Hydride Complexes of Ruthenium and Related Metals: Preparation and Structures of $Cp(PMe_3)_2RuH$ and $[Cp(PMe_3)_2RuH_2]BF_4$

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The reaction of $Cp(PMe_3)_2RuCl$ with either KOMe in MeOH or $LiAlH_4$ in Et_2O produces the hydride $Cp(PMe_3)_2RuH$ (**1**) in high yield. Protonation of **1** with HX quantitatively generates the dihydrides $[Cp(PMe_3)_2RuH_2]X$ (X = Cl (**2**), BF_4 (**3**), $B[3,5\text{-}(CF_3)_2C_6H_3]_4$ (**4**)). The spectroscopic data on **3** indicate a classical dihydride configuration with no evidence for a dihydrogen tautomer. The pK_a of **3** in CH_2Cl_2 is 13.9, and the contribution of the ancillary ligands to the pK_a value is discussed. X-ray crystal structures of hydride **1** and dihydride **3** have been determined. Hydride **1** exhibits a "three-legged piano stool" geometry, while the cation of **3** exhibits a "four-legged piano stool" geometry, consistent with the classical dihydride configuration. A comparison of the structures of **1** and **3** with related d^6 $Cp'L_2MH$, d^4 $Cp'L_2MH_2$, and d^6 $Cp'L_2M(\eta^2\text{-}H_2)$ complexes ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$, $\eta^5\text{-}C_5H_5Me$) reveals several general structural trends. First, the angle between the Cp′ plane and the ML_2 plane lies in the range 59−79° (mean 67.6(13)°) for d^6 $Cp'L_2MH$ complexes but is in the range 86−90° (mean 87.6(4)°) for d^4 $Cp'L_2MH_2$ complexes and has a mean value of 56.1(8)° for known d^6 $Cp'L_2M(\eta^2\text{-}H_2)$ complexes. Second, the angle between the M−H vector and the normal to the ML_2 plane is generally less than 10° (mean 7.9(12)°) for the d^6 $Cp'L_2MH$ complexes, while in d^4 $Cp'L_2MH_2$ complexes the M−H vector is shifted toward the ML_2 plane, increasing this angle by ca. 20° (mean 30.0(20)°). The corresponding angle in d^6 $Cp'L_2M(\eta^2\text{-}H_2)$ complexes has a mean value of 15.5(18)°. Third, the L−M−L′ angles in d^6 $Cp'L_2MH$ complexes (range 84−101°, mean 93.0(19)°) are typically smaller that the corresponding angles in d^4 $Cp'L_2MH_2$ complexes (range 101−111°, mean 107.2(10)°).

Introduction

For many years there has been great interest in transition metal hydrides because of their unusual reactivity and their involvement in many stoichiometric and catalytic processes.[1−6] Recently, ruthenium(II) hydrides of the type $Cp'L_2RuH$ ($Cp' = C_5H_5$ (Cp), C_5Me_5 (Cp*); L = CO, PR_3, PAr_3; L_2 = diphosphines) have been the focus of considerable interest. The reactivity of $Cp'L_2RuH$ is largely dependent on the ancillary ligands. $Cp(PMe_3)_2RuH$ reacts with electron-deficient chlorosilanes R_3SiCl ($SiR_3 = SiCl_3$, $SiHCl_2$, $SiMeCl_2$, SiMeHCl, and $SiMe_2Cl$) to form the ruthenium silyl complexes $Cp(PMe_3)_2RuSiR_3$ and the ruthenium dihydride $[Cp(PMe_3)_2RuH_2]Cl$, while $Cp(PPh_3)_2RuH$, under similar conditions, shows no reactivity with chlorosilanes.[7] This difference in reactivity was attributed to the enhanced electron donor ability of PMe_3 compared to PPh_3. Protonation of $Cp'L_2RuH$ has proven to be a useful route to cationic ruthenium(II) dihydrogen complexes $[Cp'L_2Ru(\eta^2\text{-}H_2)]^+$ and/or cationic ruthenium(IV) dihydride complexes $[Cp'L_2RuH_2]^+$.[8−16] The nature of the ancillary ligands dictates the protonation product. Electron-withdrawing ligands, like CO, favor dihydrogen formation while electron-donating ligands, like C_5Me_5 and PMe_3, favor dihydride formation; many protonation reactions lead to equilibrium mixtures of the two tautomers.

In contrast to this great interest in the hydrides of ruthenium, very few have been the subject of a crystallographic investigation. In this paper, we report the synthesis and ^1H NMR spectra of the electron-rich

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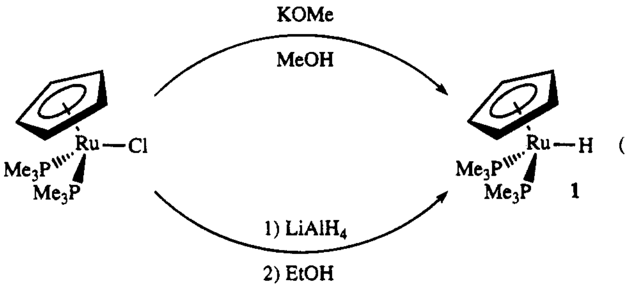
hydride $Cp(PMe_3)_2RuH$ and the dihydrides $[Cp(PMe_3)_2RuH_2]X$ (X = Cl, BF_4, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$) and the crystal structures of $Cp(PMe_3)_2RuH$ and $[Cp(PMe_3)_2RuH_2]BF_4$. The availability of these structures provides a unique opportunity to investigate the structural changes that occur upon converting a ruthenium(II) hydride to a ruthenium(IV) dihydride.

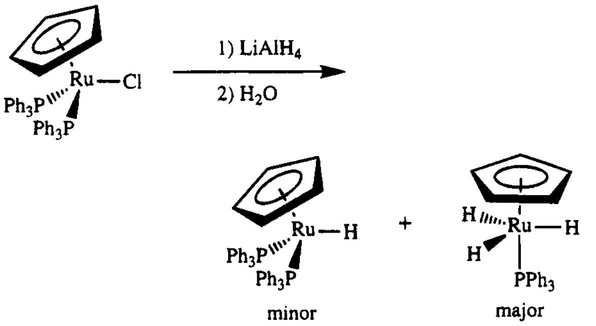
Results and Discussion

Synthesis of $Cp(PMe_3)_2RuH$. The neutral hydride $Cp(PMe_3)_2RuH$ (**1**) was prepared in high yields by a modification of the reported procedure.[17] Hydride **1** was readily prepared by reacting $Cp(PMe_3)_2RuCl$ with KOMe in refluxing MeOH (eq 1). Due to the extreme solubility of **1** in common organic solvents, crystallization of **1** from cold solvents results in low yields. However, hydride **1** readily sublimes and can be obtained as a bright yellow microcrystalline solid in high yields (ca. 90%). Similarly, reacting $Cp(PMe_3)_2RuCl$ with $KOCD_3$ in refluxing CD_3OD yields the deuteride $Cp(PMe_3)_2RuD$ (**1**-d_1) in good yields with ca. 90% deuterium incorporation at the metal hydride position. Hydride **1** can also be prepared by reacting $Cp(PMe_3)_2RuCl$ with $LiAlH_4$ in Et_2O followed by an EtOH quench (eq 1). Using $LiAlD_4$ in Et_2O followed by an EtOD quench also produces **1**-d_1 but with only 70−75% deuterium incorporation at the metal hydride position.



(1)

The difference between the reactivity of $Cp(PMe_3)_2RuCl$ and $Cp(PPh_3)_2RuCl$ with $LiAlH_4$ is noteworthy Hydride **1** can be prepared in high yields (ca. 90%) from $Cp(PMe_3)_2RuCl$ and $LiAlH_4$ (eq 1). On the other hand, the reaction of $LiAlH_4$ with $Cp(PPh_3)_2RuCl$ generates the hydride $Cp(PPh_3)_2RuH$ in low yields with the major product being the trihydride $Cp(PPh_3)RuH_3$ (eq 2).[18]

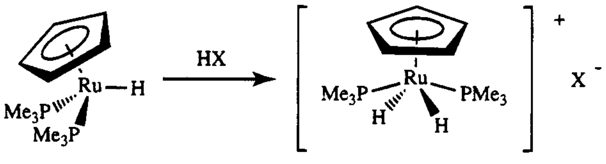


(2)

This difference in reactivity can be attributed to a difference in phosphine lability. The lability of the PPh_3 ligands in $Cp(PPh_3)_2RuCl$ is well documented, and $Cp(PPh_3)_2RuCl$ is a useful synthon for preparing a variety of other ruthenium(II) complexes,[19] including $Cp(PMe_3)_2RuCl$.[20,21] Furthermore, Nolan and co-workers, using anaerobic solution calorimetry, have recently determined that the Ru−PMe_3 bond is stronger than the Ru−PPh_3 bond by 7−8 kcal/mol.[22]

Hydride **1** is extremely air sensitive, turning blue upon exposure to air, and undergoes hydride/chloride metathesis with chlorocarbons. In $CDCl_3$, yellow **1** is completely converted to orange $Cp(PMe_3)_2RuCl$ within minutes, while in CD_2Cl_2 this conversion requires more than a day at room temperature. In the ^1H NMR spectrum (CD_2Cl_2), the hydride resonance of **1** is observed at −13.99 ppm as a triplet ($^2J_{PH}$ = 36.8 Hz). A broad band in the IR spectrum (CH_2Cl_2) at 1892 cm^{-1} is assignable to ν(Ru−H) (cf. ν(Ru−H) = 1900 cm^{-1} in KBr[17]). This assignment is confirmed by the absence of this band in **1**-d_1 and the appearance of a band at 1365 cm^{-1} assigned to ν(Ru−D). ν(Ru−H)/ν(Ru−D) = 1.39 is observed, close to the calculated ratio of 1.41.

Synthesis of $[Cp(PMe_3)_2RuH_2]X$ (X = Cl, BF_4, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$). Protonation of $Cp(PMe_3)_2RuH$ with HX (X = Cl, BF_4, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$) in Et_2O or CH_2Cl_2 (eq 3) produces the cationic dihydrides $[Cp(PMe_3)_2RuH_2]X$ [X = Cl (**2**), BF_4 (**3**), $B[3,5\text{-}(CF_3)_2C_6H_3]_4$ (**4**)], respectively, as white or light purple solids in high yields (ca. > 90%). Dihydride **2** was previously reported as a product from the reaction of **1** with chlorosilanes.[7] The isotopomers $[Cp(PMe_3)_2RuHD]BF_4$ (**3**-d_1) and $[Cp(PMe_3)_2RuD_2]BF_4$ (**3**-d_2) were prepared by protonating **1**-d_1 with $HBF_4{\cdot}Et_2O$ and $HBF_4{\cdot}Et_2O$ in D_2O, respectively. Deuterium incorporation at the metal hydride positions was 45% for **3**-d_1 and >95% for **3**-d_2.



(3)

X = Cl, **2**
BF_4, **3**
$B[3,5\text{-}(CF_3)_2C_6H_3]_4$, **4**

In the ^1H NMR spectra (CD_2Cl_2), the dihydride resonances for **2**-**4** are observed around −9.9 ppm (t, $^2J_{PH}$ = 29 Hz). A small dependence on the counterion is observed for the dihydride resonances [**2** (−9.87 ppm) > **3** (−9.90) > **4** (−9.93)] which parallels the coordinating ability of the counterions;[23] no affect on $^2J_{PH}$ is observed. The HD isotopomer **3**-d_1 displayed a triplet at −9.88 ppm ($^2J_{PH}$ = 29 Hz), corresponding to a downfield isotopic shift of ~20 ppb, with no observable HD coupling. T_1 measurements for **3** at 400 MHz in CD_2Cl_2 gave a value of 9.41 s at 293 K which decreased to 1.96 s at 208 K. The broad bands in the IR spectra (CH_2Cl_2) of **2**-**4** at ~1990 cm^{-1} are assigned to ν(Ru−

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Table 1. pK_a Values for Cationic $[Cp'L_2RuH_2]^+$ Dihydride Complexes

complex[a]	pK_a	ref
$[Cp(PPh_3)_2RuH_2]^+$	8.3,[b] 8.0[c]	15
$[Cp(dppp)RuH_2]^{+}$ [d]	8.4,[b] 8.6[c]	15
$[Cp^*(dppp)RuH_2]^{+}$ [d]	10.4[c]	16
$[Cp^*(PPh_3)_2RuH_2]^+$	11.1[c]	16
$[Cp^*(PMePh_2)_2RuH_2]^+$	12.2[c]	15, 16
$[Cp(PMe_3)_2RuH_2]^+$	13.9[b]	this work
$[Cp^*(PMe_2Ph)_2RuH_2]^+$	14.3[c]	16
$[Cp^*(PMe_3)_2RuH_2]^+$	16.3[c]	16

[a] The complexes are listed in order of increasing pK_a value. [b] In CH_2Cl_2. [c] In THF. [d] dppp = $Ph_2P(CH_2)_3PPh_2$.

H). This band is absent in **3**-d_2 and has been replaced by a band at 1422 cm^{-1} assigned to ν(Ru−D). In the IR spectrum (CH_2Cl_2) of the HD isotopomer **3**-d_1, a weak broad ν(Ru−H) at 1987 cm^{-1} as well as a strong ν(Ru−D) at 1422 cm^{-1} is observed (ν(Ru−H)/ν(Ru−D) = 1.40). The spectroscopic data described above are consistent with a classical ruthenium(IV) dihydride configuration for complexes **2-4** with no evidence for a dihydrogen tautomer. Conroy-Lewis and Simpson had previously noted that $[Cp(PMe_3)_2RuH_2]^+$ was a classical dihydride but without giving any supporting details.[9] The classical dihydride configuration was also confirmed by a single-crystal X-ray diffraction study on **3** (*vide infra*).

The pK_a of $[Cp(PMe_3)_2RuH_2]^+$ in CH_2Cl_2 was determined to be 13.9 using Proton Sponge as a reference base (see Experimental Section). Table 1 lists the pK_a values for several other classical ruthenium(IV) dihydrides. The low acidity of $[Cp(PMe_3)_2RuH_2]^+$ is consistent with the electron-rich donor ligands (Cp and PMe_3) present on the ruthenium. From the data in Table 1, several observations on ruthenium(IV) dihydride acidity can be made. First, replacing a Cp group with a Cp* group decreases the acidity by 2−3 pH units. Second, replacing two PPh_3 groups with two PMe_3 groups decreases the acidity by 5−6 pH units. Third, replacing a Ph group on the phosphines with a Me group decreases the acidity by approximately 2 pH units.

The $[Cp(PMe_3)_2RuH_2]^+$ fragment is readily deprotonated by a variety of strong bases such as $LiNR_2$ (R = Me, Pr^i, $SiMe_3$) (the pK_a's for HNR_2 cover the range 30−35[24]). Complications in this deprotonation reaction have been observed when halides (Cl^- in **2** and F^- from BF_4^- in **3**) are present. For example, the deprotonation of **2** with $LiN(SiMe_3)_2$ produces a mixture of $Cp(PMe_3)_2RuH$ and $Cp(PMe_3)_2RuCl$. This complication has been overcome by using excess KOMe as the deprotonating agent (pK_a of MeOH is 15.2[25]) in refluxing MeOH. Any $Cp(PMe_3)_2RuCl$ which may form will then be converted to $Cp(PMe_3)_2RuH$ as described in eq 1.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Cp(PMe_3)_2RuH$ (1)

atom	*x*	*y*	*z*	*U*(eq)[a]
Ru	167(1)	2099(1)	2737(1)	26(1)
H	887(90)	2374(56)	3932(83)	60
P(1)	−929(3)	3469(1)	2425(2)	32(1)
P(2)	2211(2)	2520(2)	2235(2)	34(1)
C(1)	−491(10)	877(5)	3662(8)	41(4)
C(2)	434(10)	586(5)	2930(9)	49(4)
C(3)	−310(11)	798(5)	1636(9)	47(4)
C(4)	−1683(10)	1202(5)	1569(8)	39(3)
C(5)	−1759(10)	1244(5)	2824(8)	41(3)
C(11)	−1046(13)	4155(7)	1036(11)	80(6)
C(12)	−364(13)	4300(7)	3681(12)	96(9)
C(13)	−2887(12)	3444(6)	2271(12)	74(6)
C(21)	2109(13)	2950(8)	640(10)	84(6)
C(22)	3567(12)	1596(7)	2351(11)	69(5)
C(23)	3434(11)	3374(7)	3218(11)	69(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Cp(PMe_3)_2RuH_2]BF_4$ (3)

atom	*x*	*y*	*z*	*U*(eq)[a]
Ru	0	1975(1)	0	14(1)
P(1)	1006(1)	218(1)	394(1)	15(1)
P(2)	722(1)	3887(1)	738(1)	15(1)
C(1)	−1040(3)	2222(5)	−1704(4)	27(1)
C(2)	−1315(3)	3071(4)	−843(5)	28(1)
C(3)	−1528(3)	2268(5)	93(5)	30(1)
C(4)	−1377(3)	917(5)	−205(5)	30(1)
C(5)	−1068(3)	909(5)	−1302(4)	28(1)
C(11)	551(3)	−1108(4)	1199(4)	23(1)
C(12)	1264(3)	−647(4)	−886(3)	23(1)
C(13)	2180(3)	520(4)	1210(3)	20(1)
C(21)	−55(3)	4899(4)	1476(4)	25(1)
C(22)	1039(3)	5033(4)	−335(4)	27(1)
C(23)	1805(3)	3793(4)	1793(4)	23(1)
B	−1703(4)	7390(4)	−1394(5)	24(1)
F(1)	−806(3)	7714(4)	−1613(4)	49(1)
F(2)	−1792(4)	7867(3)	−294(3)	51(1)
F(3)	−2371(4)	7950(4)	−2253(5)	61(2)
F(4)	−1806(3)	6041(3)	−1410(3)	45(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Structures of $Cp(PMe_3)_2RuH$ (1), $[Cp(PMe_3)_2RuH_2]BF_4$ (3), and Related Metal Hydrides. The crystal structures of $Cp(PMe_3)_2RuH$ (**1**) and $[Cp(PMe_3)_2RuH_2]BF_4$ (**3**) have been determined by low-temperature X-ray diffraction at 220 and 123 K, respectively. Atomic coordinates are listed in Tables 2 and 3, and pertinent interatomic distances and angles are presented in Table 4. The molecular structures of **1** and the cation of **3** are shown in Figures 1 and 2.

The geometries of **1** and the cation of **3** are best described in terms of "three- and four-legged piano stools", respectively, with the "legs" comprising the phosphine and hydride ligands. Both structures have approximate C_s symmetry. Although the hydride ligands were not located for **3**, from the comparison with related structures it can readily be inferred that the hydride ligands occupy a *trans* configuration (*vide infra*). Thus, the crystal structure of **3** confirms the absence of an η^2-H_2 ligand as is indicated by the ^1H NMR data (*vide supra*).

The geometries of related d^6 $Cp'L_2MH$, d^6 $Cp'L_2M(\eta^2\text{-}H_2)$, and d^4 $Cp'L_2MH_2$ complexes are compared in Table 5 with those of **1** and **3**. Although there is some variation among complexes of each type, certain trends clearly emerge. In both the three-legged and four-legged piano stool geometries the plane of the ring

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Table 4. Selected Interatomic Distances (Å), Angles (deg), and Torsion Angles (deg) for $Cp(PMe_3)_2RuH$ (1) and $[Cp(PMe_3)_2RuH_2]BF_4$ (3)

	1	3
	Interatomic Distances[a]	
Ru−H	1.36(8)	
Ru−P(1)	2.248(2)	2.283(1)
Ru−P(2)	2.238(3)	2.288(1)
Ru−X	1.899	1.889
Ru−C(ring)	2.239(9)−2.271(8)	2.219(4)−2.274(5)
C−C	1.385(11)−1.430(12)	1.409(7)−1.433(7)
P(1)−C	1.806(11)−1.808(12)	1.809(4)−1.816(5)
P(2)−C	1.835(10)−1.845(11)	1.807(4)−1.826(5)
	Angles[a]	
H−Ru−P(1)	88(4)	
H−Ru−P(2)	86(4)	
P(1)−Ru−P(2)	96.0(1)	110.6(1)
X−Ru−H	118.0	
X−Ru−P(1)	127.6	125.3
X−Ru−P(2)	128.2	124.1
	Torsion Angles[a]	
X−Ru−P(1)−C(11)	−103.2	−55.5
X−Ru−P(1)−C(12)	13.3	61.5
X−Ru−P(1)−C(13)	128.8	−177.9
X−Ru−P(2)−C(21)	88.1	42.7
X−Ru−P(2)−C(22)	−30.6	−73.5
X−Ru−P(2)−C(23)	−147.0	163.8

[a] X refers to the Cp(centroid).

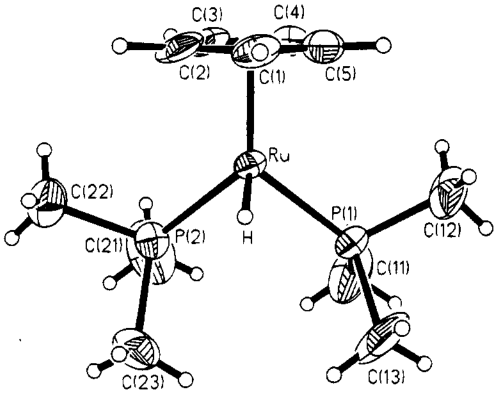

Figure 1. Molecular structure of $Cp(PMe_3)_2RuH$ (**1**) at 220 K shown with 50% probability ellipsoids for non-hydrogen atoms.

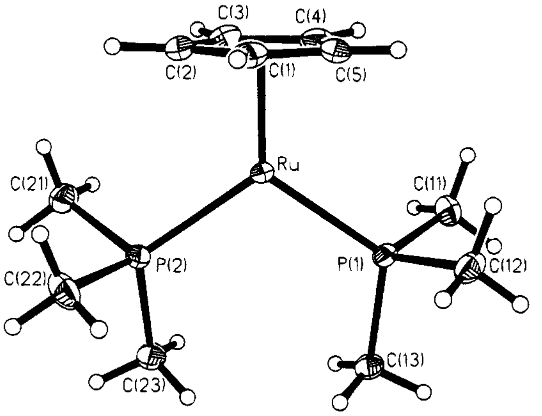

Figure 2. Molecular structure of the cation of **3**, $[Cp(PMe_3)_2RuH_2]^+$, at 123 K shown with 50% probability ellipsoids for non-hydrogen atoms.

centroid/metal atom/hydride ligand(s) lies perpendicular to the ML_2 plane. It is also evident that the two ligands, L and L′ (in **1** and **3**, L = L′ = PMe_3), must move away from the Cp′ ring in order to accommodate the second hydride ligand. This is clearly demonstrated by considering the angle between the C_5 plane and the ML_2 plane. For the d^6 $Cp'L_2MH$ complexes this angle has a mean value of 67.6(13)° but has a mean value of 87.6(4)° for the d^4 $Cp'L_2MH_2$ complexes. The larger esd for the former reflects the larger distribution of observed angles. The geometries of d^6 $Cp'L_2M(\eta^2\text{-}H_2)$ complexes (mean value 56.1(8)°) can also be distinguished from those of the mono- and dihydride complexes on the basis of this interplanar angle. The corresponding interplanar angles for complexes **1** (67.1°) and **3** (87.3°) lie close to the means for the mono- and dihydride complexes, respectively (Figure 3). This observation confirms the formulation of **3** as a dihydride complex with a four-legged piano stool geometry, even in the absence of locating the hydride ligands crystallographically.

There is little evidence that in general the position of the first hydride ligand changes substantially *relative to the cyclopentadienyl ring* upon protonation to yield the dihydride species. However, repositioning of the L and L′ ligands is quite evident from examination of the angle between the M−H vector(s) and the normal to the ML_2 plane. While the mean value of this angle is 7.9(12)° for the d^6 $Cp'L_2MH$ complexes, the ML_2 plane moves toward the M−H vector by ca. 20° upon protonation to yield the corresponding d^4 $Cp'L_2MH_2$ complexes with a mean angle of 30.0(20)°. The change in this angle is less dramatic when protonation yields the dihydrogen complexes d^6 $Cp'L_2M(\eta^2\text{-}H_2)$ (mean angle 15.5(18)°). Protonation of **1** to yield **3** also results in a reorientation of the methyl groups on phosphorus by a rotation of ca. 40−50° about the Ru−P bonds (Figure 3, Table 4).

Another identifiable structural trend is the increase in the L−M−L′ angle in the course of the protonation reaction. Such angles for d^6 $Cp'L_2MH$ complexes are in the range 84−101° (mean 93.0(19)°), with the exception of a few complexes for which the angle is strongly constrained, as in the dppm ligand. The corresponding angle is enlarged to 101−111° (mean 107.2(10)°) in the d^4 $Cp'L_2MH_2$ complexes, presumably to accommodate the *trans* hydride ligands.

Some complexes listed in Table 5 have geometries that deviate somewhat from the general trends described here. In some cases there appear to be chemical reasons for these deviations; in others these are probably ascribable to erroneous structures. Most notable are the structures of Cp(CO)(PPhFc)FeH (PPhFc = PhP-$\{Fe[(\eta^5\text{-}C_5H_4)_2]\}$)[31] and $[Cp^*(dppe)FeD]PF_6{\cdot}CH_2Cl_2$ (dppe = $Ph_2P(CH_2)_2PPh_2$).[38] In the former, the direction of

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Table 5. Geometries of d^6 Cp′L$_2$MH, d^6 Cp′L$_2$M(η^2-H$_2$), and d^4 Cp′L$_2$MH$_2$ Complexes (deg)[a]

compd	Cp′−ML$_2$[b]	L−M−L′	X−M−H[c]	MH−ML$_2$[d]	XMH−ML$_2$[c,e]	CSD REFCODE[f]	ref
			d^6 Cp′L$_2$MH				
$Cp^*(PPh_3)(OPr^i)IrH$	59.1	84.0	124.8	4.2	87.0	KIVPIO	26
$Cp^*(PMe_3)(SBu^t)IrH$	60.5	87.4	129.5	10.7	84.0	KELDIO	27
$Cp^*(PMe_3)(CH{=}CH_2)IrH$	61.3	85.8	127.5	8.0	88.5	DAMLOS10	28
$Cp(PPh_3)_2RuH$	65.5	100.7	124.8	16.4	76.5	PEYDUS	29
$Cp^*(PMe_3)(C_6H_{11})IrH$[g]	66.8	89.2	122.8	9.0	85.2	DOPWAG	30
	67.1	88.6	118.6	5.2	86.1		
$Cp(PMe_3)_2RuH$	67.1	96.0	118.0	4.9	88.8		this work
Cp(CO)(PPhFc)FeH	67.8	91.3	99.4	−13.3	89.9	FOHGEO	31
Cp(dppp)RuH	67.9	91.8	120.0	7.9	87.4	VUBXUL	32, 33
Cp(dppFc)RuH[g]	68.9	99.1				GIGCAA	34
	71.7	95.5					
$Cp(PPh_3)_2FeH$	69.4	100.9	116.5	6.9	85.7	JUNYUM	35
$Cp^*(PPh_3)LRhH$[h]	69.8	94.5				WEHCAN	36
Cp(dppm)FeH	72.3	75.2	121.1	12.8	89.4	JUNYOG	35
$[Cp^*(PPh_3)_2RhH]PF_6$	79.2	99.9				MCTPRH	37
$[Cp^*(dppe)FeD]PF_6{\cdot}CH_2Cl_2$[i]	89.6	88.4	120.4	28.4	83.2	KUCFET	38
mean dimensions[j]	67.6(13)[k]	93.0(19)[l]	122.4(15)[k,m]	7.9(12)[k,m]	85.9(12)[k,m]		
			d^6 Cp′L$_2$M(η^2-H$_2$)				
$[Cp^{‡}(dppm)Ru(\eta^2\text{-}H_2)]PF_6$[g]	55.6	71.5	120.6, 128.9	9.2, 15.7	74.5, 81.9		33
	55.1	71.5	119.4, 124.2	14.3, 31.9	60.0, 75.7		
$[Cp^*(dppm)Ru(\eta^2\text{-}H_2)]BF_4$[n]	57.7	71.3	118.6, 119.4	18.8, 19.3	71.5, 71.8		39
mean dimensions[j]	56.1(8)		121.9(16)	15.5(18)[o]	72.6(29)		
			d^4 Cp′L$_2$MH$_2$				
$[Cp^{‡}(dppe)RuH_2]PF_6$	85.7	87.0	116.6, 117.2	22.6, 31.4	87.3, 88.4		33
$Cp^*(PPhMe_2)_2ReH_2$	86.5	101.6	114.0, 115.1	23.8, 25.8	85.7, 88.0	SAWNUZ	40
$Cp^*(SiEt_3)_2RhH_2$[n]	86.7	107.9	131.8, 133.4	37.7, 47.5	90.0, 90.0	CONFEQ01	41
$Cp^*(SiEt_3)_2IrH_2$[n]	87.2	109.5	129.8, 130.7	35.8, 44.7	90.0, 90.0	CIWJAT10	42
$[Cp(PMe_3)_2RuH_2]BF_4$	87.3	110.7					this work
$[Cp(PPh_3)_2OsH_2]CF_3SO_3{\cdot}CH_2Cl_2$	87.5	105.7	118.1, 119.7	27.3, 31.7	82.7, 85.6	PESGEZ	43
$[Cp^*(dippe)FeH_2]BPh_4$	87.8	90.6	114.0, 115.1	21.1, 28.2	87.6, 88.2		44
$[Cp^{‡}(PPh_3)_2RuH_2]PF_6{\cdot}CH_2Cl_2$	88.9	105.6	111.8, 116.1	22.7, 25.4	85.9, 90.0		33
$Cp(PPh_3)_2ReH_2{\cdot}C_6H_6$	89.2	108.6	107.4, 114.6	16.0, 26.2	88.3, 87.5	FIZLUV	45
$Cp^*(SiHClMes)(PPr^i_3)RuH_2$	89.6	107.7	121.9, 125.3	33.8, 38.6	73.5, 77.8	YAGKAS	46
mean dimensions[j]	87.6(4)	107.2(10)[l]	119.6(18)	30.0(20)	87.8(6)[p]		

[a] Cp′ = Cp (C_5H_5), Cp* (C_5Me_5), Cp‡ (C_5H_4Me); L = CO, PR_3, PAr_3, PR_2^-, R^-, OR^-, SR^-, SiR_3^-; L_2 = diphosphines. PPhFc = $PhP\{Fe[(\eta^5\text{-}C_5H_4)_2]\}$, dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2P(CH_2)_2PPh_2$, dippe = $Pr^i_2P(CH_2)_2PPr^i_2$, dppFc = $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$. [b] Angle between mean planes of the C_5 ring and the ML_2 fragment. [c] Centroid(Cp′)−M−H angle. X refers to the centroid. [d] Angle between the M−H vector and the normal to the ML_2 plane. A negative value indicates that the M−H vector points toward the Cp′ ring when viewed from the ML_2 plane. [e] Angle between the XMH plane and the ML_2 plane. [f] Reference code for the Cambridge Structural Database (see: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146). [g] Two crystallograpically independent molecules. [h] L = $(PPC(Bu^t)PC(Bu^t))$. [i] Reported as d^5 Fe(III), may actually be d^4 $[Cp^*(dppe)FeXD]^+$ (see text). [j] Sample esd's, reported in the last significant digit, are calculated according to $[\sum_i(d_i - \langle d\rangle)^2/n(n-1)]^{1/2}$. [k] The value for $[Cp^*(dppe)FeD]PF_6{\cdot}CH_2Cl_2$ was excluded as this is believed to be incorrect (see text). [l] Compounds for which L_2 = diphosphine are excluded from the calculation of the mean. [m] The value for Cp(CO)(PPhFc)FeH was excluded as this is believed to be incorrect (see text). [n] Neutron diffraction studies. [o] The angle 31.9° was excluded on the basis that it is a statistical outlier. [p] The values for $Cp^*(SiHClMes)(PPr^i_3)RuH_2$ were excluded on the basis that these are statistical outliers.

the M−H bond deviates by ca. 20° *toward* the Cp ring from that observed in all the other d^6 Cp′L$_2$MH complexes, even though the relative positions of the other ligands fit the general trend very well. The authors report that the hydride was included in a calculated position. It appears that this calculated position is in error. Perhaps more interesting is the structure of the 17-electron d^5 $[Cp^*(dppe)FeD]^+$ cation. The unusual feature of the structure is that the FeP_2 plane is orthogonal (89.6°) to the plane of the C_5 ring, *i.e.* the geometry strongly resembles that of the d^4 Cp′L$_2$MH$_2$ complexes rather than the d^6 Cp′L$_2$MH complexes, even though only one hydride ligand is reported as present. The structure is also inconsistent with the structure of the related d^5 $[Cp^*(dppe)Fe(CH_2OMe)]^+$ cation, in which the Cp*−FeP$_2$ interplanar angle is only 62.1°.[47] This suggests that the structure reported as $[Cp^*(dppe)FeD]PF_6{\cdot}CH_2Cl_2$ may in fact be $[Cp^*(dppe)Fe(D)(X)]PF_6{\cdot}CH_2Cl_2$, where X = H or D, and was not observed crystallographically.

In all but two of the mono- and dihydride structures listed in Table 5, the M−H vector lies in a plane that is essentially perpendicular to both the C_5 ring plane and the ML_2 plane. In addition, little variation arises in the direction of the M−H vector within that plane, as is indicated by the relatively small esds calculated for the means of the X−M−H angle. This is consistent with the fact that, in general, X-ray diffraction has been successful in indicating the *direction* of the M−H bond, even though the M−H bond lengths may be subject to considerable inaccuracy. For the two structures in which the M−H vector lies out of the aforementioned plane, $Cp(PPh_3)_2RuH$[29] and $Cp^*(PPr^i_3)RuH_2(SiHClMes)$,[46] it appears reasonable to suggest that the steric requirements of the ligands, L and L′, give rise to the deviation of the hydride position from that in related structures.

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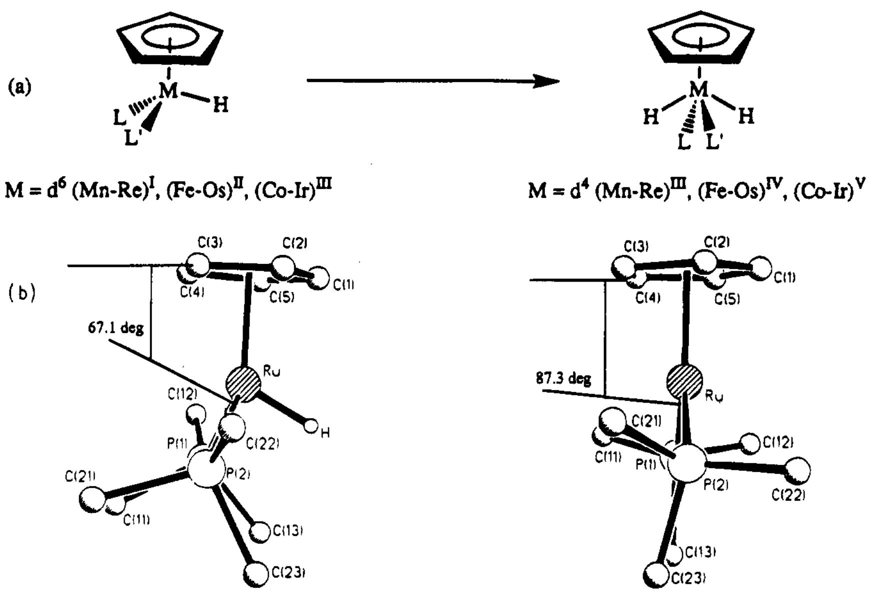

Figure 3. (a) Schematic representation of the change in geometry that occurs at the metal center during the protonation of a d^6 Cp'L_2MH complex. (b) Corresponding change in geometry that occurs in the protonation of **1** to give **3**. The Cp'–ML_2 interplanar angle is indicated; the corresponding mean angle in related dihydrogen complexes [Cp'(dppm)Ru(η^2-H_2)]$^+$ is 56.1(8)°.

Conclusions

The protonation of the electron-rich hydride Cp(PMe_3)$_2$RuH (**1**) cleanly generates the cationic dihydride [Cp(PMe_3)$_2$RuH_2]$^+$ in high yields. The classical dihydride configuration of [Cp(PMe_3)$_2$RuH_2]$^+$ was confirmed spectroscopically and crystallographically. A quantitative relationship between the pK_a of classical dihydrides [Cp'(PMe_xPh_{3-x})$_2$RuH_2]$^+$ (Cp' = C_5H_5, C_5Me_5; x = 0–3) and the ancillary ligands (Cp' and PMe_xPh_{3-x}) on ruthenium has been investigated. The structural changes that occur upon converting a "three-legged piano stool" d^6 Cp'L_2MH to either a "four-legged piano stool" d^4 Cp'L_2MH_2 complex or a d^6 Cp'L_2M(η^2-H_2) complex have been investigated. Several geometric trends have been established for these complexes. This study also confirms that X-ray diffraction is often useful for indicating the direction of the M–H bond, even though the M–H bond lengths may be subject to considerable systematic error.

Experimental Section

General Procedures. All manipulations of oxygen- or water-sensitive compounds were carried out either under an atmosphere of argon by using Schlenk or vacuum-line techniques or under a helium/argon atmosphere in a Vacuum Atmospheres drybox.[48] ^{1}H NMR (400 and 250 MHz) spectra were recorded on a Varian VXR 400S and a Bruker AC-250 spectrometer, respectively. The PMe_3 resonances in these compounds do not appear as a simple first-order pattern in the ^{1}H NMR spectra. The PMe_3 resonances appear as a $A_9XX'A'_9$ pattern; the appearance of which is a "filled-in-doublet" with the separation of the outer lines being equal to $^2J_{PH}$ + $^4J_{PH}$.[49,50] The ^{1}H chemical shifts were referenced to the residual proton peak of the solvent: C_6D_5H, δ 7.15, and $CDHCl_2$, δ 5.32. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer or a Perkin-Elmer 1600 Series FT-IR spectrometer. Elemental analyses were carried out by Oneida Research Services or Galbraith Laboratories.

Materials. Cp(PMe_3)$_2$RuCl was prepared by a modification of previously reported procedures.[20,21] Severe face rashes have been reported to result from exposure to Cp(PMe_3)$_2$RuCl, so adequate precautions should be taken.[51] [H(Et_2O)$_2$][B(3,5-(CF_3)$_2C_6H_3$)$_4$] was prepared according to a literature procedure.[52] Anhydrous diethyl ether was stored over [Cp_2TiCl]$_2ZnCl_2$[53] and vacuum transferred immediately prior to use. Dichloromethane was distilled from and stored over CaH_2 and vacuum transferred immediately prior to use. Methanol and methanol-d_4 were dried over Mg and vacuum transferred immediately prior to use. Benzene-d_6 was dried over NaK and stored over [Cp_2TiCl]$_2ZnCl_2$. Dichloromethane-d_2 was dried over P_2O_5 and stored over CaH_2. Acetonitrile-d_3 was dried over CaH_2, stored over Cp_2Zr(Me)Cl,[54] and vacuum transferred prior to use. Anhydrous HCl(g) was prepared by slowly adding H_2SO_4(l) to NaCl(s) and stored over anhydrous $CaSO_4$(s) prior to use. KOMe was prepared by reacting solid K with excess MeOH in Et_2O, collecting the solid by filtration, and drying the white solid under vacuum. $KOCD_3$ was prepared *in situ* by reacting solid K with excess CD_3OD. PMe_3 (Strem), $LiAlH_4$ (1 M in Et_2O; Aldrich), $LiAlD_4$ (Aldrich), EtOD (Aldrich), $HBF_4 \cdot Et_2O$ (85%, Aldrich), D_2O (Cambridge Isotope Laboratories), and Proton Sponge (Aldrich) were used as received.

Cp(PMe_3)$_2$RuH (1). Method A. From Cp(PMe_3)$_2$RuCl and KOMe. This method involves a modification of the literature procedure.[17] MeOH (25 mL) was added by vacuum transfer to a flask charged with Cp(PMe_3)$_2$RuCl (840 mg, 2.38 mmol) and KOMe (675 mg, 9.63 mmol). The reaction mixture was heated to reflux 2–3 h, after which time the reaction mixture was evaporated to dryness under vacuum. The reaction residue was extracted with hexanes until the extracts were colorless. The combined hexane extracts were filtered through Celite and evaporated to dryness under vacuum. The yellow residue was sublimed at 60 °C (<0.03 mmHg) to give **1** as a bright yellow solid (675 mg, 88% yield). Typical yields were 85–95%.

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Method B. From $Cp(PMe_3)_2RuCl$ and $LiAlH_4$. Et_2O (30 mL) was added by vacuum transfer to a Schlenk flask charged with $Cp(PMe_3)_2RuCl$ (1.531 g, 4.33 mmol) and cooled to −78 °C. $LiAlH_4$ (6.5 mL, 1.0 M in Et_2O) was added dropwise by syringe under argon. The orange reaction mixture was allowed to warm to room temperature, during which time it became a yellow solution with a white solid. After 2 h, the yellow slurry was cooled in an ice-water bath, and EtOH (5 mL, 95%, degassed) was added slowly to decompose unreacted $LiAlH_4$. Reaction volatiles were removed under vacuum. The yellowish residue was extracted with hexanes until the extracts were colorless. The hexane extracts were filtered through Celite and evaporated to dryness under vacuum. The yellow residue was sublimed at 60 °C (<0.03 mmHg) to give **1** as a bright yellow solid (1.245 g, 90% yield). Typical yields were 80–90%. ^1H NMR (400 MHz, CD_2Cl_2): δ 4.54 (s, 5H, Cp), 1.37 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 8.0$ Hz, 18H, PMe_3), −13.99 (t, $^2J_{PH} = 36.8$ Hz, 1H, RuH). IR (CH_2Cl_2): ν(Ru−H) 1892 (br) cm^{-1}. IR (KBr): ν(Ru−H) 1906 (br) cm^{-1}. Anal. Calcd for $C_{11}H_{24}P_2Ru$: C, 41.37; H, 7.58. Found: C, 41.57; H, 7.15. Crystals of **1** suitable for X-ray diffraction analysis were grown by slow sublimation at 50 °C under vacuum in a sealed tube.

$Cp(PMe_3)_2RuD$ (1-d_1). Method A. The reaction of $Cp(PMe_3)_2RuCl$ (202 mg, 0.57 mmol) and $KOCD_3$ (190 mg, 2.6 mmol) in refluxing CD_3OD (5 mL), as described in Method A for **1**, gave **1**-d_1 as a yellow sublimable solid (160 mg, 87% yield, >90% D by ^1H NMR).

Method B. The reaction of $Cp(PMe_3)_2RuCl$ (200 mg, 0.57 mmol) and $LiAlD_4$ (35 mg, 0.83 mmol) in Et_2O (20 mL) followed by an EtOD (2 mL, degassed) quench, as described in Method B for **1**, gave **1**-d_1 as a yellow sublimable solid (148 mg, 81% yield, 72% D by ^1H NMR). ^1H NMR (250 MHz, CD_2Cl_2): δ 4.55 (s, 5H, Cp), 1.37 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 8.4$ Hz, 18H, PMe_3). IR (CH_2Cl_2): ν(Ru−D) 1365 (br) cm^{-1}.

$[Cp(PMe_3)_2RuH_2]Cl$ (2). An excess of anhydrous HCl(g) was added to an ethereal solution (10 mL) of $Cp(PMe_3)_2RuH$ (84 mg, 0.26 mmol) at −78 °C. A white precipitate formed immediately. After 1 h, the reaction mixture was evaporated to dryness and the residue washed with hexanes. Filtration of the solid followed by vacuum drying gave **2** (91 mg, 97% yield) as a white solid. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.38 (s, 5H, Cp), 1.69 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 10.9$ Hz, 18H, PMe_3), −9.87 (t, $^2J_{PH} = 29.1$ Hz, 2H, RuH). IR (CH_2Cl_2): ν(Ru−H) 1989 (br) cm^{-1}. Anal. Calcd for $C_{11}H_{25}ClP_2Ru$: C, 37.13; H, 7.08. Found: C, 36.11; H, 7.31. We were not successful at getting a good elemental analysis for this complex, even though the spectra indicated complete purity of the product.

$[Cp(PMe_3)_2RuH_2]BF_4$ (3). Et_2O (15 mL) was added by vacuum transfer to a flask charged with **1** (192 mg, 0.60 mmol). $HBF_4{\cdot}Et_2O$ (100 μL, 0.58 mmol) was added to this solution dropwise using a microliter syringe. The resulting precipitate was isolated by filtration, washed with Et_2O, and dried under vacuum to give a light purple solid (232 mg, 99% yield). ^1H NMR (400 MHz, CD_2Cl_2): δ 5.31 (s, 5H, Cp), 1.64 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 10.9$ Hz, 18H, PMe_3), −9.90 (t, $^2J_{PH} = 29.3$ Hz, 2H, RuH). IR (CH_2Cl_2): ν(Ru−H) 1989 (br) cm^{-1}. Anal. Calcd for $C_{11}H_{25}BF_4P_2Ru$: C, 32.45; H, 6.19. Found: C, 32.25; H, 6.52. Crystals of **3** suitable for X-ray diffraction analysis were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution at room temperature.

$[Cp(PMe_3)_2RuHD]BF_4$ (3-d_1). $[Cp(PMe_3)_2RuHD]BF_4$ was prepared from **1**-d_1 (49 mg, 0.15 mmol) and $HBF_4{\cdot}Et_2O$ (26 μL, 0.15 mmol) in Et_2O as described for **3**. This gave a light purple solid (57 mg, 92% yield, 45% D by ^1H NMR). ^1H NMR (250 MHz, CD_2Cl_2): δ 5.31 (s, 5H, Cp), 1.65 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 10.9$ Hz, 18H, PMe_3), −9.88 (t, $^2J_{PH} = 29.2$ Hz, 1H, RuH). IR (CH_2Cl_2): ν(Ru−H) 1987 (br w) cm^{-1}, ν(Ru−D) 1422 (br s) cm^{-1}.

$[Cp(PMe_3)_2RuD_2]BF_4$ (3-d_2). DBF_4 (100 μL, prepared by mixing $HBF_4{\cdot}Et_2O$ and D_2O in a 1:3 ratio by volume[15]) was added dropwise to a solution of **1**-d_1 (56 mg, 0.17 mmol) in Et_2O. The reaction mixture was evaporated to dryness. The reaction residue was dissolved in CH_2Cl_2, and then Et_2O was added dropwise to initiate precipitation. The resulting solid was filtered out, washed with Et_2O, and dried under vacuum. This gave **3**-d_2 as a light purple solid (54 mg, 77% yield, >95% D by ^1H NMR). ^1H NMR (250 MHz, CD_2Cl_2): δ 5.31 (s, 5H, Cp), 1.64 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 10.9$ Hz, 18H, PMe_3). IR (CH_2Cl_2): ν(Ru−D) 1422 (br s) cm^{-1}.

$[Cp(PMe_3)_2RuH_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (4). Methylene chloride (15 mL) was added by vacuum transfer to a flask charged with **1** (75 mg, 0.23 mmol) and $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (238 mg, 0.24 mmol) at −78 °C. The reaction solution was allowed to warm to room temperature. After 30 min, the solution was concentrated, and hexane was added to initiate precipitation. The precipitate was isolated, washed with hexane, and dried under vacuum to give a white solid (246 mg, 90% yield). ^1H NMR (250 MHz, CD_2Cl_2): δ 7.72 (br, 8H, $(CF_3)_2C_6H_3$), 7.57 (br, 4H, $(CF_3)_2C_6H_3$), 5.24 (s, 5H, Cp), 1.60 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 10.9$ Hz, 18H, PMe_3), −9.93 (t, $^2J_{PH} = 29.4$ Hz, 2H, RuH). IR (CH_2Cl_2): ν(Ru−H) 1992 (br) cm^{-1}. Anal. Calcd for $C_{43}H_{37}BF_{24}P_2Ru$: C, 43.64; H, 3.15. Found: C, 43.58; H, 3.04.

T_1 Measurements on $[Cp(PMe_3)_2RuH_2]BF_4$ (3). T_1 values for the hydride protons of **3** (34 mM in CD_2Cl_2, 400 MHz) were determined by using a 180−τ−90 pulse sequence. The T_1 value of 9.41 s at 293 K for the hydride resonance decreases to 6.33 s at 263 K and 1.96 s at 208 K.

pK_a of $[Cp(PMe_3)_2RuH_2]^+$. For the equilibrium described in eq 4, where $K_{eq} = [Cp(PMe_3)_2RuH][BH^+]/[Cp(PMe_3)_2RuH_2{}^+][B]$, the acidity of $[Cp(PMe_3)_2RuH_2]^+$ (pK_a) can be expressed by the equation

$$Cp(PMe_3)_2RuH_2{}^+ + B \rightleftharpoons Cp(PMe_3)_2RuH + BH^+ \quad (4)$$

$$pK_a = pK_{eq} + pK_{BH^+}$$

For BH^+, where B = Proton Sponge (1,8-bis(dimethylamino)naphthalene), a $pK_{BH^+} = 12.34$ in H_2O was determined by Alder *et al.*[55] Kristjánsdóttir and Norton observed the following relationship between acidities in aqueous and acetonitrile media: $pK_a(CH_3CN) = pK_a(H_2O) + 7.5$.[56] Dissolving equimolar quantities of **3** and Proton Sponge ($pK_a(CH_3CN) = 19.8$) in CD_3CN gave a $pK_{eq} = 1.6$, as determined by ^1H NMR spectroscopy using $Si(SiMe_3)_4$ as an internal standard, and thus a $pK_a(CH_3CN) = 21.4$ for $[Cp(PMe_3)_2RuH_2]^+$. This corresponds to a $pK_a(CH_2Cl_2) = 13.9$ for $[Cp(PMe_3)_2RuH_2]^+$ assuming that $pK_a(H_2O)$ approximately equals $pK_a(CH_2Cl_2)$.[15]

Converting Dihydrides 2–4 to Hydride 1. The dihydrides **2**-**4** may be deprotonated by a variety of strong bases, like $LiNR_2$ (R = Me, Pr^i, $SiMe_3$), but KOMe in MeOH worked the best. For example, MeOH (20 mL) was added by vacuum transfer to a flask charged with **2** (600 mg, 1.69 mmol) and KOMe (500 mg, 7.13 mmol) and equipped with a reflux condenser. The reaction mixture was heated to reflux for 1 h, after which time the reaction was evaporated to dryness under vacuum. The reaction residue was worked-up as described above for **1** in Method A. This gave **1** (496 mg, 92% yield) as a bright yellow solid.

X-ray Crystal Structure Determinations of $Cp(PMe_3)_2RuH$ (1) and $[Cp(PMe_3)_2RuH_2]BF_4$ (3). Both crystal structures were solved by direct methods and refined to convergence by full-matrix least-squares using the SHELXTL suite of programs.[57] Data for **3** were corrected for absorption

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(55) Alder, R. W.; Bowman, P. S.; Steele, W. R. S.; Winterman, D. R. *Chem. Commun.* **1968**, 723–724.

(56) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1992; pp 309–359.

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Table 6. Data Collection, Structure Solution, and Refinement Parameters for $Cp(PMe_3)_2RuH$ (1) and $[Cp(PMe_3)_2RuH_2]BF_4$ (3)

	1	**3**
cryst system	monoclinic	monoclinic
space group, *Z*	$P2_1/n$, $Z = 4$	Cc, $Z = 4$
a (Å)	9.429(4)	14.310(3)
b (Å)	14.719(7)	10.105(3)
c (Å)	11.002(5)	11.584(4)
β (deg)	106.62(3)	99.73(2)
V ($Å^3$)	1463.2(11)	1651.1(9)
density (g cm^{-3})	1.450	1.638
temp (K)	220(5)	123(5)
X-ray wavelength (Å)	0.710 73	0.710 73
μ(Mo Kα) (mm^{-1})	1.258	1.166
2θ range (deg)	4.0–45.0	4.0–70.0
reflcns collcd	1935	3948
indepdt reflcns (R_{int})	1712 (0.072)	3769 (0.062)
obsd ($F > 3.0\sigma(F)$)	1478	3563
L. S. params	130	178
$R(F)$, $R_w(F)$	0.046, 0.058	0.034, 0.040
$S(F)$	1.26	1.04

by semi-empirical methods.[57] All non-hydrogen atoms were refined anisotropically; methyl and cyclopentadienyl hydrogens were included in calculated positions and refined using a riding model with fixed isotropic displacement parameters. The hydride ligand for **1** was located from the difference map and refined with no positional constraints but with a fixed isotropic displacement parameter. Experimental data pertinent to both structure determinations are given in Table 6.

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Supporting Information Available: Tables of X-ray crystallographic data, hydrogen positional and displacement parameters, anisotropic displacement parameters, and interatomic distances and angles (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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