Ligand Effect on the Structures and Acidities of $[TpOs(H_2)(PPh_3)_2]BF_4$ and $[CpOsH_2(PR_3)_2]BF_4$

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The new molecular dihydrogen complex $[TpOs(H_2)(PPh_3)_2]BF_4$ was prepared by protonation of $TpOsH(PPh_3)_2$ with HBF_4. The pseudo-aqueous pK_a values of $[CpOsH_2(PR_3)_2)]BF_4$ ($(PR_3)_2$ = $(PPh_3)_2$, dppm, dppe, dppp) and $[TpOs(H_2)(PPh_3)_2]BF_4$ have been determined in dichloromethane. $[TpOs(H_2)(PPh_3)_2]BF_4$ was found to be more acidic than *trans*-$[CpOsH_2(PPh_3)_2]BF_4$. While $[TpOs(H_2)(PPh_3)_2]BF_4$ is less acidic than $[TpRu(H_2)(PPh_3)_2]BF_4$ by 1.3 pK_a units, *trans*-$[CpOsH_2(PPh_3)_2]BF_4$ is less acidic than *trans*-$[CpRuH_2(PPh_3)_2]BF_4$ by 5.1 pK_a units.

Introduction

Complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2(L)(L')]^+$ (M = Ru,[1−9] Os;[10−14] (L)(L′) = $(CO)_2$, (CO)(PR_3), $(PR_3)_2$) and $[TpM(H_2)(L)(L')]^+$ (M = Ru,[15,16] Os;[15] Tp = hydridotris(pyrazolyl)borate) have attracted considerable attention recently for their structural, chemical and physical properties. Previous studies on ruthenium complexes show that $[(\eta^5\text{-}C_5R_5)RuH_2(L)(L')]^+$ can adopt either the dihydride form *trans*-$[(\eta^5\text{-}C_5R_5)RuH_2(L)(L')]^+$ or the dihydrogen form $[(\eta^5\text{-}C_5R_5)Ru(H_2)(L)(L')]^+$ or a mixture of both forms, depending on the ligands used. The dihydrogen form is adopted by the CO-containing complexes $[(\eta^5\text{-}C_5R_5)Ru(H_2)(CO)(PR_3)]^+$ and $[(\eta^5\text{-}C_5Me_5)Ru(H_2)(CO)_2]^+$. The Tp complexes $[TpRu(H_2)(L)(L')]^+$ always adopt the dihydrogen form.[15,16] As expected, the acidities of these ruthenium complexes vary with the ligands. Interestingly, $[TpRu(H_2)(PPh_3)_2]^+$ was found to be more acidic than *trans*-$[CpRuH_2(PPh_3)_2]^+$,[16b] although Tp is usually believed to be more electron-releasing than Cp.[17] The acidity of $[CpRu(H_2)(Ph_2P(CH_2)_nPh_2)]^+$ (n = 1, 2) increases as the chelating ring size increases, but that of *trans*-$[CpRuH_2(Ph_2P(CH_2)_nPPh_2)]^+$ (n = 2, 3) decreases as the chelating ring size increases.[7b] The latter trend is opposite to that inferred from the basicities of $Fe(CO)_3(Ph_2P(CH_2)_nPh_2)$[18] and $M(CO)_2(Ph_2P(CH_2)_nPPh_2)_2$ (M = Mo, W).[19]

In comparison to that of ruthenium, the chemistry of the osmium homologues is less developed. The reported osmium complexes of the formula $[CpOsH_2(L)(L')]^+$ include $[Cp^*Os(H_2)(CO)_2]^+$/*trans*-$[Cp^*OsH_2(CO)_2]^+$,[11] *trans*-$[CpOsH_2(CO)(P(i\text{-}Pr)_3)]BF_4$,[10] *trans*-$[CpOsH_2(PR_3)_2]^+$ ($(PR_3)_2$ = $(PPh_3)_2$, $(Ph_2PMe)_2$, $(PPh_3)(P(OEt)_3)$),[13,14] and $[CpOsH_2(Ph_2P(CH_2)_nPPh_2)]^+$ (n = 1, 2, 3).[12] The osmium Tp complex is limited to $[TpOs(H_2)(CO)(P(i\text{-}Pr)_3)]BF_4$, which was reported recently by Esteruelas et al.[15] Very few studies have been carried out on the acidity properties of these osmium hydride complexes.[15,20] To systematically compare the structural and acidity properties of ruthenium and osmium

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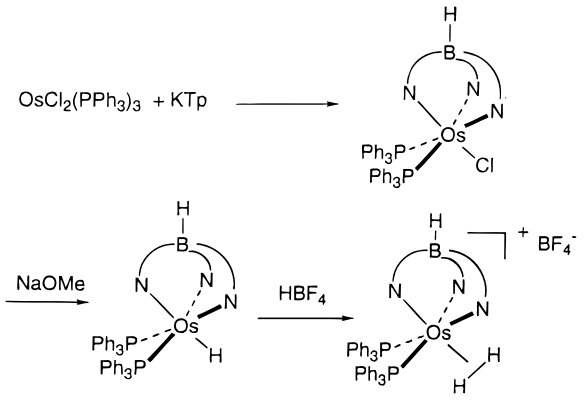
Scheme 1



hydride complexes, we have synthesized the new dihydrogen complex $[TpOs(H_2)(PPh_3)_2]BF_4$ and investigated the acidity properties of this complex and *trans*-$[CpOsH_2(PR_3)_2]BF_4$ ($(PR_3)_2 = (PPh_3)_2$, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), and $Ph_2P(CH_2)_3PPh_2$ (dppp)). The results obtained here, together with those of ruthenium complexes, allow us to see how the structural and acidity properties of these hydride complexes are varied when ruthenium is changed to osmium, Cp is changed to Tp, and the size of the chelating ring is increased.

Results and Discussion

Synthesis and Characterization of $[TpOs(H_2)(PPh_3)_2]BF_4$. The dihydrogen complex $[TpOs(H_2)(PPh_3)_2]BF_4$ was synthesized according to the sequence shown in Scheme 1. Reaction of $OsCl_2(PPh_3)_3$ with KTp in 2-propanol produced the yellow compound $TpOsCl(PPh_3)_2$. Treatment of $TpOsCl(PPh_3)_2$ with NaOMe in methanol produced the monohydride complex $TpOsH(PPh_3)_2$, which upon protonation with $HBF_4 \cdot Et_2O$ in dichloromethane gave the molecular dihydrogen complex $[TpOs(H_2)(PPh_3)_2]BF_4$.

The existence of the η^2-H_2 moiety in $[TpOs(H_2)(PPh_3)_2]BF_4$ was confirmed by the variable-temperature T_1 measurements and the observation of a large $^1J(HD)$ value for the corresponding isotopomer $[TpOs(HD)(PPh_3)_2]BF_4$.[21] The ^1H NMR spectrum of $[TpOs(H_2)(PPh_3)_2]BF_4$ in CD_2Cl_2 showed a broad hydride signal ($w_{1/2} = 31$ Hz, at room temperature) at δ −7.10 ppm. A minimum T_1 value of 31.3 ms (400 MHz) was obtained for the broad signal at −7.10 ppm, assignable to $Os(H_2)$, at 231 K. Acidification of $TpOsH(PPh_3)_2$ with DBF_4 gave the η^2-HD isotopomer $[TpOs(HD)(PPh_3)_2]BF_4$, which showed a 1:1:1 triplet ($^1J(HD) = 24.8$ Hz) of a 1:2:1 triplet ($^2J(HP) = 8.8$ Hz) centered at δ −7.12 ppm in the ^1H NMR spectrum.

The related osmium hydridotris(pyrazolyl)borate dihydrogen complex $[TpOs(H_2)(CO)(P(i\text{-}Pr)_3)]BF_4$ has been reported recently.[15] It is interesting to note that although Cp^- and Tp^- are both $6e^-$ donors, *trans*-$[CpOsH_2(PPh_3)_2]^+$ and *trans*-$[CpOsH_2(CO)(P(i\text{-}Pr)_3)]^+$ are classical dihydride complexes, but the analogous Tp complexes $[TpOs(H_2)(PPh_3)_2]^+$ and $[TpOs(H_2)(CO)(P(i\text{-}Pr)_3)]^+$ are dihydrogen complexes. That the Tp ligand has a higher tendency to stabilize the dihydrogen ligand relative to Cp has also been noted for other analogous Tp and Cp (or Cp*) complexes,[22−24] as exemplified by the structures of $Cp^*RuH_3(PCy_3)$[25] vs $TpRuH(H_2)(PCy_3)$,[22] $[Cp^*IrH_3(PMe_3)]^+$ vs $[TpIrH(H_2)(PMe_3)]^+$,[23] and *trans*-$[CpRuH_2(PPh_3)_2]^+$ vs $[TpRu(H_2)PPh_3)_2]^+$.[16b]

The fact that *trans*-$[CpOsH_2(PPh_3)_2]^+$ is a classical dihydride complex but the analogous Tp complex $[TpOs(H_2)PPh_3)_2]^+$ is a dihydrogen complex may imply that the $[CpOs(PPh_3)_2]^+$ fragment is more electron rich than $[TpOs(PPh_3)_2]^+$. To assess the relative electron richness of the TpOs and CpOs fragments, we have studied the electrochemistry of $CpOsH(PPh_3)_2$ and $TpOsH(PPh_3)_2$ (see below). The experiments indeed indicate that $TpOsH(PPh_3)_2$ undergoes oxidation at a potential slightly less negative than that of $CpOsH(PPh_3)_2$. However, the difference in the oxidation potentials is small, and therefore $CpOsH(PPh_3)_2$ is only slightly more electron rich than $TpOsH(PPh_3)_2$. The small difference in the electron richness of the metal centers may not be the major cause for the structural difference. It has been suggested that the TpM fragment has strongly directional frontier orbitals to bind three additional ligands to form octahedral complexes, while cyclopentadienyl ligands are rather ineffective in promoting strongly directional frontier orbitals due to their symmetry and diffuse electron clouds.[26] Thus, CpM can form seven-coordinated complexes easily, but TpM has a low tendency to do so in order to achieve strong σ-bonding interaction with the other three ligands. This argument can at least partially account for *trans*-$[CpOsH_2(PPh_3)_2]^+$ being a classical dihydride complex (formally a seven-coordinate complex) and the analogous Tp complex $[TpOs(H_2)PPh_3)_2]^+$ being a dihydrogen complex (formally a six-coordinate complex).

Acidity Studies. In this study, the acidity properties of $[CpOsH_2(PR_3)_2)]BF_4$ ($(PR_3)_2 = (PPh_3)_2$, dppm, dppe, dppp) and $[TpOs(H_2)(PPh_3)_2]BF_4$ have been investigated. It has been shown that $[CpOsH_2(dppm)]BF_4$ and $[CpOsH_2(dppe)]BF_4$ exist as mixtures of cis and trans isomers and that $[CpOsH_2(PPh_3)_2]BF_4$ and $[CpOsH_2(dppp)]BF_4$ only adopt the trans form.[12] The relative acidities of the hydride complexes were investigated by studying the equilibrium shown in eq 1 in CD_2Cl_2 using

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Table 1. Determination of Relative Acidities of Osmium Hydride Complexes[a]

entry no.	MH_2^+	B	K_{eq}	$pK_a(MH_2^+)$
1	*trans*-$[CpOsH_2(dppm)]BF_4$	$CpRuH(PPh_3)_2$	0.020	10.0
2	*cis*-$[CpOsH_2(dppm)]BF_4$	$CpRuH(PPh_3)_2$	0.0025	10.9
3	*trans*-$[CpOsH_2(dppe)]BF_4$	$CpRuH(PPh_3)_2$	3.4×10^{-4}	11.8
4	*cis*-$[CpOsH_2(dppe)]BF_4$	$CpRuH(PPh_3)_2$	0.023	9.9
5	*trans*-$[CpOsH_2(dppp)]BF_4$	CpOsH(dppe)	0.023	13.4[b]
6	*trans*-$[CpOsH_2(PPh_3)_2]BF_4$	CpOsH(dppp)	1.0	13.4
7	$[TpOs(H_2)(PPh_3)_2]BF_4$	$CpRuH(PPh_3)_2$	0.29	8.8

[a] In CD_2Cl_2. The pK_a value of $[CpRuH_2(PPh_3)_2]BF_4$ was taken as 8.3. [b] In reference to *trans*-$[CpOsH_2(dppe)]BF_4$.

NMR spectroscopy. A similar approach has been used previously by other investigators.[15,20,27−31]

$$MH_2^+ + B \rightleftarrows MH + BH^+ \quad (1)$$

In principle, the pK_a values of MH_2^+ can be estimated if that of BH^+ is known by using the relationship $pK_a(MH_2^+) = pK_a(BH^+) + pK_{eq}$, where K_{eq} is the equilibrium constant. In this study, *trans*-$[CpRuH_2(PPh_3)_2]BF_4$ was used as the reference acid. The pseudo-aqueous pK_a value of *trans*-$[CpRuH_2(PPh_3)_2]BF_4$ has been estimated to be 8.3, in reference to the aqueous pK_a value of $HPCy_3^+$, from the equilibrium constant of the reaction of *trans*-$[CpRuH_2(PPh_3)_2]BF_4$ with PCy_3 in CD_2Cl_2.[6a] Equilibrium mixtures were obtained from the reactions of $[TpOs(H_2)(PPh_3)_2]BF_4$, $[CpOsH_2(dppm)]BF_4$, and $[CpOsH_2(dppe)]BF_4$ with $CpRuH(PPh_3)_2$. Therefore, the pseudo-aqueous pK_a values of $[TpOs(H_2)(PPh_3)_2]BF_4$, $[CpOsH_2(dppm)]BF_4$, and $[CpOsH_2(dppe)]BF_4$ could be easily obtained in reference to *trans*-$[CpRuH_2(PPh_3)_2]BF_4$. The complexes *trans*-$[CpOsH_2(PPh_3)_2]BF_4$ and *trans*-$[CpOsH_2(dppp)]BF_4$ must be significantly less acidic than *trans*-$[CpRuH_2(PPh_3)_2]BF_4$, as *trans*-$[CpRuH_2(PPh_3)_2]BF_4$ protonated $CpOsH(PPh_3)_2$ and CpOsH(dppp) completely. The pK_a value of *trans*-$[CpOsH_2(dppp)]BF_4$ was estimated in reference to *trans*-$[CpOsH_2(dppe)]BF_4$, from the equilibrium constant for the reaction of *trans*-$[CpOsH_2(dppp)]BF_4$ with CpOsH(dppe). The pK_a value of *trans*-$[CpOsH_2(PPh_3)_2]BF_4$ was in turn estimated in reference to *trans*-$[CpOsH_2(dppp)]BF_4$, from the equilibrium constant for the reaction of *trans*-$[CpOsH_2(PPh_3)_2]BF_4$ with CpOsH(dppp). The results are summarized in Table 1. The reliability of the equilibrium constants is indicated by the fact that similar equilibrium constants were obtained when the equilibria were approached from both sides. The internal consistency of the pK_a values has also been confirmed by cross experiments, for example, by the reactions of CpOsH(dppm) with $[CpOsH_2(dppe)]BF_4$ and $[CpOsH_2(dppp)]BF_4$, respectively.

It should be stressed that the pK_a values of the hydride complexes in CD_2Cl_2 were obtained on the basis of the pseudo-aqueous pK_a value of *trans*-$[CpRuH_2(PPh_3)_2]BF_4$. As the true pK_a of *trans*-$[CpRuH_2(PPh_3)_2]BF_4$ in CD_2Cl_2 or water is unknown, the pseudo-aqueous pK_a values of the hydride complexes may be different from the true pK_a values in CD_2Cl_2 or water. However, the pseudo-aqueous pK_a values can still provide valuable information on the relative acidities of the complexes in dichloromethane.

Electrochemistry. The acidity property of a metal hydride complex is related to the electron richness of the metal center, which can be probed by electrochemistry. Thus, we have collected the cyclic voltammograms of the neutral osmium complexes in dichloromethane. For comparison purposes, cyclic voltammograms of $LRuH(PPh_3)_2$ (L = Cp, Tp) have also been collected. Except for CpOsH(dppm) and CpOsH(dppe), which undergo irreversible oxidation, all the complexes gave partially reversible waves in our hands. The peak potentials for the hydride complexes obtained in this study are collected in Table 2. The E_{ox} values for $[CpOsH(PPh_3)_2]^+/CpOsH(PPh_3)_2$[13c,20] and $[CpRuH(PPh_3)_2]^+/CpRuH(PPh_3)_2$[5a,6b,13c] in solvents such as dichloroethane, THF, and acetonitrile have been previously reported. Our values in dichloromethane are close to the reported ones.

It has been suggested that Tp is more electron releasing than Cp.[17] The electrochemical data of $[LM(CO)_3]^-$ (M = Cr, Mo, W; L = Tp, Cp) and the IR data of $LMH(CO)_3$ (M = Cr, Mo, W, L = Tp, Cp) support this proposition.[30,31] However, there is evidence that this may not be always true. For example, complexes of the type $LRuX(CO)(PPh_3)$ ($X = Cl, CO^+, PMe_3^+, H$; L = Cp, Tp)[32] and $LMH(CO)P(i\text{-}Pr)_3$ (M = Ru, Os; L = Tp, Cp)[15] have very similar ν(CO) stretching frequencies; the ν(CO) stretching frequency of $CpRuCl(CO)(PPh_3)$ is actually lower than that of $TpRuCl(CO)(PPh_3)$.[32] Our electrochemistry data for $LMH(PPh_3)_2$ (M = Ru, Os) show that it is slightly easier to oxidize $CpMH(PPh_3)_2$ than $TpMH(PPh_3)_2$, which implies that Tp is slightly less electron releasing than Cp.

The complexes $CpOsH(Ph_2P(CH_2)_nPPh_2)$ become more susceptible to oxidation when the size of the chelating ring is increased. The order is probably not surprising, as the basicities of the chelating ligands increase in this order.[33] Similar trends have been observed for CpRuH(PP) (PP = dppm, dppe, dppp)[5a,6c] and $Fe(CO)_3(PP)$ (PP = dppp, dppm).[13c] The E_{ox} value of the PPh_3 complex $CpOsH(PPh_3)_2$ is similar to that of the dppp complex CpOsH(dppp). The observation is also similar to that observed for the analogous ruthenium complexes.[5a,6c]

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Table 2. pK_a Values, Oxidation Potentials, and Bond Energies of Selected Osmium and Ruthenium Complexes

entry no.	complex, MH_2^+	pK_a(MH_2^+)	E_{ox}(MH)[a]	BDE(MH_2^+)[b]
1	*trans*-[$CpOsH_2$(dppm)]BF_4	10.0	−0.16[c]	76.0 ± 3
2	*trans*-[$CpOsH_2$(dppe)]BF_4	11.8	−0.17[c]	78.2 ± 3
3	*trans*-$CpOsH_2$(dppp)]BF_4	13.4	−0.35[d]	76.3 ± 2
4	*trans*-[$CpOsH_2(PPh_3)_2$]BF_4	13.4	−0.38[d]	75.6 ± 2
5	*cis*-[$CpOsH_2$(dppm)]BF_4	10.9	−0.16[c]	77.7 ± 3
6	*cis*-[$CpOsH_2$(dppe)]BF_4	9.9	−0.17[c]	75.6 ± 3
7	[$TpOs(H_2)(PPh_3)_2$]BF_4	8.9	−0.22[d]	73.1 ± 2
8	*trans*-[$CpRuH_2(PPh_3)_2$]BF_4	8.3[e]	−0.36[d]	69.1 ± 2
9	[$TpRu(H_2)(PPh_3)_2$]BF_4	7.6[f]	−0.12[d]	73.6 ± 2

[a] Oxidation potential for the oxidation of MH in V vs Fc^+/Fc, measured by cyclic voltammetry in CH_2Cl_2 containing 0.10 M *n*-Bu_4NPF_6 with a scan rate of 100 mV/s. [b] Calculated using the equation BDE(MH_2^+) = 1.37pK_a(MH_2^+) + 23.06E_{ox}(MH) + 66 kcal/mol. The errors are estimated on the basis of the uncertainties of E_{ox} and pK_a values. [c] Irreversible peak. [d] Partially reversible peak, taken as the midpoint between anodic and cathodic peaks. [e] Reference 6a. [f] Reference 16b.

Estimation of M−H Bond Energy. The acidity of a protic acid HA is related to the ionization energy of A^- (which is in turn related to the oxidation potential of A^-) and the H−A bond energy. To better understand the acidity properties of the hydride complexes, we have estimated the metal−hydrogen bond energies. The pK_a value and M−H bond energy of a hydride complex MH_2^+ can be related to the oxidation potential (E_{ox}) of the deprotonated species MH using eq 2.[20,28b,34]

$$\text{BDE}(MH_2^+) = 1.37\text{p}K_a + 23.06E_{ox}(\text{MH}) + C(\text{kcal/mol}) \quad (2)$$

The constant *C* in eq 2, which is related to free energy changes for solvation of hydrogen atom, formation of hydrogen atom from H_2 gas, and transfer of proton from water to the solvent under consideration, is dependent on the choice of reference electrode and solvent in which the pK_a and E_{ox} values are measured. The constant has been estimated in solvents such as acetonitrile and DMSO.[34] In dichloromethane or THF solutions, a constant of 66 kcal/mol has been previously suggested, based on the pseudo-aqueous pK_a values of hydride complexes in the solvents.[20,28b]

Table 2 summarizes the estimated M−H bond energies of several hydride complexes using eq 2, where *C* was taken as 66 kcal/mol. The larger uncertainty occurs for dppm and dppe complexes due to the irreversibility of the oxidation peaks; the true values should be smaller than the estimated ones. The estimated M−H bond energies of [$CpMH_2(PPh_3)_2$]$^+$ (without considering the statistical difference) are all slightly larger than those reported by Angelici.[13c] For example, the Os−H bond energy of *trans*-[$CpOsH_2(PPh_3)_2$]$^+$ was estimated to be 75.6 kcal/mol in this work but was reported to be 73.6 kcal/mol by Angelici;[13c] the Ru−H bond energy of *trans*-[$CpRuH_2(PPh_3)_2$]$^+$ was estimated to be 69.1 kcal/mol but was reported to be 68.3 kcal/mol by Angelici.[13c] The choices of the constant *C* in eq 2 may contribute to the slight difference in the estimated bond energies.

Comments on the Acidity Properties. The pseudo-aqueous pK_a values indicate that [$TpM(H_2)(PPh_3)_2$]$^+$ species (M = Ru, Os) are more acidic than [$CpM(H_2)(PPh_3)_2$]$^+$, which is consistent with the relative electron richness of the metal centers as indicated by electrochemistry. The group 6 complexes $TpMH(CO)_3$ (M = Cr, Mo, W) are also found to be more acidic than $CpMH(CO)_3$ (M = Cr, Mo, W).[30,31]

As stated previously, [$CpOsH_2$(dppm)]$^+$ and [$CpOsH_2$(dppe]$^+$ exist as mixtures of cis and trans isomers, whereas [$CpOsH_2(PPh_3)_2$)]$^+$ and [$CpOsH_2$(dppp)]$^+$ exist only in the trans form.[12] The pseudo-aqueous pK_a values indicate that the acidities of *trans*-[$CpOsH_2$(PP)]BF_4 (PP = dppm, dppe, dppp) decrease as the size of the chelating ring increases. The trend in the acidity is in line with the relative electron-donating ability of the chelating ligands. Such a trend has also been observed for *trans*-[$CpRuH_2$(PP)]BF_4 (PP = dppm, dppe, dppp),[6b] *trans*-[Cp*RuH_2(PP)]BF_4 (PP = dppm, dppp),[6c] and [$CpOsHBr$(PP)]BF_4 (PP = dppm, dppp).[13a] The change in the pK_a values of *trans*-[$CpOsH_2$(PP)]BF_4 upon variation of the chelating ring is larger than that observed for the analogous ruthenium complexes *trans*-[$CpRuH_2$(PP)]BF_4.[6b] For both ruthenium and osmium complexes, those containing PPh_3 have acidities comparable to those supported by dppp.

cis-[$CpOsH_2$(dppm)]BF_4 has been proved to be less acidic than *cis*-[$CpOsH_2$(dppe)]BF_4. Increases in the acidity with increasing chelating ring size has also been observed for [$CpRu(H_2)$(PP)]$^+$ (PP = dppm, dppe),[6b] [$RuCl(H_2)(PP)_2$]$^+$ (PP = dppe,[28c] dppp[27]), [$FeH(CO)_2$(PP)]$^+$,[18] and [$MH(CO)_2(PP)_2$]$^+$ (M = Mo, W).[19] The trend in the acidities of the metal complexes is opposite to that expected from the basicities of the chelating ligands. For [$FeH(CO)_3$(PP)]$^+$ and [$MH(CO)_2(PP)_2$]$^+$ (M = Mo, W), a steric effect has been proposed as the cause for the increased acidity of metal complexes with larger chelating rings.[18,19]

The pseudo-aqueous pK_a values of the osmium complexes are consistently larger than those of the corresponding ruthenium analogues. These results are not unusual, as the acidity of closely related complexes generally decreases on going down a group.[35] It is interesting to note that the difference in the pK_a values of [$TpM(H_2)(PPh_3)_2$]BF_4 (M = Ru, Os; ΔpK_a = 1.3) is smaller than that of the Cp analogues *trans*-[$CpMH_2(PPh_3)_2$]BF_4 (M = Ru, Os; ΔpK_a = 5.1). The difference in the metal effect could be at least partially attributed to the stronger H−H bonding in the TpRu complex. The

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stronger H−H bonding in $[TpRu(H_2)(PPh_3)_2]BF_4$ is indicated by the $^1J(HD)$ coupling constants for the isotopomers $[TpM(HD)(PPh_3)_2]BF_4$ (32.0 Hz, M = Ru; 24.8 Hz, M = Os).[16b] The idea is supported by the estimated M−H bond energy. As shown in Table 2, the estimated Ru−H bond energy for $[TpRu(H_2)(PPh_3)_2]BF_4$ (73.6 kcal/mol) is comparable to or slightly larger than the estimated Os−H bond energy for $[TpOs(H_2)(PPh_3)_2]BF_4$. For isostructural classic hydride complexes (for example, *trans*-$[CpMH_2(PPh_3)_2]^+$), Os−H bonds are usually stronger than Ru−H bonds. The relatively larger Ru−H bond energy in $[TpRu(H_2)(PPh_3)_2]BF_4$ could be attributed to the stronger H−H interaction in the ruthenium complex. The effect of H−H bonding on acidity has been noted previously.[20] In fact, the effect of H−H interaction in $[MH(H_2)(dppe)_2]^+$ on the acidity appears to be so important that the pK_a values of the dihydrogen complexes $[MH(H_2)(dppe)_2]^+$ are on the order of Fe < Os < Ru, due to the presence of strong H−H bonding in the ruthenium complex.

Experimental Section

All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under dinitrogen from sodium−benzophenone (hexane, diethyl ether, THF), sodium (benzene), and calcium hydride (dichloromethane). The complexes $OsCl_2(PPh_3)_3$,[36] KTp,[37] $CpRuH(PPh_3)_2$,[38] $[CpRuH_2(PPh_3)_2]BF_4$,[9] $CpOsH(PR_3)_2$ ($(PR_3)_2$ = $(PPh_3)_2$, dppm, dppe, dppp),[12] and $[CpOsH(PR_3)_2]BF_4$ ($(PR_3)_2$ = $(PPh_3)_2$, dppm, dppe, dppp)[12,14] were prepared according to literature methods. All other reagents were used as purchased from Aldrich.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H and ^{31}P{^{1}H} NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 (300 MHz) or DPX-400 spectrometer (400 MHz). ^{1}H chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

The electrochemical measurements were performed with a PAR Model 273 potentiostat. A two-component electrochemical cell was used with a glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, and a Ag/$AgNO_3$ (0.1 M in CH_3CN) electrode as the reference electrode. The cyclic voltammograms were collected with a scan rate of 100 mV/s in CH_2Cl_2 containing 0.10 M n-Bu_4NPF_6 as the supporting electrolyte. Ferrocene was added as the internal standard, and the peak potentials reported were referenced to ferrocenium/ferrocene ($Cp_2Fe^{+/0}$).

$TpOsCl(PPh_3)_2$. Samples of 0.25 g (0.25 mmol) of $OsCl_2(PPh_3)_3$ and 0.93 g (0.37 mmol) of K[Tp] were added to a two-necked round-bottom flask. The setup was evacuated and flushed with nitrogen. Degassed 2-propanol (30 mL) was added through a syringe, and the suspension was stirred for 2 days, during which time the green suspension gradually turned to yellow. At the end of the reaction, the yellow solid was collected by filtration under nitrogen. The solid was washed with a few portions of degassed methanol and then dried under vacuum for 8 h. Yield: 0.23 g (98%). IR (KBr, cm^{-1}): ν(B−H) 2480 (br med). ^{1}H NMR ($CDCl_3$, 20 °C): δ 5.13 [d, 1 H, H^5(pz′)], 5.64 [s, 2 H, H^4(pz)], 6.80 [d, 2H, H^5(pz)], 7.1 [m, 30 H, PPh_3], 7.46 [d, 2 H, H^3(pz)], 7.48 [d, 1 H, H^3(pz′)], (pz = pyrazole trans to PPh_3; pz′ = pyrazole trans to Cl; all coupling constants for pyrazolyl proton resonances, if measurable, were about 2 Hz (1.5−2.4 Hz)). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ −9.5. FAB-MS (nba matrix): m/z 964 [M$^+$]. Anal. Calcd for $C_{45}H_{40}BClN_6P_2Os$: C, 56.11; H, 4.19; N, 8.72. Found: C, 55.93; H, 4.35; N, 8.69.

$TpOsH(PPh_3)_2$. A sample of 0.37 g (0.39 mmol) of $TpOsCl(PPh_3)_2$ was added to a two-necked round-bottom flask fitted with a condenser, and the system was evacuated and flushed with nitrogen. A degassed solution of sodium methoxide in methanol (0.1 g Na in 6 mL degassed methanol) was added through a syringe. The resulting suspension was refluxed for 5 days. After the mixture was cooled to room temperature, a pale yellow solid settled down and it was filtered under nitrogen. The solid was washed with a few portions of degassed methanol. Finally, the crude product thus obtained was extracted with degassed acetone, the extract was brought to dryness, and the solid obtained was further dried under vacuum for 8 h. Yield: 0.21 g (75%). IR (KBr, cm^{-1}): ν(B−H) 2482 (br med); ν(Os−H) 2062 (sh, med). ^{1}H NMR (CD_2Cl_2, 20 °C): δ −15.65 [t, ^2J(P, H) = 18.4 Hz, 1 H, OsH], 5.04 [d, 1 H, H^5(pz′)], 5.08 [t, 1H, H^4(pz′)], 5.56 [d, 2 H, H^5(pz)], 6.70 [s, 2 H, H^4(pz)], 7.1 [m, 30 H, PPh_3], 7.42 [d, 2 H, H^3(pz)], 7.43 [d, 1 H, H^3(pz′)] (pz = pyrazole trans to PPh_3; pz′ = pyrazole trans to H; all coupling constants for pyrazolyl proton resonances, if measurable, were about 2 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 20.7. FAB-MS (nba matrix): m/z 930 [M$^+$]. Anal. Calcd for $C_{45}H_{41}BN_6P_2Os$: C, 58.19; H, 4.45; N, 9.05. Found: C, 58.25; H, 4.53; N, 9.14.

$[TpOs(H_2)(PPh_3)_2]BF_4$. In Situ. A 5 mm NMR tube which was filled with nitrogen was charged with ca. 6.6 mg (0.007 mmol) of $TpOsH(PPh_3)_2$ and 0.5 mL of degassed CD_2Cl_2. A stoichiometric amount of tetrafluoroboric acid (0.97 μL, 0.007 mmol, 54% in diethyl ether) was added at −60 °C, the tube was capped with a rubber septum, and the NMR spectrum of the solution was measured immediately.

Preparative. A sample of $TpOsH(PPh_3)_2$ (0.10 g, 0.10 mmol) was dissolved in degassed THF (20 mL) to give a yellow solution. Tetrafluoroboric acid (13.8 μL, 0.10 mmol, 54% in diethyl ether) was added at room temperature to give a white precipitate. The reaction mixture was further stirred for 15 min. The product was collected by filtration, washed with hexane, and dried under vacuum. Yield: 93 mg, 85%. Mass spectrum (EI, 10% CH_3OH in CH_2Cl_2): m/z 929 [M − H_2]$^+$, 961 [M − CH_3OH − H_2]$^+$. ^{1}H NMR (CD_2Cl_2, 20 °C): δ −7.07 [br t, ^2J(HP) = 8.2 Hz, 2 H, Os(H_2)], 5.65 [br s, 3 H, H^4(pz)], 6.25 [br s, 3 H, H^5(pz)], 6.98−7.36 [m, 30 H, PPh_3], 7.61 [br s, 3 H, H^3(pz)]. ^{1}H NMR (CD_2Cl_2, −60 °C): δ −7.10 [br, $w_{1/2}$ = 31 Hz, 2 H, Os(H_2)], 5.39 [t, 1 H, H^4(pz′)], 5.65 [d, 1 H, H^5(pz′)], 5.69 [t, 2 H, H^4(pz)], 6.30 [d, 2 H, H^5(pz)], 6.91 [m, 30 H, PPh_3], 7.55 [d, 2 H, H^3(pz)], 7.66 [d, 1 H, H^3(pz′)] (pz = pyrazole trans to PPh_3; pz′ = pyrazole trans to H_2; all coupling constants for pyrazolyl proton resonances, if measurable, were about 2 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, − 60 °C): δ 6.52. Variable-temperature T_1 measurements on the broad hydride signal were taken using the inversion recovery method. T_1 (400 MHz, ms): 34.4 (213 K), 31.9 (223 K), 31.3 (233 K), 31.8 (243 K), 31.7 (348 K), 33.9 (253 K), 36.8 (263 K), 45.8 (283 K), 51.3 (293 K). T_1(min) (400 MHz, 231 K): 31.3 ms.

$[TpOs(HD)(PPh_3)_2]BF_4$. Preparation of the HD isotopomer was analogous to that of $[TpOs(H_2)(PPh_3)_2]BF_4$, except that DBF_4, which was prepared by mixing HBF_4·Et_2O with D_2O in a volume ratio of 3:1, was used in place of HBF_4·Et_2O. The η^2-HD signal was observed after nulling the η^2-H_2 peak by the inversion recovery method. ^{1}H NMR (CD_2Cl_2, 20 °C): δ −7.12 (1:1:1 t, 1 H, J(HD) = 24.8 Hz, J(HP) = 8.8 Hz, Os(HD)). ^{31}P NMR (CD_2Cl_2, −60 °C): δ 6.45.

Acidity Measurement. In a typical experiment, appropriate amounts of a neutral hydride complex and a cationic

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hydride complex were loaded into an NMR tube; then CD_2Cl_2 was added. After a suitable period of time, ^1H and ^{31}P NMR spectra were collected. The equilibrium is confirmed by monitoring the reactions with NMR spectroscopy. By measuring the intensity of the hydride signals in the ^1H NMR spectra, one can estimate the relative concentrations of species in equilibrium and therefore the equilibrium constants. The pK_a values of the cationic hydride complexes were calculated on the basis of the assumption that the pK_a value of $[CpRuH_2(PPh_3)_2]^+$ is 8.3 in dichloromethane.

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