.091(7) Å, H(2)···F(4) 2.078(8) Å, C(2)···F(4) 3.140(5) Å, C(2)−H(2)···F(4) 163.6(7)°]. The hydrogen-bonding network is shown in Figure 3. Recent studies have begun to highlight the importance of C−H···X (X = N, O, S, Cl) in the packing of organic[22] and organometallic[23] molecules and thus in their mutual recognition. We have previously demonstrated from a neutron diffraction

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(21) (a) Brammer, L.; Zhao, D.; Bullock, R. M.; McMullan, R. K. *Inorg. Chem.* **1993**, *32*, 4819−4824. (b) Kubácek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

(22) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

study[23a] that $C-H\cdots Cl$ hydrogen bonds are more readily deformed than stronger $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds, and, thus, show a wider range of angles at the hydrogen. Furthermore, the study also suggests[23a] that the Cl lone pairs are less directional than those of oxygen atoms, although a recent study by Crabtree and co-workers[24] suggests that a greater degree of Cl lone pair directionality may be present in some ($N-H\cdots Cl$ hydrogen bonded) systems. The features of our previous study of $C-H\cdots Cl$ hydrogen bonds are also seen in the $C-H\cdots F$ hydrogen bonds documented in the present study. Thus $C-H\cdots F$ bond angles vary in the range 128.0−176.4°, indicating ease of deformation, and $B-F\cdots H$ angles, which are an indication of fluorine lone pair directionality, encompass the range 98.1−155.6°.

A survey of the Cambridge Structural Database (CSD)[25] indicates a number of structures in which $C-H\cdots F$ interactions are present, including ca. 100 intermolecular $C-H\cdots F$ contacts characterized by neutron diffraction, in which $H\cdots F < 2.6$ Å. Of these interactions only 5 have $H\cdots F$ separations less than 2.3 Å, the shortest being 2.192 and 2.243 Å in the compound $[Cp(PMe_3)IrH_3]BF_4$[26] and as in **2** involving the C−H bonds of the Cp ring. Additionally, **3** shows four $H\cdots F$ contacts at separations of less than 2.3 Å, the shortest being $C(8)-H(8a)\cdots F(4)$ at 2.203 Å. Thus, the $C(2)-H(2)\cdots F(4)$ hydrogen bond observed in **2** is by over 0.1 Å the shortest characterized by neutron diffraction to date.

Atomic Vibrational Motion. It has been shown in previous neutron diffraction studies of transition metal hydride complexes that analysis of the atomic displacement parameters (ADPs) for accurate structures determined at very low temperatures can provide information on the hydride vibrational modes in good agreement with spectroscopic data.[17b,27] The rigid bond test,[28] which can be used to examine for consistency the components of the ADPs along bonds between atoms of similar mass, indicates that the displacement parameters are of sufficient quality for the application of vibrational analysis.[29] In both **1** and **2** (cation), the largest discrepancies are for the P−C bonds, as might be anticipated. Application of the rigid body test of Schomaker and Trueblood[30,31] for the non-hydrogen atoms of **1** and **2** (cation) yielded fits to the rigid body model of $R_w = 0.180$ and 0.237, respectively, indicating that these molecules show some degree of flexibility even at 20 K. Further investigation using a segmented rigid-body fit[31] reveals that neither **1** nor **2** shows large torsional motion about the $Ru-X_c$ vector (i.e. Cp ring rotation) and that **1** but not **2** shows appreciable torsional motion about the Ru−P bonds. The corresponding fits for two-segment rigid-body models are $R_w = 0.177$ for **1** and 0.229 for **2**, and for the four-segment rigid-body model $R_w = 0.112$ for **1** and 0.219 for **2**. The magnitudes of torsional motion are consistent with the metal center being more sterically crowded in **2**, leading to a more restricted motion of the phosphine ligands.

As has been previously shown, the mean-square amplitudes (msa) of motion of the hydride ligands, when corrected for the motion of the attached metal atom (here Ru), can be considered to be described as a quantum harmonic oscillator, for which the msa of vibration is related to the frequency by the equation $\langle x^2 \rangle = (h/8\pi^2 c\mu\nu)[\coth(hc\nu/2kT)]$, where $\langle x^2 \rangle$ is the msa of motion, h is Planck's constant, k is Boltzmann's constant, T is the temperature (K), c is the velocity of light, ν is the vibration frequency (cm^{-1}), and μ is the reduced mass of the oscillator. A further approximation that the hyperbolic cotangent term is unity can be made assuming that only the ground-state vibrational level is populated at the experimental temperature. The corrected msa values for motion parallel to the Ru−H bond are 0.0088(20) $Å^2$ for **1** and 0.0082(30) $Å^2$ (H) and 0.0072(40) Å (H′) for **2** (esd's are estimated as the maximum individual U_{ii} esd for each hydride hydrogen atom). This corresponds to a Ru−H stretch of 1919(436) cm^{-1} for **1**, in remarkable agreement with IR measurements[3] 1906 cm^{-1} (KBr) and 1892 cm^{-1} (CH_2Cl_2). For **2** the mean value for the Ru−H stretch derived from the two hydride ligands is 2203(143) cm^{-1} (esd derived from scatter of the observations for the two hydrides) and within the precision of this determination is also in agreement with solution IR data[3] (1989 cm^{-1}, CH_2Cl_2). Thus the trend of increased stretching frequency of going from an Ru(II)−H bond to Ru(IV)−H bonds is qualitatively reproduced.

Conclusions

The first single-crystal neutron diffraction studies of terminal ruthenium hydride complexes are described. The structures of **1** and **2** provide important benchmarks in the study of the activation of dihydrogen by the "$Cp'L_2Ru$" moiety and by comparison with **3** provide for a complete picture of three of the four structural types pertinent to this area of chemistry (the fourth, a *cis*-dihydride, has not yet been isolated to our knowledge). Moreover, greater insight can be gained into the ligand rearrangements that take place in the formation of the dihydrogen and dihydride species from the monohydride.

Of interest to the field of molecular recognition in organometallic chemistry is the observation that a network of $C-H\cdots F$ hydrogen bonds links the anion and cation moieties in **2**. With an $H\cdots F$ separation of 2.078(8) Å, the $C(2)-H(2)\cdots F(4)$ hydrogen bond is the shortest such interaction characterized to date by neutron diffraction. Finally we note that the structure determinations of **1** and **2** are of sufficient quality to facilitate a more detailed analysis of the vibrational motion of the hydride ligands. This analysis yields estimates for the stretching frequencies of the terminal Ru−H bonds which are in good agreement with IR measurements.

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[29] The rms differences in mean square amplitude (msa) of vibration for pairs of bonded carbon atoms are 0.0015 and 0.0026 $Å^2$ for **1** and **2**, respectively, compared with esd's of individual C U_{ii} values of ca. 0.001 and 0.002 $Å^2$. The rms differences in msa of vibration for P−C bonded atom pairs are 0.0032 and 0.0083 $Å^2$ for **1** and **2**, respectively, compared with esd's of individual C and P U_{ii} values of ca. 0.001 and 0.002 $Å^2$.

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Supporting Information Available: For **1** and **2**, anisotropic displacement parameters (Tables S1 and S2) and interatomic distances and angles (Tables S3−S6) (6 pages). Ordering information is given on any current masthead page.

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