Synthesis, Characterization, and Acidity Properties of $[MCl(H_2)(L)(PMP)]BF_4$ (M = Ru, L = PPh_3, CO; M = Os, L = PPh_3; PMP = 2,6-$(Ph_2PCH_2)_2C_5H_3N$)

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Treatment of $RuCl_2(PPh_3)_3$ with PMP (PMP = 2,6-$(Ph_2PCH_2)_2C_5H_3N$) in acetone produced $RuCl_2(PPh_3)$(PMP), which has been characterized by X-ray diffraction. Treatment of $RuCl_2(PPh_3)$(PMP) with $NaBH_4$ in methanol gave $RuHCl(PPh_3)$(PMP), acidification of which with HBF_4·Et_2O produced the molecular dihydrogen complex $[RuCl(H_2)(PPh_3)(PMP)]BF_4$. Treatment of $RuHCl(CO)(PPh_3)_3$ with PMP in benzene produced RuHCl(CO)(PMP), which reacted with HBF_4·Et_2O to give the molecular dihydrogen complex $[RuCl(H_2)(CO)(PMP)]BF_4$. The osmium molecular dihydrogen complex $[OsCl(H_2)(PPh_3)(PMP)]BF_4$ was prepared by protonation of $OsHCl(PPh_3)$(PMP) with HBF_4·Et_2O. Relative acidities of the dihydrogen complexes were investigated by NMR spectroscopy of equilibrium reactions conducted in CD_2Cl_2. $[RuCl(H_2)(CO)(PMP)]BF_4$ is more acidic than $[RuCl(H_2)(PPh_3)(PMP)]BF_4$, which is in turn more acidic than its osmium analog $[OsCl(H_2)(PPh_3)(PMP)]BF_4$.

Introduction

The acid−base properties of transition metal hydride complexes have attracted considerable attention.[1] It is now well-established that the acidity of hydride complexes is strongly influenced by the metal as well as the auxiliary ligands. With a few exceptions,[1c,2] 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.[3−6]

Dihydrogen complexes are an interesting class of hydride complexes[7] for which a wide range of pK_a values have been reported.[8−11] However, a generalization in the trend in the acidity of isostructural dihydrogen complexes is complicated by the fact that H−H interactions could have a significant effect on the acidity. The presence of a strong H−H interaction may make dihydrogen complexes less acidic than may be suggested by the general trend in the acidity of classic hydride

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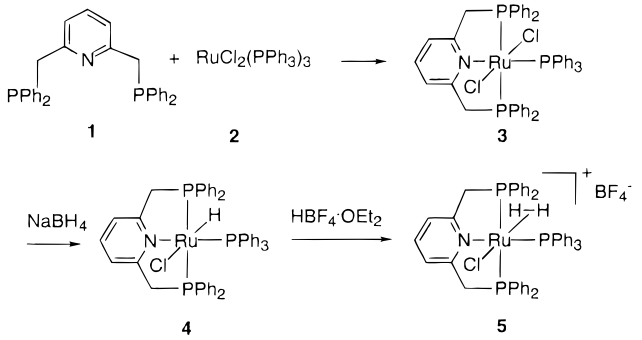
Scheme 1



complexes. A good example of the effect of H−H interactions on the acidity is provided by the observation that the more electron-rich trihydride complex $[RuH_3(dppf)_2]^+$ (dppf = $(Ph_2PC_5H_4)_2Fe$)[8c] is more acidic than the less electron-rich dihydrogen complex $[RuH(H_2)(dppe)_2]^+$.[8d] It has been noted that the relative acid strengths of a series of isostructural dihydrogen complexes may depart from the trend observed for classic hydride complexes. For example, $[CpRu(H_2)(dppm)]^+$ [8h] is more acidic than $[CpRu(H_2)(dmpe)]^+$,[9a] as expected from the relative electron-richness of the metal centers; the ruthenium dihydrogen complex $[RuCl(H_2)(dppe)_2]^+$ [8a,c] is more acidic than the corresponding osmium complex, as expected from the general trend in M−H bond strength and from the pK_a values of $MH_2(CO)_4$ (M = Fe, Ru, Os).[3d] In contrast, the effect of H−H interaction in $[MH(H_2)(dppe)_2]^+$ on the acidity is so important that the pK_a values of the dihydrogen complexes $[MH(H_2)(dppe)_2]^+$ are now in the order of Fe < Os < Ru,[8d] due to the presence of strong H−H bonding in the ruthenium complex. Due to the limited pK_a data available for dihydrogen complexes, a distinctive trend in the acidity of isostructural dihydrogen complexes is not apparent. In this regard Morris *et al.* have recently proposed that H−H interactions will have a negligible effect on the acidity of dihydrogen complexes when *d*(HH) is longer than 1.0 Å.[8a]

In order to further study the acidity properties of dihydrogen complexes and to delineate trends in relative acidities, we have prepared the molecular dihydrogen complexes $[MCl(H_2)(L)(PMP)]BF_4$ (M = Ru, L = PPh_3, CO; M = Os, L = PPh_3; PMP = 2,6-$(Ph_2PCH_2)_2C_5H_3N$) and have measured their pK_a values. Reported dihydrogen complexes closely related to the $[MCl(H_2)(L)(PMP)]BF_4$ complexes are the bis(diphosphine) complexes $[MCl(H_2)(PP)_2]^+$ (M = Ru, Os; PP = diphosphines).[8a,c,10,12] Our system differs from the bis(diphosphine) system in that it contains a tridentate ligand with one nitrogen and two phosphorus donor atoms and a monodentate ligand L. This system enables us to evaluate how the acidity of dihydrogen complexes changes when L is changed from PPh_3 to CO and when the metal is changed from Ru to Os.

Results and Discussion

Synthesis and Characterization of $[RuCl(H_2)(PPh_3)(PMP)]BF_4$ and Related Complexes. The molecular dihydrogen complex $[RuCl(H_2)(PPh_3)(PMP)]BF_4$ (**5**) was prepared according to the sequence shown in Scheme 1. Treatment of $RuCl_2(PPh_3)_3$ (**2**) with PMP (**1**) in acetone produced $RuCl_2(PPh_3)(PMP)$ (**3**). The related complex $RuCl_2(PPh_3)(EtN(CH_2CH_2PPh_2)_2)$ has been reported.[13] It is of interest to note that reactions of $RuCl_2(PPh_3)_3$ with the related triphosphine ligands such as $PhP(CH_2CH_2PPh_2)_2$ (etp)[14] and $PhP(CH_2CH_2CH_2PCy_2)_2$ (Cyttp)[15] lead to $[Ru_2Cl_3(etp)_2]Cl$ and $RuCl_2$(Cyttp), respectively. These observations may indicate that PMP and $EtN(CH_2CH_2PPh_2)_2$ ligands are sterically less demanding than the triphosphine ligands etp and Cyttp. The structure of complex **3** can be readily assigned based on the ^{31}P and ^1H NMR data. The ^1H NMR spectrum in $CDCl_3$ showed only one virtual triplet at 4.52 ppm for the methylene protons, indicating that the geometry of the PMP ligand is meridional[16] and that the complex has a symmetric structure. Consistent with the structure, the ^{31}P NMR spectrum in $CDCl_3$ showed a doublet at 29.6 ppm (d, J(PP) = 27.7 Hz) for the PPh_2 groups and a triplet at 35.9 ppm for the PPh_3 ligand.

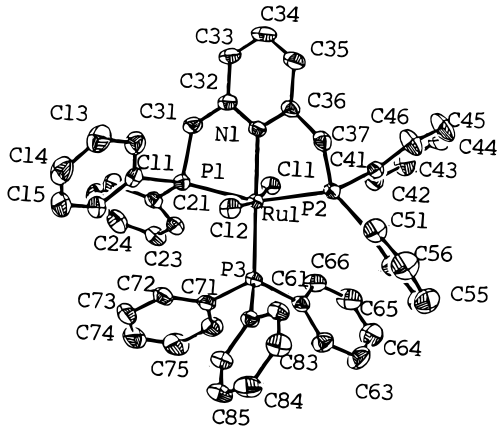


Figure 1. Molecular structure for $RuCl_2(PPh_3)(PMP)\cdot CH_2Cl_2$. Hydrogen atoms and the solvent molecule are omitted for clarity.

The structure of compound **3** has been confirmed by X-ray diffraction (see Figure 1). Selected bond lengths and angles are given in Table 2. The geometry around ruthenium can be described as a distorted octahedron with a meridional PMP ligand, two mutually *trans* Cl atoms, and a PPh_3 ligand *trans* to the nitrogen atom. The distortion from an idealized octahedral geometry can be attributed to the bending of the two PPh_2 groups toward nitrogen (P(1)−Ru−N(1) = 79.6(1)°, P(2)−Ru−N(1) = 78.6(1)°), probably due to the size of the chelating bite angle. Overall the structure is very similar to that of $RuCl_2(PPh_3)(EtN(CH_2CH_2PPh_2)_2)$.[13a] The Ru−$PPh_3$ bond (2.346(1) Å) is slightly shorter than the mutually *trans* Ru−P(1) (2.360(1) Å) and Ru−P(2) (2.369(1) Å) bonds, which may be related to the smaller trans

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Table 1. Crystal Data and Refinement Details for $RuCl_2(PPh_3)(PMP)\cdot CH_2Cl_2$

formula	$C_{50}H_{44}Cl_4NP_3Ru$
fw	994.6
color and habit	pale orange trapezoid
cryst dimens, mm	0.50 × 0.45 × 0.15
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	10.831(2)
b, Å	13.729(2)
c, Å	17.483(2)
α, deg	71.98(2)
β, deg	88.65(2)
γ, deg	67.97(2)
V, Å^3	2279.1(6)
Z	2
d_{calc}, g cm^{-3}	1.449
abs coeff, mm^{-1}	0.720
F(000)	1016
radiation	Mo Kα (λ = 0.071 073 Å)
T, K	213
2*θ* range, deg	3.0−50.0
scan type	2*θ*−*θ*
scan range (*ω*)	0.80° plus Kα-separation
standard reflections	3 measured every 150 reflns
index range	$-1 \le h \le 14$, $-16 \le k \le 17$, $-23 \le l \le 23$
no. of reflns collected	12 664
no. of independent reflns	11 282 (R_{int} = 1.72%)
no. of obsd reflns	9198 ($F > 4.0\sigma(F)$)
abs corr	semi-empirical
system used	Siemens SHELXTL IRIS
no. of params refined	534
hydrogen atoms	riding model, fixed isotropic *U*
final *R* indices (obsd data)	*R* = 3.36%, R_w = 4.11%
R indices (all data)	*R* = 4.44%, R_w = 4.40%
goodness of fit	1.27
data to parameter ratio	17.2:1
largest difference peak	0.45 e Å^{-3}
largest difference hole	−0.51 e Å^{-3}

influence of the pyridine ligand. The Ru−N(1) bond distance (2.161(2) Å) is comparable to those in the pyridine complex $[Ru(C{\equiv}CC_6H_{11})(CO)(py)_2(PPh_3)_2]ClO_4$ (2.16(2), 2.21(2) Å)[17] and shorter than that (2.337(4) Å) in $RuCl_2(PPh_3)(EtN(CH_2CH_2PPh_2)_2)$.[13a] The Ru−Cl bond distances (2.430(1) and 2.411(1) Å) agree well with the reported values for *trans*-dichlororuthenium complexes such as $RuCl_2(PPh_3)(EtN(CH_2CH_2PPh_2)_2)$,[13a] $RuCl_2(CO)(PMePh_2)_3$,[18] and $RuCl_2(PhAs(CH_2PPh_2)_2)_2$.[19]

Compound **3** reacted with $NaBH_4$ in refluxing methanol to give $RuHCl(PPh_3)(PMP)$ (**4**). The ^{1}H NMR spectrum in C_6D_6 showed a hydride signal at −16.55 ppm as an apparent quartet with $J(PH)$ = 22.2 Hz; this indicates that the hydride is *cis* to the three phosphorus atoms, the PMP ligand is meridionally coordinated to ruthenium, and the PPh_3 is *cis* to the two PPh_2 groups. Consistent with this structural assignment, the ^{31}P NMR spectrum in C_6D_6 contained a doublet at 47.2 ppm (d, $J(PP)$ = 27.8 Hz) for the PPh_2 groups and a triplet at 57.9 ppm for the PPh_3 ligand. On the basis of the ^{1}H and ^{31}P NMR data, two possible structures can be proposed for **4**, with the hydride *trans* to the pyridine ring or *trans* to the chloride. The latter structure was confirmed by a NOE experiment in which irradiation of the hydride signal induced enhancement of one of the signals for the methylene protons.

Treatment of complex **4** with $HBF_4\cdot Et_2O$ in dichloromethane produced the molecular dihydrogen complex $[RuCl(H_2)(PPh_3)(PMP)]BF_4$ (**5**), which is stable in both the solid state and in solution under a dihydrogen or argon atmosphere. Although the dihydrogen complex can be pumped briefly without decomposition, upon overnight evacuation it partially loses the dihydrogen ligand to give uncharacterized products. The existence of the η^2-H_2 moiety in **5** was confirmed by variable-temperature T_1 measurements and the observation of a large ^1J(HD) for the corresponding isotopomer.[7] The ^{1}H NMR spectrum of **5** in CD_2Cl_2 showed a broad hydride signal at δ −10.49 ppm. A minimum T_1 value of 21 ms (400 MHz) was obtained for this hydride signal at 236 K. Acidification of $RuHCl(PPh_3)(PMP)$ with DBF_4 gave the η^2-HD isotopomer, $[RuCl(HD)(PPh_3)(PMP)]BF_4$, which showed a 1:1:1 triplet ($^1J(HD)$ = 28.0 Hz) of quartets ($^2J(HP)$ = 8.0 Hz) centered at −10.56 ppm in the ^{1}H NMR spectrum.

The stereochemistry of complex **5** shown in Scheme 1 is supported by the NMR spectroscopic data and its deprotonation reaction with $CpRuH(PPh_3)_2$ at low temperature. The meridional geometry of the PMP ligand in **5** is indicated by the AM_2 pattern for the signals in the ^{31}P NMR spectrum and its ^{1}H NMR spectrum which showed two doublet of triplet signals for the methylene protons. The position of the dihydrogen ligand in complex **5** is inferred from the structure of its precursor **4** and the fact that deprotonation of complex **5** at 200 K with $CpRuH(PPh_3)_2$ gave complex **4** (in which the hydride is *trans* to chloride and *cis* to PPh_3) as the only deprotonation product. The position of the dihydrogen ligand in a dihydrogen complex is expected to be the same as that of the hydride ligand in the kinetic deprotonation product. For example, the kinetic deprotonation product of *trans*-$[RuH(H_2)(dppe)_2]^+$ is *trans*-$RuH_2(dppe)_2$ which isomerizes to the thermodynamically stable mixture of *cis*- and *trans*-$RuH_2(dppe)_2$.[8d] The structure of complex **5** has been confirmed by a NOE experiment. In this experiment, a positive NOE effect was observed for one of the signals of the methylene protons when the dihydrogen signal was irradiated.

The H−H distance in complex **5** can be estimated from the T_1(min) value[20] and J(HD) data.[8a] On the basis of the T_1(min) value of 21 ms (at 400 MHz), d(HH) was estimated to be 1.13 Å for complex **5** with a slow spinning dihydrogen ligand or 0.89 Å for a fast spinning dihydrogen ligand. It should be mentioned that the calculated d(HH) values are the minimum H−H distances, as contributions to T_1(min) from other groups are not corrected for here. A d(HH) value of 0.95 Å can be obtained by use of the relationship $d(HH) = -0.0167J(HD) + 1.42$ and $J(HD)$ = 28.0 Hz.[8a]

Related dihydrogen complexes $[RuCl(H_2)(PP)_2]^+$ (PP = dppe, depe, dcpe, dppp) have been reported.[8c,10,12] It is of interest to note that the J(HD) values for the isotopomers of $[RuCl(HD)(PP)_2]^+$ (16−26 Hz) are smaller than that of $[RuCl(HD)(PPh_3)(PMP)]^+$ (28.0 Hz). The J(HD) data may indicate that $[RuCl(HD)(PPh_3)(PMP)]^+$ is less electron-rich than $[RuCl(HD)(PP)_2]^+$ and that the H−H bond in complex **5** is stronger than those in

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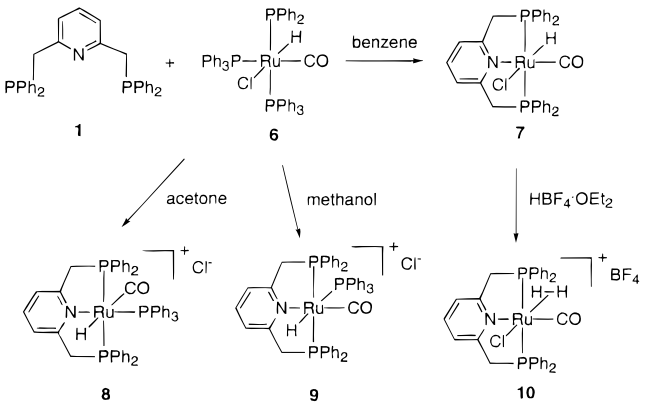
Table 2. Selected Bond Distances (Å) and Angles (deg) for $RuCl_2(PPh_3)(PMP)\cdot CH_2Cl_2$

		Interatomic Distances			
Ru−P(1)	2.360(1)	Ru−P(2)	2.369(1)	Ru−P(3)	2.346(1)
Ru−Cl(1)	2.430(1)	Ru−Cl(2)	2.411(1)	Ru−N(1)	2.161(2)
		Intermolecular Angles			
P(1)−Ru−P(2)	158.1(1)	P(1)−Ru−P(3)	102.4(1)	P(1)−Ru−Cl(1)	82.3(1)
P(1)−Ru−Cl(2)	90.9(1)	P(1)−Ru−N(1)	79.6(1)	P(2)−Ru−P(3)	99.5(1)
P(2)−Ru−Cl(1)	95.1(1)	P(2)−Ru−Cl(2)	89.1(1)	P(2)−Ru−N(1)	78.6(1)
P(3)−Ru−Cl(1)	96.5(1)	P(3)−Ru−Cl(2)	90.8(1)	P(3)−Ru−N(1)	176.7(1)
Cl(1)−Ru−Cl(2)	170.9(1)	Cl(1)−Ru−N(1)	86.4(1)	Cl(2)−Ru−N(1)	86.5(1)

Scheme 2



$[RuCl(H_2)(PP)_2]^+$. The difference may be attributed to the presence of the pyridine ligand which is a poorer σ-electron-pair donor. In this regard, it is noted that the J(HD) for Tp*RuH(HD)(PCy_3) (21.0 Hz) is also reported to be smaller than that of Tp*RuH(HD)(py) (26.7 Hz) (Tp* = hydrotris(3,5-dimethylpyrazolyl)-borate).[21] Related to this is the report that the CO stretching frequencies of $[CpFe(CO)_2(py)]PF_6$ are higher than those of $[CpFe(CO)_2(PPh_3)]PF_6$ and $[Cp(CO)_2Fe(\mu\text{-dppe})Fe(CO)_2Cp](PF_6)_2$.[22]

Synthesis and Characterization of $[RuCl(H_2)(CO)(PMP)]BF_4$. The molecular dihydrogen complex $[RuCl(H_2)(CO)(PMP)]BF_4$ (**10**) was prepared by protonation of RuHCl(CO)(PMP) (**7**) with $HBF_4\cdot Et_2O$ in dichloromethane. Complex **7** was in turn prepared by the substitution reaction of $RuHCl(CO)(PPh_3)_3$ with PMP in benzene (see Scheme 2). The dihydrogen complex **10** is stable at room temperature in dichloromethane solution under a hydrogen atmosphere. However, attempts to isolate pure samples of **10** using diethyl ether as the precipitating solvent failed; the predominant phosphorus-containing species of the solid eventually isolated was in fact the monohydride complex **7**. Thus, the dihydrogen complex **10** is deprotonated by excess diethyl ether. There are several reported examples of dihydrogen complexes or intermediates that can be deprotonated by diethyl ether, for example, $[Os(H_2)(CH_3CN)(dppe)_2]^{2+}$,[8b] $[Cp^*Ru(H_2)(CO)_2]^+$,[9b] $[Cp^*Re(H_2)(CO)(NO)]^+$,[9b] $[CpRu(H_2)(dfepe)]^+$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$),[23] and $[Os(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$.[11j]

The monohydride complex **7** was characterized by ^1H and ^{31}P NMR spectroscopy and elemental analysis. The ^{31}P NMR spectrum in CD_2Cl_2 showed a singlet at 50.4 ppm for the PPh_2 groups. The ^1H NMR spectrum in CD_2Cl_2 showed a triplet hydride signal at −13.65 ppm with J(PH) = 19.9 Hz and two doublets of triplets for the methylene protons at 4.13 and 4.64 ppm. The NMR data are consistent with a structure in which the PMP ligand is meridionally coordinated to ruthenium. The chemical shift (−13.65 ppm) of the hydride signal indicates that the hydride is *trans* to Cl or pyridine rather than to CO. In comparison, the signal for the hydride *trans* to CO is at −5.15 ppm for $RuHCl(CO)_2(P(i\text{-}Pr)_3)_2$[24] and at −3.68 to −7.25 ppm for $[RuH(CO)(PP)_2]^+$ (PP = dppm, dppe, dppe);[25] the signal for the hydride *trans* to pyridine is at −11.3 ppm for $[RuH(CO)(bpy)_2]^+$ [26] and at −12.10 ppm for $[RuH(CO)(py)_2(PPh_3)_2]ClO_4$;[27] the signal for the hydride *trans* to Cl is at −13.5 to −15.4 ppm for $RuHCl(CO)(PPh_3)(PP)$ (PP = dppm, dppp).[25] In the present case, the *trans* disposition of the hydride and the chloride was established by a NOE experiment in which a positive enhancement was observed for one of the signals of the methylene protons upon irradiation of the hydride signal.

Due to its low stability, complex **10** was primarily characterized by ^1H and ^{31}P NMR spectroscopy. Consistent with the meridional geometry of the PMP ligand, the ^{31}P NMR spectrum displayed a singlet at 40.6 ppm. A signal assignable to $Ru(H_2)$ was observed at −8.50 ppm (in CD_2Cl_2). Formulation of complex **10** as a dihydrogen complex is supported by the observation of a short T_1(min) of the hydride signal (11 ms, 400 MHz at 232 K) and a large ^1J(HD) (30.1 Hz) for the corresponding isotopomer $[RuCl(HD)(CO)(PMP)]BF_4$. The H−H distance in **10** was estimated to be 0.92 Å by use of the relationship $d(HH) = -0.0167J(HD) + 1.42$ and J(HD) = 30.1 Hz.

The J(HD) coupling constant for $[RuCl(HD)(CO)(PMP)]BF_4$ (30.1 Hz) is surprisingly close to that of $[RuCl(HD)(PPh_3)(PMP)]BF_4$ (28.0 Hz). Replacement of PR_3 in $[MH_2(PR_3)L_n]^{x+}$ with CO are known to have drastic effect on the structure. For example, the dihydrogen form is stable for complexes such as $[CpRu(H_2)(CO)(PR_3)]^+$,[9a,c] $Os(H_2)H_2(CO)(PR_3)_2$,[28] $[Re(H_2)H_2(CO)(PR_3)_3]^+$ (PR_3 = PMe_3, PMe_2Ph),[29,30] and $[Re(H_2)(CO)_2(PR_3)_3]^+$,[30−32] but the classic hydride form is adopted

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by $[CpRuH_2(PR_3)_2]^+$,[33,34] $OsH_4(PR_3)_4$,[20a,35] $[ReH_4(PR_3)_4]^+$,[36] and $[ReH_2(CO)(PR_3)_4]^+$ (PR_3 = PMe_3, PMe_2Ph).[30,31] In the cases where both $[M(H_2)(CO)L_n]^{x+}$ and $[M(H_2)(PR_3)L_n]^{x+}$ are stable, the H−H interaction in $[M(H_2)(CO)L_n]^{x+}$ is so strong that the J(HD) coupling constants for the HD isotopomers $[M(HD)(CO)L_n]^{x+}$ are usually larger than (or equal to) 32 Hz.[30,37]

A small change in J(HD) coupling constants for η^2-HD complexes upon variation of the electron-donating ability of the ligands is known for complexes lying at the early stage of the oxidative addition of dihydrogen at metal centers. For example, the J(HD) values for $[RuH(HD)(PP)_2]^+$ (PP = dtfpe, dppe, depe, dcpe)[8d,12] and $[RuH(HD)(PR_3)(PhP(CH_2CH_2PPh_2)_2)]^+$ (PR_3 = PMe_2Ph, $P(OCH_2)_3CEt$)[38] are in the range of 31−33 Hz. The same argument can be used to explain the similarity in the J(HD) values observed for [RuCl(HD)(CO)(PMP)]-BF_4 (30.1 Hz) and $[RuCl(HD)(PPh_3)(PMP)]BF_4$ (28.0 Hz). Alternatively, the similarity may be related to the fact that the dihydrogen ligand is *trans* to chloride. Morris *et al.* have noted that the H−H distances in *trans*-$[OsH(H_2)(PP)_2]^+$ change significantly when PP is changed from dppe to depe and dcpe, but the H−H distances in *trans*-$[OsCl(H_2)(PP)_2]^+$ only change slightly when the ligand is varied.[8a] The insensitivity of the H−H bond distance to the change in the ligands in *trans*-$[OsCl(H_2)(PP)_2]^+$ has been attributed to the buffer effect of the *trans* chloride.

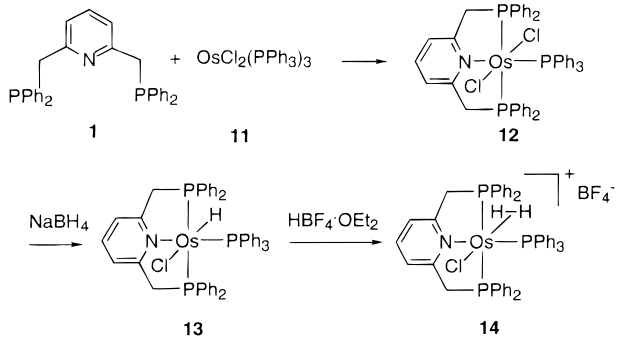
Other Reactions of PMP with RuHCl(CO)(PPh$_3$)$_3$. During the attempts to prepare RuHCl(CO)-(PMP) from the reaction of $RuHCl(CO)(PPh_3)_3$ and PMP, it was found that other compounds can also be isolated from the reaction (see Scheme 2). Thus, the cationic complex [RuH(CO)(PPh_3)(PMP)]Cl (**8**) was formed when the reaction was carried out in refluxing acetone. The isomeric cationic complex [RuH(CO)(PPh_3)(PMP)]Cl (**9**) was formed when the reaction was carried out in refluxing benzene, followed by treatment with methanol. The stereochemistry of complexes **8** and **9** was readily assigned on the basis of the ^{1}H and ^{31}P NMR data.

Synthesis and Characterization of [OsCl(H$_2$)(PPh$_3$)(PMP)]BF$_4$ and Related Complexes. The molecular dihydrogen complex $[OsCl(H_2)(PPh_3)(PMP)]BF_4$ (**14**) was prepared according to the sequence shown in Scheme 3.

Treatment of $OsCl_2(PPh_3)_3$ (**11**) with PMP (**1**) in acetone produced the orange complex $OsCl_2(PPh_3)(PMP)$ (**12**). Compound **12** was converted by $NaBH_4$ in refluxing THF into the yellow monohydride complex OsHCl-(PPh_3)(PMP) (**13**). These compounds were characterized by their NMR and analytical data.

Acidification of $OsHCl(PPh_3)(PMP)$ (**13**) with HBF_4·Et_2O in CH_2Cl_2 produced $[OsCl(H_2)(PPh_3)(PMP)]BF_4$

Scheme 3



(**14**), a white compound which showed a hydride signal at −9.04 ppm with J(PH) = 11.8 Hz (in CD_2Cl_2). Variable-temperature T_1 measurements gave a T_1(min) of 39 ms for the hydride signal at 300 MHz and 220 K. Protonation of **13** with DBF_4 produced [OsCl(HD)-(PPh_3)(PMP)]BF_4, which exhibited a hydride signal at −9.10 ppm with J(HD) = 17.7 Hz. The J(HD) value of 17.7 Hz is larger than those observed for [OsCl(HD)-$(PP)_2]^+$ (PP = dppe, depe, dcpe).[8a] The T_1(min) and J(HD) data imply that complex **14** contains an elongated dihydrogen ligand. On the basis of the T_1(min) value, the minimum H−H distance in **14** was estimated to be 1.26 Å for **14** with a slow spinning dihydrogen ligand and 1.00 Å for **14** with a fast spinning dihydrogen ligand. The H−H distance was estimated to be 1.12 Å based on the J(HD) value of 17.7 Hz. As expected, the H−H distance in **14** is longer than that in **5**. The stereochemistry of complex **14** is similar to that of complex **5**, as inferred by its spectroscopic data and results of a NOE experiment. In contrast to the case with complex **5**, the dihydrogen ligand in complex **14** cannot be removed under vacuum.

Acidity Properties of Complex 5. The pK_a value of **5** was estimated by studying the equilibrium shown in eq 1 by using ^{1}H and ^{31}P NMR spectroscopy. Due to

$$RuHCl(PPh_3)(PMP) + HP(p\text{-tolyl})_3^+ \rightleftharpoons [RuCl(H_2)(PPh_3)(PMP)]^+ + P(p\text{-tolyl})_3 \quad (1)$$

the tendency of complex **5** to lose H_2, the equilibrium measurements were conducted under 1 atm of H_2. Equilibrium mixtures were obtained by mixing RuHCl-(PPh_3)(PMP) with $HP(p\text{-tolyl})_3BF_4$ or by protonation with a limited amount of HBF_4·Et_2O of a mixture of $RuHCl(PPh_3)(PMP)$ and $P(p\text{-tolyl})_3$ in CD_2Cl_2. As indicated by both the ^{1}H and ^{31}P NMR spectroscopy, minor side products, one of which was identified as $RuCl_2$-(PPh_3)(PMP), were also present in the mixture. Owing to proton exchange, the signals of $P(p\text{-tolyl})_3$ and $HP(p\text{-tolyl})_3^+$ merged at room temperature to give a broad peak but separated into two peaks below 270 K. Thus, the equilibrium constant cannot be obtained at room temperature but can be estimated at lower temperatures. The relative concentrations of $P(p\text{-tolyl})_3$ and $HP(p\text{-tolyl})_3^+$ can be estimated from integrations of the ^{31}P signals in the ^{31}P NMR spectrum, and those of the hydride species can be obtained from both the ^{31}P and ^{1}H NMR spectroscopy. At 253 K, the equilibrium constant was determined to be 16 from the mixture obtained by mixing $RuHCl(PPh_3)(PMP)$ with $HP(p\text{-tolyl})_3^+$ and 18 from the mixture obtained by protonation

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of a mixture of $RuHCl(PPh_3)(PMP)$ and P(*p*-tolyl)$_3$ with a limited amount of $HBF_4{\cdot}OEt_2$. The pK_a value of HP(*p*-tolyl)$_3^+$ (on the aqueous scale) has been reported to be 3.84.[39] Thus, a pK_a value of 5.1 was calculated based on an equilibrium constant of 17 for eq 1. For comparison, the pK_a value of the closely related dihydrogen complex $[RuCl(H_2)(dppe)_2]^+$ is 6.0[8c] and that of $[RuCl(H_2)(dppp)_2]^+$ is 4.4.[10]

To verify the equilibrium study, we also studied reactions of $[RuCl(H_2)(PPh_3)(PMP)]^+$ (or $RuHCl(PPh_3)$(PMP)) with other bases (or acids) (see eq 2). The

$$RuHCl(PPh_3)(PMP) + HPPh_3^+ \rightarrow [RuCl(H_2)(PPh_3)(PMP)]^+ + PPh_3 \quad (2)$$

equilibrium for eq 2 must lie to the far right as reaction of $RuHCl(PPh_3)(PMP)$ with a slight excess of $HPPh_3$-BF_4 leads to complete consumption of $RuHCl(PPh_3)$-(PMP) to give the dihydrogen complex **5**. No deprotonation was observed when the dihydrogen complex **5** was treated with PPh_3. These observations are consistent with the fact the $HPPh_3^+$ (pK_a = 2.73 on aqueous scale)[39] is much more acidic than the dihydrogen complex **5** (pK_a = 5.1 on aqueous scale).

$[CpRuH_2(PPh_3)_2]^+$ is reported to have an aqueous pK_a value of 8.3 in CD_2Cl_2.[8h] As expected, the more acidic dihydrogen complex $[RuCl(H_2)(PPh_3)(PMP)]BF_4$ in CD_2Cl_2 was completely deprotonated with a slight excess of $CpRuH(PPh_3)_2$ to give the monohydride complex $RuHCl(PPh_3)(PMP)$ and the dihydride complex $[CpRuH_2(PPh_3)_2]BF_4$. It should be mentioned that $CpRuCl(PPh_3)_2$ was also observed if the reaction mixture was set at room temperature for over 30 min.

Acidity Properties of Complex 10. We mentioned in the previous section that the dihydrogen complex **10** is so acidic that it was deprotonated to give the monohydride complex **7** during the attempted isolation using diethyl ether as the precipitating solvent. Deprotonation of complex **10** by diethyl ether to give **7** can also be demonstrated by an NMR experiment. These observations prompted us to estimate the equilibrium constant by NMR for the protonation reaction of complex **7** with $HBF_4{\cdot}Et_2O$. A ^{1}H NMR spectrum (in CD_2Cl_2) of a commercially available sample of $HBF_4{\cdot}Et_2O$ at 203 K indicated that the sample contained both $HBF_4{\cdot}Et_2O$ and Et_2O in an approximate molar ratio of 1:0.7 (corresponding to ca. 76% $HBF_4{\cdot}Et_2O$). No appreciable reaction was observed when 1 μL of this commercially available acid (containing *ca.* 0.0056 mmol $HBF_4{\cdot}Et_2O$) was added to a solution of RuHCl(CO)(PMP) (*ca.* 10 mg, 0.016 mmol) at 243 K. Further addition of another 2 μL of the acid caused the hydride signal at -13.65 ppm of RuHCl(CO)(PMP) to become broad (at 243 K). This signal remained broad at 203 K. A small hydride signal due to $[RuCl(H_2)(CO)(PMP)]BF_4$ became observable (at 203 K) after the addition of another 2 μL of the acid to the reaction mixture. A mixture containing both $[RuCl(H_2)(CO)(PMP)]BF_4$ and RuHCl(CO)(PMP) (in a molar ratio of 0.3:1) formed after adding a total of 7 μL of the acid (ca 0.039 mmol $HBF_4{\cdot}Et_2O$), as indicated by both the ^{31}P and ^{1}H NMR spectroscopy at 203 K. The ^{1}H NMR spectrum also showed a broad signal at 11.5 ppm assignable to $HBF_4{\cdot}Et_2O$. From the integration of the acid and diethyl ether signals, it was estimated that the relative amounts of $HBF_4{\cdot}Et_2O$ and Et_2O were in a molar ratio of 1:0.93. The relative molar concentrations of $HBF_4{\cdot}Et_2O$, Et_2O, RuHCl(CO)(PMP), and $RuCl(H_2)$-(CO)(PMP)]BF_4 were 3.0, 2.8, 1.0, and 0.33 based on ^{1}H NMR integrations. Thus, an equilibrium constant of 0.3 for eq 3 can be estimated. The pK_a values of protonated

$$RuHCl(CO)(PMP) + HBF_4{\cdot}Et_2O \rightleftharpoons [RuCl(H_2)(CO)(PMP)]BF_4 + Et_2O \quad (3)$$

ether are in the range from -2.39 (at 25 °C) to -2.48 (at 90 °C) in aqueous sulfuric acid.[40] Thus, the pK_a value of $[RuCl(H_2)(CO)(PMP)]BF_4$ was calculated to be -2.8 at 203 K if that of $HBF_4{\cdot}OEt_2$ is taken as -2.4. Although the uncertainty in the estimated pK_a value may be significant, the pK_a value is consistent with the fact that the dihydrogen complex **10** was formed from the reaction of RuHCl(CO)(PMP) in dichloromethane with excess $HBF_4{\cdot}Et_2O$ but was deprotonated by excess ether to give the monohydride complex **7**. Interestingly, it was reported recently that the CO-containing complex $[Ru(H_2)(CO)(dppp)_2]^{2+}$ has a pK_a value close to -6.[10]

Attempts to study the acid properties of complex **10** with phosphines (or protonated phosphines) were unsuccessful, due to the formation of $[RuH(CO)(PR_3)$-$(PMP)]^+$. For example, reaction of RuHCl(CO)(PMP) with $HPPh_3BF_4$ did not lead to the dihydrogen complex **10** but rather to the phosphine adduct $[RuH(CO)(PPh_3)$-$(PMP)]BF_4$ (**9**).

Acidity Properties of Complex 14. The pK_a value of **14** was estimated by studying the equilibrium shown in eqs 4 and 5, using ^{1}H and ^{31}P NMR spectroscopy. In

$$CpRuH(PPh_3)_2 + [OsCl(H_2)(PPh_3)(PMP)]^+ \rightleftharpoons [CpRuH_2(PPh_3)_2]^+ + OsHCl(PPh_3)(PMP) \quad (4)$$

$$CpRuH(dppm) + [OsCl(H_2)(PPh_3)(PMP)]^+ \rightleftharpoons [CpRu(H_2)(dppm)]^+ + OsHCl(PPh_3)(PMP) \quad (5)$$

these experiments, all the relevant species can be readily detected by ^{1}H and ^{31}P NMR spectroscopy, although very small amounts of unidentified species were also present in the reaction mixture. The relative concentrations of the relevant species can be readily obtained by integration of the hydride signals. An equilibrium constant of 6.8 for eq 4 was obtained from the mixture obtained by protonation with $HBF_4{\cdot}Et_2O$ of a mixture of $CpRuH(PPh_3)_2$ and $OsHCl(PPh_3)(PMP)$. An equilibrium constant of 2.2 for eq 5 was obtained for the mixture obtained by protonation with $HBF_4{\cdot}$ Et_2O of a mixture of CpRuH(dppm) and $OsHCl(PPh_3)$-(PMP). The pK_a values (aqueous scale) of $[CpRuH_2$-$(PPh_3)_2]BF_4$ and $[CpRu(H_2)(dppm)]^+$ have been reported to be 8.3 and 7.1, respectively.[8h] Thus, the pK_a value for complex **14** was estimated to be 7.5 from eq 4 and 6.8 from eq 5. It could be concluded that the pK_a value of complex **14** is close to 7.2 on an aqueous scale.

To further verify the acidity of complex **14**, we have directly compared the acidity of $[RuCl(H_2)(PPh_3)$-$(PMP)]^+$ with $[OsCl(H_2)(PPh_3)(PMP)]^+$. When RuHCl-$(PPh_3)(PMP)$ was mixed with $[OsCl(H_2)(PPh_3)(PMP)]^+$ in CD_2Cl_2, no signals of $OsHCl(PPh_3)(PMP)$ could be

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Table 3. Spectroscopic Properties and Acidities of Selected Hydride Complexes

complexes	T_1(min), ms[a]	J(HD)	d(HH), Å[b]	pK_a[c]	refs
$[RuCl(H_2)(PPh_3)(PMP)]^+$	21	28.0	0.95	5.1[d]	this work
$[OsCl(H_2)(PPh_3)(PMP)]^+$	39[e]	17.7	1.12	7.2	this work
$[RuCl(H_2)(dppe)_2]^+$	25	25.9	0.99	6.0	8c
$[OsCl(H_2)(dppe)_2]^+$	53	13.9	1.19	7.4	8a
$[RuCl(H_2)(dppp)_2]^+$	8.2[f]	24	1.0	4.4	10
$[OsCl(H_2)(dppp)_2]^+$	23.7[f]	11	1.2	12.5	10
$[RuH(H_2)(dtfpe)_2]^+$	10	33	0.87	10.0[g]	8d
$[OsH(H_2)(dtfpe)_2]^+$	15	28	0.95	9.2[g]	8d
$[RuH(H_2)(dppe)_2]^+$	20	32	0.89	15.0[g]	8a,d
$[OsH(H_2)(dppe)_2]^+$	40	25.5	0.99	13.6[g]	8a,d
$[RuH(H_2)(depe)_2]^+$	16	32.3	0.88	17.5[g]	8a,d
$[OsH(H_2)(depe)_2]^+$	80	11	1.23	17.3[g]	8a,d
$[RuH(H_2)(dppp)_2]^+$	5.5[f]	32	0.89	10.2	10
$[OsH_3(dppp)_2]^+$	72[f]	0		10.3[h]	10
$[RuCl(H_2)(CO)(PMP)]^+$	11	30.1	0.92	−2.8[i]	this work
$[Ru(H_2)(CO)(dppp)_2]^{2+}$	5.0[f]	34	0.85	*ca.* −6	10
$[Os(H_2)(CO)(dppp)_2]^{2+}$	5.5[f]	32	0.89	−5.7	10
$[Os(H_2)(CH_3CN)(dppe)_2]^{2+}$	28	21.4	1.06	−2	8b

[a] At 400 MHz, unless otherwise stated. [b] Calculated based on J(HD) values. [c] pK_a values were determined in CD_2Cl_2, but reported on pseudo aqueous scale. [d] Determined at 253 K. [e] At 300 MHz. [f] At 200 MHz. [g] Conjugated bases are *trans*-$MH_2(PP)_2$. [h] The conjugated base is *cis*-$OsH_2(dppp)_2$. [i] Determined at 203 K.

observed by ^1H and ^{31}P NMR spectroscopy, although small signals due to $[RuCl(H_2)(PPh_3)(PMP)]^+$ could be observed. The latter compound could be produced from traces of acid present in the sample of $[OsCl(H_2)(PPh_3)(PMP)]BF_4$. When a mixture of $OsHCl(PPh_3)(PMP)$ and $RuHCl(PPh_3)(PMP)$ was protonated with a limited amount of $HBF_4 \cdot Et_2O$, only $OsHCl(PPh_3)(PMP)$ was protonated to give the molecular dihydrogen complex **14**. These experiments clearly indicate that $[RuCl(H_2)(PPh_3)(PMP)]BF_4$ is more acidic than $[OsCl(H_2)(PPh_3)(PMP)]BF_4$.

Comments on the Acidities of Complexes 5, 10, and 14. It should be stressed that the pseudo aqueous pK_a values of complexes **5**, **10**, and **14** are obtained based on the assumption that the differences in the pK_as of the dihydrogen complexes and the reference acids are the same in water and CD_2Cl_2. Because 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. However, the pseudo aqueous pK_a values can still provide valuable information on the trend in the acidities of the complexes. For comparison, the pseudo aqueous pK_a values of complexes **5**, **10**, **14**, and related dihydrogen complexes are listed in Table 3.

Substitution of PPh_3 for CO is known to change the acidity of related classic hydride complexes by 5−8 pK_a units. For example, $MnH(CO)_5$[3d] has a pK_a(CH_3CN) of 15.1 vs 20.4 for $MnH(CO)_4(PPh_3)$;[3b] $CpCrH(CO)_3$[3e] has a pK_a(CH_3CN) of 13.3 vs 21.8 for $CpCrH(CO)_2(PPh_3)$,[4c] and $HCo(CO)_4$[3d] has a pK_a(CH_3CN) of 8.3 vs 15.4 for $HCo(CO)_3(PPh_3)$.[3d] The pK_a values of closely related molecular dihydrogen complexes $L_nM(H_2)(CO)$ and $L_nM(H_2)(PPh_3)$ have not been reported previously. Due to the presence of the stronger H−H bond in $L_nM(H_2)(CO)$ as compared to $L_nM(H_2)(PPh_3)$, the difference in the acidity of $L_nM(H_2)(CO)$ and $L_nM(H_2)(PPh_3)$ may be reduced. This study shows that complex **10** is more acidic than complex **5** by *ca.* 7.9 pK_a (pseudo aqueous) units. The difference is quite similar to that of classic hydride complexes. Thus, it appears that the difference in the H−H interaction has less importance than the inductive effect of the ligands in determining the acidity of $[RuCl(H_2)(L)(PMP)]^+$.

The observation that $[RuCl(H_2)(PPh_3)(PMP)]BF_4$ (pK_a = 5.1) is more acidic than the osmium analog $[OsCl(H_2)(PPh_3)(PMP)]BF_4$ (pK_a = 7.2) is consistent with the trend reported for $[MCl(H_2)(dppe)_2]^+$ (pK_a = 6.0, M = Ru;[8c] pK_a = 7.4, M = Os[8a]) and $[MCl(H_2)(dppp)_2]^+$ (pK_a = 4.4, M = Ru; pK_a = 12.5, M = Os).[10] The trend is also similar to those observed for classic hydride complexes such as $[CpMH_2(PPh_3)_2]^+$ (M = Ru, Os)[8d] and $H_2M(CO)_4$ (pK_a(CH_3CN) = 18.7, M = Ru; pK_a = 20.8, M = Os).[3d] Such a trend is expected as the Os−H bond is usually stronger than the Ru−H bond. In contrast, the pK_a values of $[MH(H_2)(PP)_2]^+$ (PP = dppe, dtfpe, depe) are in the order of Os < Ru.[8d] The distinctive order in the acidity of complexes $[MH(H_2)(PP)_2]^+$ has been attributed to the stronger H−H interactions present in $[RuH(H_2)(PP)_2]^+$ complexes. Indeed, the strong H−H interactions in $[RuH(H_2)(PP)_2]^+$ complexes are reflected in the J(HD) (≥32 Hz) for their corresponding isotopomers. To explain the distinctive trend in the acidity of $[MH(H_2)(PP)_2]^+$, it was suggested that as the d(HH) bond stretches above 1.0 Å, the M−H bond energy drops to that of dihydride and the acidity becomes the same as the classic complexes.[8a] Although the H−H interactions in $[RuCl(H_2)(PP)_2]^+$ and $[RuCl(H_2)(PPh_3)(PMP)]^+$ (H−H distance is likely shorter than 1.0 Å) are also substantially stronger than that in the osmium analogs, as reflected in the J(HD) coupling constants (see Table 3), the H−H interactions in the ruthenium complexes are not strong enough to give a distinctive trend in the acidity of $[MCl(H_2)(PP)_2]^+$ and $[MCl(H_2)(PPh_3)(PMP)]^+$. For comparison, J(HD) is 28.0 Hz for $[RuCl(HD)(PPh_3)(PMP)]^+$ and 32 Hz for $[RuH(H_2)(dppe)_2]^+$.

Conclusion. We have successfully synthesized and characterized the dihydrogen complexes $[MCl(H_2)(L)(PMP)]BF_4$ (**5**, M = Ru, L = PPh_3; **10**, M = Ru, CO; **14**, M = Os, L = PPh_3). Complex **10** is so acidic that it is deprotonated by diethyl ether. Equilibrium studies show that the acidity decreases in the order of **10** > **5** > **14**. The trend is the same as that expected for classic hydride complexes.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under dinitrogen from sodium-benzophenone (hexane, diethyl ether, THF, benzene) and calcium hydride (CH_2Cl_2). The starting materials $RuCl_2(PPh_3)_3$,[41] $RuHCl(CO)(PPh_3)_3$,[42] $CpRuH(PPh_3)_2$,[43] $[CpRuH_2(PPh_3)_2]BF_4$,[34] PMP,[44] and $OsCl_2(PPh_3)_3$[45] were prepared according to literature methods. All other reagents were used as purchased from Aldrich.

Microanalysis were performed by M-H-W Laboratories (Phoenix, AZ). ^1H and $^{31}P\{^1H\}$ NMR spectra were collected on a JEOL EX-400 or Bruker ARX-300 or 400 spectrometer.

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^{1}H chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. IR spectra were collected on a Perkin-Elmer 1600 spectrometer.

$RuCl_2(PPh_3)(PMP)$ (3). A mixture of 2.00 g of $RuCl_2(PPh_3)_3$ (2.09 mmol) and 1.00 g of PMP (2.10 mmol) in acetone (30 mL) was refluxed for 1 h to give a yellow precipitate. The yellow solid was collected by filtration. A second crop of yellow solid was obtained from the filtrate by reducing the volume of the filtrate and cooling with an ice bath. The yellow solid was dried under vacuum overnight. Yield: 1.81 g, 87%. The solid was recrystallized from dichloromethane/methanol. Anal. Calcd for $C_{49}H_{42}Cl_2NP_3Ru\cdot CH_2Cl_2$: C, 60.38; H, 4.46; N, 1.41. Found: C, 60.88; H, 4.49; N, 1.41. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.52 (t, J(PH) = 4.9 Hz, 4 H, 2 CH_2), 6.83−7.52 (m, 38 H, PPh_3, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (161.70 MHz, $CDCl_3$): δ 29.6 (d, J(PP) = 27.7 Hz), 35.9 (t, J(PP) = 27.7 Hz).

$RuHCl(PPh_3)(PMP)$ (4). A mixture of 0.20 g of $RuCl_2(PPh_3)$(PMP) (0.22 mmol) and 0.10 g of $NaBH_4$ (0.24 mmol) in methanol (25 mL) was refluxed for 30 min to give an orange-brown solution. The reaction mixture was allowed to cool to room temperature to give a bright yellow precipitate. The solid was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.18 g, 91%. Anal. Calcd for $C_{49}H_{43}ClNP_3Ru$: C, 67.24; H, 4.95; N, 1.60. Found: C, 67.10; H, 5.19; N, 1.51. ^{1}H NMR (400 MHz, C_6D_6): δ −16.55 (q, J(PH) = 22.2 Hz, 1 H, RuH), 3.73 (dt, J(HH) = 15.7 Hz, J(PH) = 3.9 Hz, 2 H, C*H*H(C_5H_3N)C*H*H), 4.69 (br d, J(HH) = 15.7 Hz, 2 H, CH*H*(C_5H_3N)CH*H*), 6.41 (d, J(HH) = 7.8 Hz, 2 H, py-3,5-H), 6.59 (t, J(HH) = 7.8 Hz, 1 H, py-4-H), 6.84−8.14 (m, 35 H, PPh_3, 2 PPh_2). ^{31}P{^{1}H} NMR (161.70 MHz, C_6D_6): δ 47.2 (d, J(PP) = 27.8 Hz), 57.9 (t, J(PP) = 27.8 Hz).

$[RuCl(H_2)(PPh_3)(PMP)]BF_4$ (5). Method A. To a CD_2Cl_2 solution (0.5 mL) of 10 mg of $RuHCl(PPh_3)$(PMP) (0.01 mmol) in an NMR tube was added 3 μL of tetrafluoroboric acid−diethyl ether complex. ^{1}H and ^{31}P NMR were obtained immediately.

Method B. A dichloromethane solution (4 mL) of 0.17 g $RuHCl(PPh_3)$(PMP) (0.65 mmol) was treated with tetrafluoroboric acid−diethyl ether complex (*ca.* 0.16 mL). The color changed from bright yellow to yellow. The solution was allowed to stir for 15 min and then transferred to a solution of diethyl ether (30 mL) *via* a cannula. The white solid formed was collected on a filter frit, washed with diethyl ether, and dried under vacuum. Anal. Calcd for $C_{49}H_{44}BClF_4NP_3Ru\cdot CH_2Cl_2$: C, 57.30; H, 4.42; N, 1.33. Found: C, 57.41; H, 4.68; N, 4.68. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −10.49 (br, 2 H, Ru(H_2)), 4.19 (dt, J(HH) = 16.7 Hz, J(PH) = 4.3 Hz, 2 H, C*H*H(C_5H_3N)C*H*H), 4.81 (dt, J(HH) = 16.7 Hz, J(PH) = 4.4 Hz, 2 H, CH*H*(C_5H_3N)CH*H*), 7.02−7.55 (m, 38 H, PPh_3, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2): δ 33.4 (d, J(PP) = 25.2 Hz), 38.5 (t, J(PP) = 25.2 Hz). T_1(400 MHz, CD_2Cl_2): ms (temperature) 32 (293 K), 25 (273 K), 22 (253 K), 21 (243 K), 21 (233 K), 22 (223 K), 24 (213 K), 28 (202 K). A plot of ln T_1 vs 1000/T showed the familiar "V" shape, and T_1(min) was found to be 21 ms at 236 K.

$[RuCl(HD)(PPh_3)(PMP)]BF_4$. This complex was not isolated but was prepared in an NMR tube and characterized by NMR spectroscopy *in situ*. To a sample of 10 mg of $RuHCl(PMP)(PPh_3)$ dissolved in CD_2Cl_2 (0.5 mL) was added DBF_4. The DBF_4 was prepared by adding 0.1 mL of D_2O into 0.4 mL of $HBF_4\cdot Et_2O$. The tube was then placed in an NMR probe, and a ^{1}H NMR spectrum of the solution was taken. The η^2-HD signal was observed after nulling the η^2-H_2 peak at δ −10.49 by the inversion−recovery method. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −10.56 (tq, J(HD) = 28.0, J(PH) = 8.0 Hz, Ru(HD)).

$RuHCl(CO)(PMP)$ (7). A mixture of 0.51 g of $RuHCl(CO)(PPh_3)_3$ (0.54 mmol) and 0.30 g of PMP (0.63 mmol) in benzene (25 mL) was refluxed overnight to give a clear yellow solution. The solution was allowed to cool to room temperature. The solvent was removed completely under vacuum, and 30 mL of diethyl ether was added to give a yellow solid. The yellow solid was recrystallized using dichloromethane/diethyl ether to give a pale yellow solid. The solid was collected on a filter frit and dried under vacuum overnight. Yield: 0.29 g, 85%. Anal. Calcd for $C_{32}H_{28}ClNOP_2Ru$: C, 59.96; H, 4.40; N, 2.19. Found: C, 59.73; H, 4.66; N, 1.92. IR (KBr, cm^{-1}): ν(CO) 1916 (s). ^{1}H NMR (300 MHz, CD_2Cl_2): δ −13.65 (t, J(PH) = 19.9, 1H, RuH), 4.13 (dt, J(HH) = 16.6 Hz, J(PH) = 4.8 Hz, 2 H, C*H*H(C_5H_3N)C*H*H), 4.64 (dt, J(HH) = 16.6 Hz, J(PH) = 4.5 Hz, 2 H, CH*H*(C_5H_3N)CH*H*), 6.82−7.85 (m, 23 H, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2): δ 50.4 (s).

$[RuH(CO)(PPh_3)(PMP)]Cl$ (8). A mixture of 0.80 g of $RuHCl(CO)(PPh_3)_3$ (0.84 mmol) and 0.57 g of PMP (1.2 mmol) in 30 mL of acetone was refluxed for 45 min to give a greenish solution. The hot solution was filtered through a filter frit. The solvent was reduced to *ca.* 1 mL under vacuum, and 40 mL of diethyl ether was added to give a white solid. The solid was recrystallized with CH_2Cl_2/benzene, washed with diethyl ether and hexane, and dried under vacuum overnight. Yield: 0.52 g, 68%. Anal. Calcd for $C_{50}H_{43}ClNOP_3Ru$: C, 66.48; H, 4.80; N, 1.55. Found: C, 66.31; H, 5.01; N, 1.50. IR (KBr, cm^{-1}): ν(CO) 1978 (s), ν(Ru−H) 1885 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ −4.08 (q, J(PH) = 20.4 Hz, 1 H, RuH), 4.08 (dt, J(HH) = 16.3 Hz, J(PH) = 4.2 Hz, 2 H, C*H*H(C_5H_3N)C*H*H), 4.50 (br d, J(HH) = 16.3 Hz, 2 H, CH*H*(C_5H_3N)CH*H*), 6.94−7.56 (m, 38 H, PPh_3, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, $CDCl_3$): δ 51.3 (d, J(PP) = 26.0 Hz), 54.0 (t, J(PP) = 26.0 Hz).

$[RuH(CO)(PPh_3)(PMP)]Cl$ (9). A mixture of 0.54 g of $RuHCl(CO)(PPh_3)_3$ (0.57 mmol) and 0.30 g of PMP (0.63 mmol) in benzene (25 mL) was refluxed overnight to give a clear yellow solution. The solution was allowed to cool to room temperature. The solvent was removed completely under vacuum. Then 30 mL of methanol was added, and the mixture was stirred for 1 min to give a clear yellow solution. The solvent was removed again under vacuum, and 30 mL of diethyl ether was added to give a yellow solid. The yellow solid was collected on a filter frit, washed with diethyl ether and hexane, and dried under vacuum overnight. Yield: 0.41 g, 82%. Anal. Calcd for $C_{50}H_{43}ClNOP_3Ru$: C, 66.48; H, 4.80; N, 1.55. Found: C, 66.23; H, 4.72; N, 1.46. IR (KBr, cm^{-1}): ν(CO) 1938 (s). ^{1}H NMR (300 MHz, CD_2Cl_2): δ −6.79 (dt, J(PH) = 88.3, 21.5 Hz, 1 H, RuH), 3.72 (dt, J(HH) = 16.9 Hz, J(PH) = 3.8 Hz, 2 H, C*H*H(C_5H_3N)C*H*H), 4.45 (dt, J(HH) = 16.9 Hz, J(PH) = 5.0 Hz, 2 H, CH*H*(C_5H_3N)CH*H*), 6.72−7.70 (m, 38 H, PPh_3, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2): δ 22.9 (t, J(PP) = 14.9 Hz), 40.6 (d, J(PP) = 14.9 Hz).

$[RuCl(H_2)(CO)(PMP)]BF_4$ (10). Due to its low stability, this compound was not isolated but was characterized *in situ*. To a dichloromethane-d_2 solution (0.5 mL) of 10 mg of RuHCl(CO)(PMP) (0.016 mmol) in an NMR tube was added $HBF_4\cdot Et_2O$ until all the hydride signal of complex **7** disappeared. ^{1}H and ^{31}P NMR spectra were obtained immediately. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −8.50 (br, Ru(H_2)), 4.40−4.79 (m, CH_2), 7.01−7.74 (m, PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2): δ 40.6 (s). T_1(400 MHz, CD_2Cl_2): ms (temperature) 22 (293 K), 15 (273 K), 12 (253 K), 11 (243 K), 11 (233 K), 11 (223 K), 12 (213 K), 15 (202 K). A plot of ln T_1 vs 1000/T showed the familiar "V" shape, and T_1(min) was found to be 11 ms at 232 K.

$[RuCl(HD)(CO)(PMP)]BF_4$. The compound was prepared similarly, except that DBF_4 was used instead of $HBF_4\cdot Et_2O$. The η^2-HD signal was observed after nulling the η^2-H_2 peak at δ −8.50 ppm by the inversion−recovery method. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −8.55 (br t, J(HD) = 30.1 Hz, Ru(HD)).

$OsCl_2(PPh_3)(PMP)$ (12). A mixture of 0.21 g of PMP (0.44 mmol) and 0.35 g of $OsCl_2(PPh_3)_3$ (0.33 mmol) in 20 mL of acetone was stirred at room temperature for 2 min. The color changed immediately from green to orange. The solvent was reduced to 1 mL under vacuum, and 40 mL of diethyl ether was added to give an orange solid. The solid was collected on a filter frit, washed with diethyl ether, and dried under

vacuum overnight. Yield: 0.29 g, 87%. Anal. Calcd for $C_{49}H_{42}Cl_2NP_3Os$: C, 58.92; H, 4.24; N, 1.40. Found: C, 58.99; H, 4.48; N, 1.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.50 (t, J(PH) = 4.7 Hz, 4 H, 2 CH_2), 6.88−7.57 (m, 38 H, PPh_3, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, $CDCl_3$): δ −17.0 (t, J(PP) = 15.6 Hz), −0.1 (d, J(PP) = 15.6 Hz).

$OsHCl(PPh_3)(PMP)$ (13). A mixture of 0.21 g of $OsCl_2(PPh_3)$(PMP) (0.21 mmol) and 0.20 g of $NaBH_4$ (5.3 mmol) was refluxed in 20 mL of THF overnight. Then the reaction mixture was cooled down to room temperature. The solvent was then removed completely under vacuum, and the residue was extracted with 30 mL of benzene, which was removed subsequently under vacuum. After the addition of 30 mL of ethanol, a yellow solid was formed, which was collected on a filter frit, washed with ethanol, and dried under vacuum. The solid was recrystallized from CH_2Cl_2/ethanol and dried under vacuum. Yield: 0.14 g, 69%. Anal. Calcd for $C_{49}H_{43}ClNP_3Os\cdot CH_2Cl_2$: C, 57.23; H, 4.32; N, 1.34. Found: C, 57.33; H, 4.53; N, 1.34. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −18.53 (q, J(PH) = 17.5 Hz, 1 H, Os−H), 4.09 (dt, J(HH) = 15.8 Hz, J(HH) = 4.7 Hz, 2 H, C*H*H(C_5H_3N)C*H*H), 4.72 (dt, J(HH) = 15.8 Hz, J(PH) = 3.7 Hz, 2 H, CH*H*(C_5H_3N)CH*H*), 6.78−7.80 (m, 38 H, PPh_3, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, THF-d_8): δ 7.6 (t, J(PP) = 15.7 Hz), 16.7 (d, J(PP) = 15.7 Hz).

$[OsCl(H_2)(PPh_3)(PMP]BF_4$ (14). A few drops of $HBF_4\cdot Et_2O$ was added to a solution of 0.10 g of $OsHCl(PPh_3)$(PMP) (0.10 mmol) in 5 mL of dichloromethane, and the reaction mixture was allowed to stir at room temperature for 10 min. After the addition of 30 mL of diethyl ether, a white solid was formed. The solid was collected on a filter frit, washed with water and diethyl ether, and dried under vacuum overnight. Yield: 80 mg, 73%. Anal. Calcd for $C_{49}H_{44}BClF_4NP_3Os$: C, 55.93; H, 4.21; N, 1.33. Found: C, 55.98; H, 4.27; N, 1.25. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −9.04 (br q, J(PH) = 11.8 Hz, Os−H), 4.26 (dt, J(HH) = 16.9 Hz, J(PH) = 4.7 Hz, 2 H, C*H*H(C_5H_3N)C*H*H), 5.00 (dt, J(HH) = 16.9 Hz, J(PH) = 4.8 Hz, 2 H, CH*H*(C_5H_3N)CH*H*), 6.78−7.80 (m, 38 H, PPh_3, 2 PPh_2, py-3,4,5-H). ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2): δ −5.9 (t, J(PP) = 14.1 Hz), 6.3 (d, J(PP) = 14.1 Hz). T_1 (300 MHz, CD_2Cl_2): ms (temperature) 87 (298 K), 58 (273 K), 51 (263 K), 45 (253 K), 41 (243 K), 40 (233 K), 39 (223 K), 42 (213 K), 42 (203 K), 52 (193 K), 57 (183 K). A plot of ln T_1 vs 1000/T showed the familiar "V" shape, and T_1(min) was found to be 39 ms at 220 K.

$[OsCl(HD)(PPh_3)(PMP)]BF_4$. The compound was prepared similarly, except that DBF_4 was used instead of $HBF_4\cdot Et_2O$. The DBF_4 was prepared by mixing $HBF_4\cdot Et_2O$ and D_2O in a 3:1 volume ratio. The η^2-HD signal was observed after nulling the η^2-H_2 peak at δ −9.04 ppm by the inversion−recovery method. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.10 (tq, J(HD) = 17.7 Hz, J(PH) = 11.8 Hz, Ru(HD)).

Acidity Study. The experiments were conducted under a H_2 atmosphere. In a typical experiment, appropriate amounts of an acid and a base were loaded into an NMR tube, then CD_2Cl_2 was added. After a suitable period of time, ^{1}H and ^{31}P NMR spectra were collected. The equilibrium is confirmed by monitoring the reactions with NMR spectroscopy. In some cases, the NMR spectra were recorded below room temperature as mentioned previously. By measuring the intensity of the ^{1}H and/or ^{31}P resonances, one can estimate the relative concentration of the species in equilibrium and therefore the equilibrium constants.

Alternatively, an appropriate mixture of monohydrido complexes were dissolved in CD_2Cl_2 in an NMR tube and then a limited amount $HBF_4\cdot Et_2O$ was added. After a suitable period of time, NMR spectra were then recorded.

Crystallographic Analysis for $RuCl_2(PPh_3)(PMP)\cdot CH_2Cl_2$. Suitable crystals for X-ray diffraction study were obtained by slow diffusion of Et_2O to a saturated CH_2Cl_2 solution of $RuCl_2(PPh_3)$(PMP) at room temperature. A specimen of dimensions 0.50 × 45 × 0.15 mm was mounted on a glass fiber and used for the X-ray structure determination. The diffraction data was collected on a Siemens P4-RA diffractometer at 213 K. The crystal system was triclinic and in the space group $P\bar{1}$. A total of 12 664 intensity measurements were made using the $2\theta-\theta$ scan technique in the range $3.0 \le 2\theta \le 50°$ (Mo Kα radiation). Of these, 11 282 were unique (R_{int} = 1.72%) and 9198 observed $F \ge 4\sigma(F)$, which were used for structure solution and refinement using the SHELXTL PLUS program package. Solution by direct methods yielded the positions of all non-hydrogen atoms. Refinement by full-matrix least squares resulted in final discrepancy indices R = 3.36%, R_w = 4.11% with GOF = 1.27. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were revealed in difference Fourier maps but then placed in geometrically determined positions with d_{C-H} = 0.96 Å and refined isotropically with riding constraints and group thermal parameters. The data/parameter ratio was 17.2/1 and residual electron density/hole ratio +0.45/−0.51 e Å^{-3}. Further crystallographic details and selected bond distances and angles for $RuCl_2(PPh_3)(PMP)\cdot CH_2Cl_2$ are given in Tables 1 and 2, respectively.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, complete bond lengths and bond angles, anisotropic displacement coefficients, H-atom coordinates, and isotropic displacement coefficients for $RuCl_2(PPh_3)(PMP)\cdot CH_2Cl_2$ (7 pages). Ordering information is given on any current masthead page.

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