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Ligand and Metal Effects on the Enthalpies of Protonation of $Cp'M(PR_3)(PR'_3)X$ Complexes (M = Ru or Os)

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Abstract: Titration calorimetry has been used to determine the enthalpies of protonation (ΔH_{HM}) of 22 $Cp'M(PR_3)(PR'_3)X$ complexes ($Cp' = \eta^5\text{-}C_5H_5(Cp)$ or $\eta^5\text{-}C_5Me_5(Cp^*)$; M = Ru, Os; $PR_3 = PPh_3$, PPh_2Me, $PPhMe_2$, PMe_3, $P(OEt)_3$, dppm, dppe, dppp; X = H, Cl, Br, I) with CF_3SO_3H in 1,2-dichloroethane solution at 25.0 °C to give $Cp'M(PR_3)(PR'_3)(X)(H)^+CF_3SO_3^-$. Systematically changing the ligands and/or the metal in these complexes has yielded ΔH_{HM} values for protonation at the metal that range from −14.1 kcal/mol for $CpOs(PPh_3)_2I$ to −39.2 kcal/mol for $CpOs(PPh_2Me)_2H$. Metal basicities (ΔH_{HM}) of the $CpOs(PPh_3)_2X$ complexes correlate linearly with the gas-phase proton affinities of the X^- ligands, both of which increase in the following order: $I^- < Br^- < Cl^- \ll H^-$. Substitution of a halide ligand with a hydride causes the metal basicity to increase by as much as 23.2 kcal/mol. The basicities of $CpOs(PPh_3)(PR_3)Br$ complexes increase in the following order: $P(OEt)_3 < PPh_3 < PMe_3$. There is a linear correlation between the basicities (ΔH_{HM}) of the $CpOs(PR_3)_2Br$ complexes and the basicities (ΔH_{HP}) of their PR_3 ligands. In a series of complexes, the Cp* ligand increases the basicity of the metal by 5.5–9.0 kcal/mol over that of the corresponding Cp derivative, and Os complexes are 6.0–8.5 kcal/mol more basic than analogous Ru complexes. Basicities of the $CpOs(PR_3)_2(Br)$ and $CpRu(PR_3)_2(H)$ complexes are reduced when the protonated product is contrained to have the *cis*, rather than *trans*, structure by a small-ring chelating diphosphine ligand (dppm). These studies demonstrate that the metal, ligands, and geometry of the protonated product all substantially affect the heats of protonation (ΔH_{HM}) of $Cp'M(PR_3)(PR'_3)X$ complexes.

Introduction

There is currently much interest in quantitative relationships between properties of ligands and their transition metal complexes. Several studies[1] of ligand effects on spectroscopic, electrochemical, and kinetic properties of complexes have been reported. Especially relevant for this present paper are investigations of the acidity of transition metal hydrides.[2] For example, Norton and co-workers have determined pK_a values of organometallic complexes such as $HMn(CO)_4(PR_3)$,[3] $HCo(CO)_3(PR_3)$,[4] and $CpM(CO)_3H$ ($Cp = \eta^5\text{-}C_5H_5$; M = Cr, Mo, W).[5] Oxidation potentials of transition metal hydrides have been used to calculate acidities of the corresponding 17e⁻ hydride radical cations such as $Cp'M(CO)_2(L)H^{\bullet+}$ ($Cp' = C_5H_5(Cp)$, $C_5Me_5(Cp^*)$; M = Cr, Mo, W; L = PMe_3, PPh_3, $P(OMe)_3$, PEt_3, CO),[6] while Morris et al.[7] have determined pK_a values of $Cp'Ru(\overset{\frown}{P\ P})H_2^+$ (Cp′ = Cp, Cp*) complexes.

In these laboratories, we have determined the effects of ligand basicities on the basicities of their metal complexes, as measured by the enthalpies of protonation (ΔH_{HM}) with CF_3SO_3H in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1).[8] The basicities of phosphine ligands (PR_3) were measured by their heats of protonation (ΔH_{HP}, eq 2) under the same conditions. Excellent

$$ML_n + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} HML_n^+CF_3SO_3^-;\quad \Delta H_{HM} \qquad (1)$$

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} HPR_3^+CF_3SO_3^-;\quad \Delta H_{HP} \qquad (2)$$

linear correlations are observed between ΔH_{HM} and ΔH_{HP} values for the following series of phosphine complexes; $CpIr(CO)(PR_3)$,[9] $Fe(CO)_3(PR_3)_2$,[9] and $W(CO)_3(PR_3)_3$.[10] Similarly, increasing the number of methyl groups in the η^5-cyclopentadienyl ligand of $(\eta^5\text{-}C_5Me_xH_{5-x})Ir(COD)$,[11] where COD is 1,5-cyclooctadiene, increases the basicity (ΔH_{HM}) of the metal. In a recent communication[12] we noted that the basicities (ΔH_{HM}) of $CpOs(PR_3)_2X$ ($PR_3 = PPh_3$, PPh_2Me; X = Cl, Br, I, H) increase with changes in the X ligand in the following order: I < Br < Cl ≪ H. The most remarkable finding was that the hydride complexes are up to 23.2 kcal/mol more basic than the corresponding halide complexes. In this paper we expand upon that study to include 22 $Cp'M(PR_3)_2X$ complexes (eq 3), where the metal and the X, PR_3, and Cp′ (Cp′ = Cp or Cp*) ligands are systematically varied.

Experimental Section

All preparative reactions were carried out under an argon atmosphere following standard Schlenk techniques. The 1.0 M PMe_3 in toluene and neat PMe_3 were purchased and used as received from Aldrich. Hexanes

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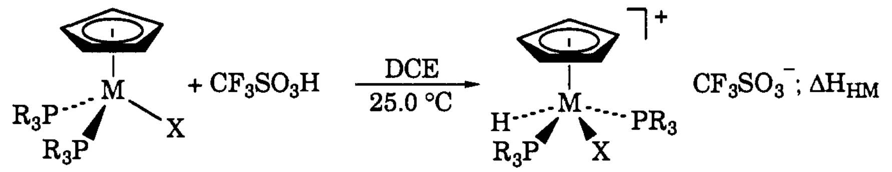

(3)

1-22 **$1H^+$-$22H^+$**

complex	M	PR_3	X	complex	M	PR_3	X	complex	M	PR_3	X
1, $1H^+$	Os	2 PPh_3	Cl	**9, $9H^+$**	Os	PPh_3, PMe_3	Br	**16, $16H^+$**	Ru	2 PMe_3	I
2, $2H^+$	Os	2 PPh_3	Br	**10, $10H^+$**	Os	2 PMe_3	I	**17, $17H^+$**	Ru	2 PPh_3	H
3, $3H^+$	Os	2 PPh_3	I	**11, $11H^+$**	Os	PPh_3, $P(OEt)_3$	H	**18, $18H^+$**	Ru*	2 PMe_3	Cl
4, $4H^+$	Os	2 PPh_3	H	**12, $12H^{+,a}$**	Os	dppm	Br	**19, $19H^+$**	Ru*	2 PPh_3	H
5, $5H^+$	Os	2 PPh_2Me	Br	**13, $13H^+$**	Os	dppp	Br	**20, $20H^{+,a}$**	Ru	dppm	H
6, $6H^+$	Os	2 PPh_2Me	H	**14, $14H^+$**	Ru	2 PMe_3	Cl	**21, $21H^{+,b}$**	Ru	dppe	H
7, $7H^+$	Os	2 $PPhMe_2$	Br	**15, $15H^+$**	Ru	2 PMe_3	Br	**22, $22H^+$**	Ru	dppp	H
8, $8H^+$	Os	2 PMe_3	Br					*=Cp* analog; all other complexes are Cp.			

[a] **$12H^+$** and **$20H^+$** have *cis*-$CpOs(dppm)(\eta^2\text{-}H_2)^+$ and *cis*-$CpRu(dppm)(\eta^2\text{-}H_2)^+$ structures, rather than the *trans* structure shown in eq 3. [b] **$21H^+$** exists as an equilibrium mixture of *trans*-$CpRu(dppe)(H)_2^+$ and *cis*-$CpRu(dppe)(\eta^2\text{-}H_2)^+$. See Results.

and CH_2Cl_2 were refluxed over CaH_2 and then distilled under N_2. Diethyl ether was purified by distillation from Na/benzophenone under N_2; the 1,2-dichloroethane solvent (99.8%, HPLC Grade) was purchased from Aldrich and was distilled from P_4O_{10} under argon immediately prior to use. The CF_3SO_3H was purchased from 3M Co. and purified as previously described.[8] Ethanol and methanol were dried over magnesium alkoxide according to the procedure given by Perrin et al.,[13] while decahydronaphthalene (decalin) was degassed with $N_2(g)$ and then stored over molecular sieves for 12 h before use. Deuterated solvents (CD_2Cl_2 and $CDCl_3$) were stored over molecular sieves in air. Brockman, activity I, neutral Al_2O_3 was deoxygenated for 18 h at room temperature under high vacuum, deactivated with 5% (w/w) Ar-saturated water, and stored under argon.

The ^1H NMR spectra were recorded in $CDCl_3$ unless otherwise noted with a Nicolet-NT 300 MHz or Varian VXR-300 MHz spectrometer with TMS (δ = 0.00 ppm) as the internal standard. T_1 values were determined by using the standard inversion recovery sequence 180–τ–90.[14] The $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer in CD_2Cl_2 with 85% phosphoric acid (δ = 0.00 ppm) as the external standard. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN, or Desert Analytics, Tuscon, AZ.

Syntheses of $CpOs(PPh_3)_2X$ (X = Cl (**1**),[15] Br (**2**),[16] I (**3**),[15] H (**4**)[17]), $CpRu(PMe_3)_2X$ (X = Cl (**14**), Br (**15**), I (**16**),[18] $CpRu(PPh_3)_2H$ (**17**),[17] $Cp^*Ru(PMe_3)_2Cl$ (**18**),[19] $Cp^*Ru(PPh_3)_2H$ (**19**),[7a] $CpRu(\overset{\frown}{P\ P})H$ ($\overset{\frown}{P\ P}$ = dppm (**20**), dppe (**21**), dppp (**22**)),[17] and CpOs(dppm)Br (**12**)[20] were carried out according to the cited literature procedures. Ligand abbreviations are dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, and dppp = $Ph_2PCH_2CH_2CH_2PPh_2$.

$CpOs(PMe_3)_2Br$ (8).[21] A suspension of $CpOs(PPh_3)_2Br$ (460 mg, 0.54 mmol) and neat PMe_3 (1.0 mL, 9.7 mmol) in 20 mL of decalin was heated to reflux for 12 h. The solution was cooled to room temperature and then placed on an alumina column (1.5 × 30 cm) packed in hexanes. The decalin and excess phosphines were eluted with 150 mL of hexanes. The desired yellow product was eluted with CH_2Cl_2; the solvent was then removed under vacuum. The residue was recrystallized by dissolving it in a minimum of CH_2Cl_2; this solution was layered with a 10-fold excess of hexanes, and the mixture was cooled to −20 °C for 24 h to yield orange crystals of $CpOs(PMe_3)_2Br$ (**8**) (150 mg, 66%). ^1H NMR ($CDCl_3$) δ 4.58 (s, 5H, Cp), 1.66 (d, $^2J_{PH}$ = 8.7 Hz, 18H, Me).

The following compounds were prepared in a manner similar to that used for **8**. Superscripts refer to literature preparations of the complexes by similar routes.

$CpOs(PPh_2Me)_2Br$ (5):[21b,c] 300 mg (0.35 mmol) of $CpOs(PPh_3)_2Br$ and 0.40 mL (2.1 mmol) of PPh_2Me in 20 mL of decalin; reaction time 12 h; yield 84%. ^1H NMR ($CDCl_3$) δ 7.1–7.3 (m, Ph), 4.51 (s, 5H, Cp), 1.72 (d, $^2J_{PH}$ = 8.1 Hz, 6H, CH_3). Anal. Calcd for $C_{31}H_{31}BrOsP_2$: C, 50.61; H, 4.25. Found: C, 50.23; H, 4.47.

$CpOs(PPhMe_2)_2Br$ (7):[21b,c] 200 mg (0.23 mmol) of $CpOs(PPh_3)_2Br$ and 0.20 mL (1.4 mmol) of $PPhMe_2$ in 20 mL of decalin; reaction time 12 h; yield, 66%. ^1H NMR ($CDCl_3$) δ 7.3–7.1 (m, Ph), 4.50 (s, 5H, Cp), 1.72 (d, $^2J_{PH}$ = 8.1 Hz, 12H, CH_3).

$CpOs(PPh_3)(PMe_3)Br$ (9):[21b,c] 200 mg (0.23 mmol) of $CpOs(PPh_3)_2Br$ and 1.0 mL (1.0 mmol) of PMe_3 (1.0 M solution in toluene) in 20 mL of toluene; reaction time 12 h; yield, 54%. ^1H NMR ($CDCl_3$) δ 7.3–7.1 (m, Ph), 4.47 (s, 5H, Cp), 1.39 (d, $^2J_{PH}$ = 9 Hz, 9H, CH_3). Anal. Calcd for $C_{26}H_{29}BrOsP_2$: C, 46.37; H, 4.34. Found: C, 46.61; H, 4.36.

$CpOs(PMe_3)_2I$ (10): 236 mg (0.23 mmol) of $CpOs(PPh_3)_2I$ and 5 mL (5.0 mmol) of PMe_3 (1.0 M solution in toluene) in 40 mL of decalin; reaction time 6 h; yield, 72%. ^1H NMR ($CDCl_3$) δ 4.59 (s, 5H, Cp), 1.72 (virtual t, $^2J_{PH}$ = 8.7 Hz, 18H, CH_3). Anal. Calcd for $C_{11}H_{23}IOsP_2$: C, 24.92; H, 4.33. Found: C, 25.12; H, 4.57.

CpOs(dppp)Br (13). Complex **13** was prepared from $CpOs(PPh_3)_2Br$ (100 mg, 0.12 mmol) and dppp (50 mg, 0.12 mmol) in a manner exactly like that used for CpOs(dppm)Br:[20] yield, 50-80%. ^1H NMR ($CDCl_3$) δ 7.5–7.1 (m, Ph), 4.58 (s, 5H, Cp), 3.08 (m, 2H, CH_2), 2.72 (m, 2H, CH_2), 2.45 (m, 1H, CH_2), 1.72 (m, 1H, CH_2). Anal. Calcd for $C_{32}H_{31}BrOsP_2$: C, 51.41; H, 4.18. Found: C, 50.94; H, 4.26.

$CpOs(PPh_3)(P(OEt)_3)H$ (11). First, $CpOs(PPh_3)(P(OEt)_3)Br$ was prepared from $CpOs(PPh_3)_2Br$ (200 mg, 0.23 mmol) and $P(OEt)_3$ (164 μL, 0.96 mmol) in a manner exactly like that used for $CpOs(PPh_3)(P(OMe)_3)Br$:[20] reaction time, 3 h; yield, a yellow oil. ^1H NMR ($CDCl_3$) δ 7.5–7.3 (m, Ph), 4.60 (s, 5H, Cp), 3.81 (q, $^2J_{HH}$ = 6.9 Hz, 6H, CH_2), 1.06 (t, $^2J_{HH}$ = 6.9 Hz, 9H, CH_3). To the $CpOs(PPh_3)(P(OEt)_3)Br$ oil was added a NaOMe solution, which was prepared by allowing 70 mg (3.0 mmol) of Na to react completely with 20 mL of MeOH. After the solution was refluxed for 9 h, the volume was reduced to 3 mL in vacuo. The pale yellow precipitate tht formed was filtered,

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washed (2 × 1 mL of MeOH), and dried in vacuo (50% overall yield). ^1H NMR ($CDCl_3$) δ 7.4–7.2 (m, Ph), 4.54 (s, 5H, Cp), 3.5 (m, ^2J = 50 Hz, 6H, CH_2), 0.87 (t, $^2J_{HH}$ = 8.7 Hz, 9H, CH_3), −15.64 (dd, $^2J_{PH}$ = 31.5 and 27.6 Hz, 1H, Os–H). Anal. Calcd for $C_{29}H_{36}O_3OsP_2$: C, 50.86; H, 5.30. Found: C, 50.68; H, 5.54.

$CpOs(PPh_2Me)_2H$ (6). Complex **6** was prepared in a manner similar to that used for **11**: 200 mg (0.23 mmol) of $CpOs(PPh_2Me)_2Br$ added to a NaOMe solution prepared by reacting 70 mg (3.0 mmol) of Na with 40 mL of MeOH: reaction time, 3 h; yield, 87%. ^1H NMR ($CDCl_3$) δ 7.0–7.6 (m, 20H, Ph), 4.42 (s, 5H, Cp), 1.83 (d, $^2J_{PH}$ = 8.1 Hz, 6H, CH_3), −14.62 (t, $^2J_{PH}$ = 29.0 Hz, 1H, Os–H).

Preparation of $[CpOs(PPh_3)_2(H)_2]CF_3SO_3$ ($4H^+CF_3SO_3^-$).[15] The complex $CpOs(PPh_3)_2H$ (**4**) was prepared by reaction of 125 mg (0.15 mmol) of $CpOs(PPh_3)_2Br$ with a NaOMe solution, which was prepared by reacting 100 mg (4.3 mmol) of Na with 10 mL of MeOH. After the solution was refluxed for 1.5 h, the off-white precipitate was filtered from the cooled solution and washed with MeOH. This white solid (87 mg) was dissolved in Et_2O and protonated with 1.1 equiv (10.8 μL, 0.12 mmol) of CF_3SO_3H. After the solution was stirred for 5 min, the off-white precipitate was filtered and rinsed with Et_2O and dried in vacuo (50% overall yield). X-ray quality crystals were formed by dissolving **$4H^+CF_3SO_3^-$** in a minimal amount of CH_2Cl_2 and layering the solution with a 5-fold volume of hexanes; the resulting mixture was cooled to −20 °C for 4 days. Anal. Calcd for $C_{42}H_{37}F_3O_3OsP_2S$: C, 54.18; H, 4.01. Found: C, 53.98, H, 3.97.

Protonation Reactions. Compounds **1–22** were protonated for NMR characterization by dissolving ~5 mg of the complex in 0.5 mL of $CDCl_3$ (or CD_2Cl_2) in an NMR tube under Ar. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe through a rubber septum. Spectroscopic data at room temperature for compounds **$1H^+$–$22H^+$** are listed below.

$[CpOs(PPh_3)_2(Cl)(H)]CF_3SO_3$ ($1H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.43 (s, 5H, Cp), −11.66 (t, $^2J_{PH}$ = 32.4 Hz, 1H, Os–H).

$[CpOs(PPh_3)_2(Br)(H)]CF_3SO_3$ ($2H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.4 (m, Ph), 5.43 (s, 5H, Cp), −12.13 (t, $^2J_{PH}$ = 34.0 Hz, 1H, Os–H).

$[CpOs(PPh_3)_2(I)(H)]CF_3SO_3$ ($3H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.4 (m, Ph), 5.35 (s, 5H, Cp), −12.74 (t, $^2J_{PH}$ = 34.7 Hz, 1H, Os–H).

$[CpOs(PPh_3)_2(H)_2]CF_3SO_3$ ($4H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.06 (s, 5H, Cp), −11.46 (t, $^2J_{PH}$ = 29.0 Hz, 2H, Os–H).

$[CpOs(PPh_2Me)_2(Br)(H)]CF_3SO_3$ ($5H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.4 (m, Ph), 5.66 (s, 5H, Cp), 1.77 (d, $^2J_{PH}$ = 8.7 Hz, 6H, CH_3), −12.70 (t, $^2J_{PH}$ = 33.4 Hz, 1H, Os–H).

$[CpOs(PPh_2Me)_2(H)_2]CF_3SO_3$ ($6H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.3 (m, Ph), 5.14 (s, 5H, Cp), 2.06 (d, $^2J_{PH}$ = 8.7 Hz, 6H, CH_3), −12.57 (t, $^2J_{PH}$ = 30.6 Hz, 2H, Os–H).

$[CpOs(PPhMe_2)_2(Br)(H)]CF_3SO_3$ ($7H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.46 (s, 5H, Cp), 2.14 (d, $^2J_{PH}$ = 9 Hz, 6H, CH_3), 1.76 (d, $^2J_{PH}$ = 9 Hz, 6H, CH_3), −13.78 (t, $^2J_{PH}$ = 36.5 Hz, 1H, Os–H).

$[CpOs(PMe_3)_2(Br)(H)]CF_3SO_3$ ($8H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 5.74 (s, 5H, Cp), 1.95 (d, $^2J_{PH}$ = 10.5 Hz, 18H, CH_3), −14.34 (t, $^2J_{PH}$ = 36.2 Hz, 1H, Os–H).

$[CpOs(PPh_3)(PMe_3)(Br)(H)]CF_3SO_3$ ($9H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.5 (m, Ph), 5.64 (s, 5H, Cp), 1.55 (d, $^2J_{PH}$ = 11.7 Hz, 9H, CH_3), −13.98 (dd, $^2J_{PH}$ = 32.4 and 36.9 Hz, 1H, Os–H).

$[CpOs(PMe_3)_2(I)(H)]CF_3SO_3$ ($10H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 5.64 (s, 5H, Cp), 2.02 (virtual t, $^2J_{PH}$ = 8.4 Hz, 18H, CH_3), −15.33 (t, $^2J_{PH}$ = 37.3 Hz, 1H, Os–H).

$[CpOs(PPh_3)(P(OEt)_3)(H)_2]CF_3SO_3$ ($11H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.34 (s, 5H, Cp), 3.71 (pentet, ^2J = 7.0 Hz, 6H, CH_2), 1.06 (t, $^2J_{HH}$ = 7.0 Hz, 9H, CH_3), −12.26 (t, $^2J_{PH}$ = 30.2 Hz, 2H, Os–H).

$[CpOs(dppm)(Br)(H)]CF_3SO_3$ ($12H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.6 (m, Ph), 5.45 (s, 5H, Cp), 6.26 (dt, 1H, CH_2), 5.70 (dt, 1H, CH_2), −10.81 (s, 1H, Os–H).

$[CpOs(dppp)(Br)(H)]CF_3SO_3$ ($13H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.70 (s, 5H, Cp), 3.30 (dt, J = 6.3, 12.9 Hz, 2H, CH_2), 2.96 (m, 2H, CH_2), 2.22 (br m, 2H, CH_2), −12.49 (t, $^2J_{PH}$ = 32.7 Hz, 1H, Os–H).

$[CpRu(PMe_3)_2(Cl)(H)]CF_3SO_3$ ($14H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 5.52 (s, 5H, Cp), 1.77 (d, $^2J_{PH}$ = 9.9 Hz, 18H, CH_3), −9.52 (t, $^2J_{PH}$ = 30.0 Hz, 1H, Ru–H).

$[CpRu(PMe_3)_2(Br)(H)]CF_3SO_3$ ($15H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 5.53 (s, 5H, Cp), 1.88 (d, $^2J_{PH}$ = 10.2 Hz, 18H, CH_3), −9.48 (t, $^2J_{PH}$ = 29.4 Hz, 1H, Ru–H).

$[CpRu(PMe_3)_2(I)(H)]CF_3SO_3$ ($16H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 5.75 (s, 5H, Cp), 2.00 (d, $^2J_{PH}$ = 10.5 Hz, 18H, CH_3), −9.60 (t, $^2J_{PH}$ = 29.4 Hz, 1H, Ru–H).

$[CpRu(PPh_3)_2(H)_2]CF_3SO_3$ ($17H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.3 (m, Ph), 4.91 (s, 5H, Cp), −7.30 (t, $^2J_{PH}$ = 23.9 Hz, 2H, Ru–H).

$[Cp^*Ru(PMe_3)_2(Cl)(H)]CF_3SO_3$ ($18H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 1.83 (s, 15H, Cp*), 1.63 (d, $^2J_{PH}$ = 9.3 Hz, 18H, CH_3), −9.91 (t, $^2J_{PH}$ = 34.2 Hz, 1H, Ru–H).

$[Cp^*Ru(PPh_3)_2(H)_2]CF_3SO_3$ ($19H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.3 (m, Ph), 1.35 (s, 15H, Cp*), −7.29 (t, $^2J_{PH}$ = 26.5 Hz, 2H, Ru–H).

$[CpRu(dppm)(H_2)]CF_3SO_3$ ($20H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.4 (m, Ph), 5.18 (s, 5H, Cp), 5.35 (m, 1H, CH_2), 4.31 (m, 1H, CH_2), −6.98 (br s, 2H, Ru–(H_2)).

$[CpRu(dppe)(H)_2]CF_3SO_3$ ($21H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 7.4 (m, Ph), 5.18 (s, 5H, Cp of *trans* complex), 4.82 (s, 5H, Cp of *cis* complex), 2.50 (br s, 2H, CH_2 of *trans* complex), 2.45 (s, 2H, CH_2 of *cis* complex), −9.09 (br s, 2H, *cis*-Ru–(H_2)), −8.49 (t, $^2J_{PH}$ = 28.0 Hz, 2H, *trans*-Ru–H).

$[CpRu(dppp)(H)_2]CF_3SO_3$ ($22H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.4 (m, Ph), 5.01 (s, 5H, Cp), 2.89 (m, 2H, CH_2), 2.24 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), −8.70 (t, $^2J_{PH}$ = 25.7 Hz, 2H, Ru–H).

Calorimetric Titrations. Calorimetric titrations were performed under an argon atmosphere with a Tronac Model 458 isoperibol calorimeter as originally described[8] and then modified.[9] In general a 2-min titration period was used for all complexes except for **3**, which was run with a 3-min titration. The titration period was preceded and followed by heat capacity calibrations. During the titration period approximately 0.8 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE solvent was added at a constant rate to 50 mL of a 1.7 mM solution of the metal complex (5–10% excess) in DCE.

The heat of dilution (ΔH_{dil}) of the acid in DCE (−0.2 kcal/mol)[9] was used to correct the reaction enthalpies. The ΔH_{HM} values were obtained with use of two different standardized acid solutions and are reported as the average of at least four titrations and as many as eight. Errors are reported as the average deviation from the mean.

The combination of CF_3SO_3H and DCE used in these and previous ΔH_{HM} studies was chosen for the following reasons. Trifluoromethanesulfonic acid is one of the strongest acids known, $H_0 = -14.1$;[22] therefore, it protonates a large number of even weakly basic metal complexes. The $CF_3SO_3^-$ anion is weakly coordinating so it has a low tendency to displace other ligands from the protonated product. 1,2-Dichloroethane (DCE) has been chosen as the solvent for these and previous ΔH_{HM} studies because it is easily purified,[8] has low volatility (bp = 83 °C), is weakly coordinating, and is weakly basic so that it is not protonated by CF_3SO_3H. It also dissolves a broad range of neutral and protonated complexes. The low dielectric constant ($\epsilon = 10.46$)[23] for DCE means that the protonated ionic products occur as ion pairs. It has been estimated that dissociation of these ion pairs, autoprotolysis, and dimerization of CF_3SO_3H contribute little to the measured ΔH_{HM} values.[8] Solvation effects, which can be substantial in hydrogen bonding solvents,[24] are assumed to be very similar for protonation reactions of related complexes in this acid–solvent system. Evidence that solvation and ion-pairing effects are not major contributors come from ΔH_{HP} values for PMe_3 (−31.6 kcal/mol)[8] and $P(cyclohexyl)_3$ (−33.2 kcal/mol).[8] As alkyl-substituted phosphines, both would be expected to have similar ΔH_{HP} values. If the protonated phosphine HPR_3^+ were stabilized by ion-pairing or solvation, one would expect this stabilization to be greater for the smaller $HPMe_3^+$ than $HP(cyclohexyl)_3^+$, which would make PMe_3 more basic than $P(cyclohexyl)_3$. That $P(cyclohexyl)_3$, is, in fact, more basic than PMe_3 indicates that solvation and ion-pairing energies for these phosphines are similar in this system. Thus, trends in ΔH_{HM} values for these complexes are likely to be determined by the energetics of protonation rather than ion-pairing or solvation effects. In addition, there is an excellent correlation[8] between ΔH_{HP} values for phosphines in DCE and their pK_a values in water, which also suggests that solvation energies do not dominate trends in their basicities. Abboud et al.[25] report that "gas-phase like behavior" can

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Table I. Crystal and Data Collection Parameters for [*trans*-CpOs(PPh$_3$)$_2$(H)$_2$]CF$_3$SO$_3$ (**4**H$^+$)

formula	[OsP$_2$C$_{41}$H$_{32}$]$^+$[SO$_3$CF$_3$]$^-$CH$_2$Cl$_2$
space group	$P\bar{1}$
a, Å	11.346(2)
b, Å	13.061(2)
c, Å	14.108(2)
α, deg	80.24 (2)
β, deg	85.88(2)
γ, deg	75.11(2)
V, Å^3	1990.3(7)
Z	2
d_{calc}, g/cm^3	1.69
cryst size, mm	0.45 × 0.15 × 0.15
μ(Mo Kα), cm^{-1}	37.2
data collection instrument	Enraf-Nonius, CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
no. of orientation reflctns; range (2θ)	25; 17.4 < θ < 32.0
temp, °C.	-50(1)
scan method	θ–2θ
data collection range, 2θ, deg	4.0–50.0
no. of data collected:	7340
no. of unique data	
total	6672
with $F_o^2 > 3.0\sigma(F_o^2)$	5811
no. of parameters refined	504
trans factors; max; min (ψ-scans)	0.994, 0.875
R^a	0.028
R_w	0.036
quality-of-fit indicator^c	1.12
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	0.93(9)

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

prevail in solution chemistry for acid–base reactions if hydrogen bonding is minimized by using saturated hydrocarbons or CH$_2$Cl$_2$ as solvents.

Equilibrium Study and ΔH_{HM} Determination of 6. Due to small amounts of decomposition in the calorimeter that made the results unreliable, the ΔH_{HM} for complex **6** was determined from equilibrium constant (K_{eq}) measurements (eq 4) at different temperatures. An air-tight 5-mm NMR tube containing 13.1 mg (0.020 mmol) of **6**, 18.6 mg (0.020 mmol) of **4**H$^+$CF$_3$SO$_3^-$, and 0.5 mL of CD$_2$Cl$_2$ was allowed to equilibrate for 8 h. After 8 h, no changes in the spectrum occurred with time, indicating that equilibrium had been achieved. Relative concentrations of the species in solution were determined by integration of the Cp resonances of the reactants and products. Calculation of the K_{eq} was done with eq 5. The K_{eq} values measured at various temperatures were 15.4 (15.0 °C), 15.3 (20.0 °C), 15.1 (22.5 °C), 14.6 (25.0 °C), 14.2 (27.5 °C), 13.2 (30.0 °C), and 12.7 (35.0 °C).

$$\mathbf{4}\text{H}^+ + \mathbf{6} \overset{K_{eq}}{\rightleftharpoons} \mathbf{4} + \mathbf{6}\text{H}^+ \tag{4}$$

$$K_{eq} = \frac{[\text{CpOs(PPh}_3)_2\text{H } (\mathbf{4})][\text{CpOs(PPh}_2\text{Me)}_2(\text{H})_2{}^+ \ (\mathbf{6}\text{H}^+)]}{[\text{CpOs(PPh}_2\text{Me)}_2\text{H } (\mathbf{6})][\text{CpOs(PPh}_3)_2(\text{H})_2{}^+ \ (\mathbf{4}\text{H}^+)]} \tag{5}$$

X-ray Diffraction Study of [*trans*-CpOs(PPh$_3$)$_2$(H)$_2$]$^+$[CF$_3$SO$_3$]$^-$·CH$_2$Cl$_2$ (4H$^+$CF$_3$SO$_3^-$). A colorless crystal of **4**H$^+$CF$_3$SO$_3^-$ was mounted on a glass fiber for data collection at -50 ± 1 °C on an Enraf-Nonius CAD4 diffractometer. The cell constants for the data collection were determined from a list of reflections found by an automated search routine. Data collection and reduction information are given in Table I. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 3.0% was applied to the data. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the averaging of observed reflections was 1.6% based on F. The triclinic space group $P\bar{1}$ was determined by intensity statistics, and the structure was solved by direct methods.[26] Most non-hydrogen atoms were placed directly from the E-map. All remaining non-hydrogen atoms were found in one successive difference-Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were of the riding-model type, and the isotropic temperature factors were fixed at the accompanying carbon atom values. One molecule of dichloromethane was found per formula unit. The hydride atoms were located at 1.19 and 1.45 Å from the Os with use of a difference-Fourier map. Selected bond distances and angles for **4**H$^+$ are given in Table II. The ORTEP drawing of the cation **4**H$^+$ has the hydride atoms placed at 1.68 Å (discussed in the Results section) in Figure 1.

Table II. Selected Bond Distances (Å)^a and Angles (deg)^a for [*trans*-CpOs(PPh$_3$)$_2$(H)$_2$]$^+$ (**4**H$^+$)

Distances (Å)					
Os–P(1)	2.310(1)	Os–C(3)	2.230(5)	C(3)–C(4)	1.425(8)
Os–P(2)	2.310(1)	Os–C(4)	2.210(5)	C(4)–C(5)	1.418(7)
Os–Cp(cent)^b	1.89	Os–C(5)	2.226(5)	C(5)–C(1)	1.398(7)
Os–C(1)	2.260(5)	C(1)–C(2)	1.408(7)		
Os–C(2)	2.267(5)	C(2)–C(3)	1.411(7)		

Bond Angles (deg)			
P(1)–Os–P(2)	105.71(4)	P(2)–Os–H$_b$	77(2)
P(1)–Os–H$_a$	66(2)	H$_a$–Os–H$_b$	121(3)
P(1)–Os–H$_b$	71(2)	P(1)–Os–Cp(cent)^b	127
P(2)–Os–H$_a$	78(2)	P(2)–Os–Cp(cent)^b	127

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] cent = centroid of Cp ring.

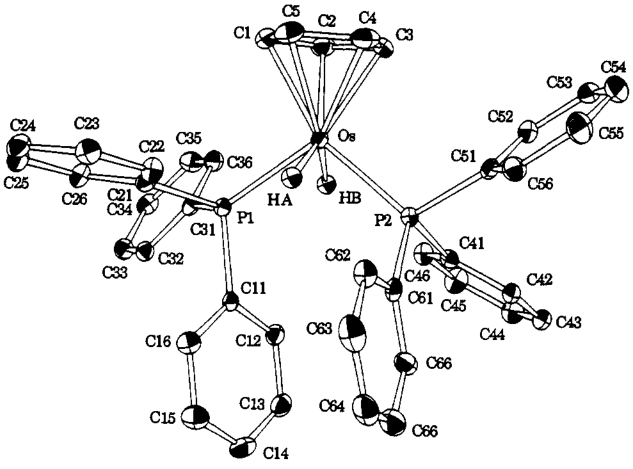

Figure 1. Molecular structure of *trans*-CpOs(PPh$_3$)$_2$(H)$_2{}^+$ (**4**H$^+$).

Results

Characterization of Complexes and Their Protonated Products. Complexes **1**–**22** have the three-legged piano-stool geometry (eq 3); X-ray structural studies of **1**[27] and **14**[28] show that there are approximately 90° angles between the PR$_3$ and X ligands. The complexes are slightly air-sensitive in the solid state, except for the osmium halides which are air-stable.

Quantitative formation of the four-legged piano-stool complexes **1**H$^+$–**22**H$^+$ occurs upon addition of 1 equiv of CF$_3$SO$_3$H to the neutral complexes **1**–**22** (eq 3) as evidenced by ^{1}H NMR spectroscopy. These protonated complexes are air-sensitive in solution; complex **4**H$^+$CF$_3$SO$_3^-$ was isolated as an off-white, air-stable solid. The ^{1}H NMR spectra of these complexes are the same as those of **2**H$^+$PF$_6^-$,[21a] **4**H$^+$BPh$_4^-$,[15] **8**H$^+$PF$_6^-$,[21a] **14**H$^+$PF$_6^-$,[28] **17**H$^+$BPh$_4^-$,[29] **18**H$^+$PF$_6^-$,[19] **19**H$^+$BF$_4^-$,[7b] and **20**H$^+$–**22**H$^+$PF$_6^-$,[30] which have previously been isolated and characterized.

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The *trans* configuration has previously been assigned to the protonated halide compounds **2H**$^+$,[21a] **8H**$^+$,[21a] and **14H**$^+$ [28] based on the triplet ($^2J_{PH}$ = 30.0–36.2 Hz) for the hydride ligand in their ^{1}H NMR spectra. The *trans* structure is also assigned to the halide complexes **1H**$^+$, **3H**$^+$, **5H**$^+$, **7H**$^+$, **9H**$^+$, **10H**$^+$, **13H**$^+$–**16H**$^+$, and **18H**$^+$, since the hydride resonances occur as triplets between −7.29 (**17H**$^+$) and −15.33 (**10H**$^+$) ppm with $^2J_{PH}$ coupling constants between 23.9 and 37.3 Hz. Although a doublet of doublets is expected for $CpOs(PPh_3)[P(OEt)_3](H)_2^+$ (**11H**$^+$), a triplet with a $^2J_{PH}$ coupling constant of 30.2 Hz is observed, which is similar to $^2J_{PH}$ values of the above complexes; apparently the $^2J_{PH}$ coupling constants for the phosphine and the phosphite ligands are similar. The complex $CpOs(PPh_3)(PMe_3)(Br)(H)^+$ (**9H**$^+$) does exhibit a doublet of doublets for the hydride resonance (−13.98 ppm, $^2J_{PH}$ = 32.4 and 26.9 Hz).

The dihydride complexes $Cp'Ru(PPh_3)_2(H)_2^+$ (Cp′ = Cp, **17H**$^+$ and Cp*, **19H**$^+$) were assigned the *trans* structure by Chinn and Heinekey[31] based on the two distinct ^{1}H NMR hydride ($^2J_{PH}$ = 29.4 and 30.7 Hz) signals observed for $CpRu[(R)\text{-}(+)\text{-}Ph_2PCH_2CH(CH_3)PPh_2](H)_2^+$, which rules out the *cis* isomer. The structures of **4H**$^+$ and **6H**$^+$ are also assigned the *trans* geometry since their $^2J_{PH}$ values (29.0 and 30.6 Hz) are very similar to those in the Ru complexes. The structure of **4H**$^+$ (Figure 1) was found to be a regular 4-legged piano-stool molecule of *trans* geometry with a P_1–Os–P_2 bond angle of 105.71(4)°. The Os–P bond lengths are both 2.310(1) Å, which is within the normal Os–P bond length range.[32] The structure solution yielded Os–H bond distances (1.19 and 1.45 Å) that are much shorter than the average Os–H bond length (1.66(2) Å) in $H_4Os(PPhMe_2)_3$, which was determined by neutron diffraction.[32] The short Os–H distances are almost certainly not real since most of the electron density located by X-ray diffraction is between the Os and hydride atoms, rather than around the hydrogen nucleus. The H_a–Os–H_b bond angle is 121°, which is somewhat smaller than the 138° H_a–Re–H_b bond angle for the isostructural $CpRe(PPh_3)_2(H)_2$ complex.[33]

Due to the small bite angle of the dppm ligand, $CpRu(dppm)(H_2)^+$ (**20H**$^+$) is constrained to have *cis* phosphorus atoms and an η^2-(H_2) ligand. This geometry has been previously established[7,30] by J_{HD} coupling constants for **20H**$^+$; **21H**$^+$ exists as a 1:2 mixture of *cis*-(η^2-H_2) and *trans*-$(H)_2$ isomers, while complex **22H**$^+$ has exclusively the *trans*-$(H)_2$ geometry as evidenced by ^{1}H NMR studies.[7,30] Molecular orbital calculations on *cis*- and *trans*-$CpRu(PR_3)_2H_2^+$ have been used to examine the tendencies of these complexes to exist with η^2-H_2 or $(H)_2$ ligands.[34]

In contrast to **20H**$^+$, the structure of $CpOs(dppm)(Br)(H)^+$ (**12H**$^+$) cannot be definitively assigned on the basis of the ^{1}H and ^{31}P NMR spectra in CD_2Cl_2. At room temperature this complex exhibits a broad singlet for the hydride resonance at −11.43 ppm in the ^{1}H NMR spectrum. If the sample is cooled to −20 °C, the fluxionality of the system is slowed and the hydride resonance appears as a triplet ($^2J_{PH}$ = 22.5 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **12H**$^+$ shows sharp doublets at −38.3 and −58.5 ppm ($^2J_{PP}$ = 101 Hz for both doublets) in the temperature range from −78 to 15 °C, which indicates that the P atoms are inequivalent. However, selective irradiation of the methylene protons (5.8 ppm in the ^{1}H NMR spectrum) while running the ^{1}H coupled ^{31}P NMR spectrum at −30 °C results in a doublet of doublets ($^2J_{PH}$ = 22.1 Hz, $^2J_{PP}$ = 101 Hz) for both phosphorus atoms. Comparing this coupling constant (22.1 Hz) with the $^2J_{PH}$ coupling constant (22.5 Hz) of the hydride peak from the ^{1}H NMR spectrum indicates that the inequivalent phosphorus nuclei are equally coupled to the hydride ligand, which would be consistent with the *cis* four-legged piano-stool geometry for **12H**$^+$ if the coupling constant $^2J_{PH}$ for the *cis* and *trans* P were coincidentally the same. On the basis of these results, we cannot confidently assign a structure to **12H**$^+$ although the other dppm complexes have *cis* structures; attempts to grow crystals for X-ray diffraction were unsuccessful.

Table III. Heats of Protonation (ΔH_{HM}) of $Cp'M(PR_3)(PR'_3)X$ Complexes

metal complex	$-\Delta H_{HM}$,[a,b] kcal/mol
$CpOs(PPh_3)_2Cl$, **1**	19.7 (±0.2)
$CpOs(PPh_3)_2Br$, **2**	16.3 (±0.1)
$CpOs(PPh_3)_2I$, **3**	14.1 (±0.1)
$CpOs(PPh_3)_2H$, **4**	37.3 (±0.1)
$CpOs(PPh_2Me)_2Br$, **5**	20.0 (±0.2)
$CpOs(PPh_2Me)_2H$, **6**	39.2 (±0.3)
$CpOs(PPhMe_2)_2Br$, **7**	26.2 (±0.1)
$CpOs(PMe_3)_2Br$, **8**	29.4 (±0.4)
$CpOs(PPh_3)(PMe_3)Br$, **9**	25.6 (±0.4)
$CpOs(PMe_3)_2I$, **10**	26.6 (±0.4)
$CpOs(PPh_3)(P(OEt)_3)H$, **11**	33.6 (±0.3)
$CpOs(dppm)Br$,[c] **12**	17.5 (±0.4)
$CpOs(dppp)Br$,[c] **13**	20.1 (±0.4)
$CpRu(PMe_3)_2Cl$, **14**	21.2 (±0.4)
$CpRu(PMe_3)_2Br$, **15**	20.9 (±0.3)
$CpRu(PMe_3)_2I$, **16**	20.6 (±0.2)
$CpRu(PPh_3)_2H$, **17**	29.7 (±0.2)
$Cp^*Ru(PMe_3)_2Cl$, **18**	30.2 (±0.2)
$Cp^*Ru(PPh_3)_2H$, **19**	35.2 (±0.2)
$CpRu(dppm)H$,[c] **20**	28.9 (±0.2)
$CpRu(dppe)H$,[c,d] **21**	29.0 (±0.1)
$CpRu(dppp)H$,[c] **22**	29.6 (±0.1)

[a] For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b] Numbers in parentheses are average deviations from the mean of at least four titrations. [c] dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2P(CH_2)_2PPh_2$, and dppp = $Ph_2P(CH_2)_3PPh_2$. [d] *Cis* and *trans* isomers of the product contribute to the ΔH_{HM} of this complex. See text for details.

Calorimetry Studies. Table III contains the heats of protonation (ΔH_{HM}) as determined by calorimetric titration of complexes **1–5** and **7–22** with CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C according to eq 3. Plots of temperature vs amount of acid added were linear, indicating that the protonations occur rapidly and stoichiometrically. There was no decomposition of either the neutral or protonated species during the titration as evidenced by the normal pre- and post-titration curves. The protonated halide complexes in DCE solution were easily deprotonated with 1.0 equiv of diphenylguanidine; the resulting complexes were recovered by passing the mixtures down a short (~5 cm) alumina column with CH_2Cl_2 as the eluent. Crystallization of the complexes from CH_2Cl_2 layered with hexanes resulted in the pure unprotonated complexes. Recovery of the original hydride complexes was unsuccessful due to the air sensitivity of the protonated compounds in solution. Attempts to determine ΔH_{HM} for $CpRu(PMe_3)_2H$ were not successful because of its high reactivity with traces of air.

Equilibrium Study of Reaction 4. A plot of ln K_{eq} vs $1/T$, where the slope = $-\Delta\Delta H_{HM}/R$, was used to determine that $\Delta\Delta H_{HM}$ = −1.9 (±0.3) kcal/mol for reaction 4; the error is one standard deviation from a linear regression line. The ΔH_{HM} for $CpOs(PPh_2Me)_2H$ (**6**) was calculated (eq 6) to be −39.2 kcal/mol by using the ΔH_{HM} for **4** and $\Delta\Delta H_{HM}$ (−1.9 kcal/mol) for reaction 4. The $\Delta\Delta S°$ at 298 K for reaction 4 was calculated to be −1.0 (±1.0) eu with eq 6a, where $\Delta\Delta G° = -RT \ln K_{eq}$ at 298 K.

$$\Delta\Delta H_{HM} = \Delta H_{HM}(\text{of } \mathbf{6}) - \Delta H_{HM}(\text{of } \mathbf{4}) \qquad (6)$$

$$\Delta\Delta G° = \Delta\Delta H_{HM} - T\Delta\Delta S° \qquad (6a)$$

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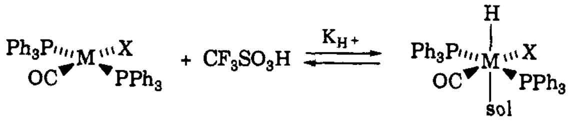
Discussion

Halide and Hydride Ligand Effects on Metal Basicity (ΔH_{HM}). The heats of protonation (ΔH_{HM}) (Table III) for the halide complexes $CpOs(PPh_3)_2X$ (**1**–**3**) increase in the following order: I^- (−14.1 kcal/mol) < Br^- (−16.3 kcal/mol) < Cl^- (−19.7 kcal/mol). One might have expected the reverse order for ΔH_{HM} since the higher electronegativity and lower polarizability of Cl^- should decrease the electron density on the metal. Previously, we showed that the basicity (ΔH_{HM}) of the metal in $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ increased with the basicity of the PR_3 ligand, as measured by its enthalpy of protonation (ΔH_{HP}) or pK_a. The simplest measure of the basicity of the halide ligand is the gas-phase proton affinity (PA) of $X^-(g)$,[35] which shows the basicities increase in the following order: I^- (314.3 kcal/mol) < Br^- (323.6 kcal/mol) < Cl^- (333.3 kcal/mol). This trend in proton affinities is the same trend followed by the basicities of the $CpOs(PPh_3)_2X$ complexes; thus, increasing the basicity of X^- increases the basicity of its complex. The increasing donor ability of the halide ligands from I^- to Cl^- is supported by equilibrium constants[1i] for halide displacement reactions (eq 7) in CH_2Cl_2 solvent, which increase with Y^- as follows: I^- (3.5×10^{-4}) < Br^- (1.3×10^{-2}) < Cl^- (0.34).

$$Rh(PPh_3)_2(CO)(F) + PPN^+Y^- \rightleftharpoons Rh(PPh_3)_2(CO)(Y) + PPN^+F^- \quad (7)$$

While the basicity (ΔH_{HM}) of the metal in $CpOs(PPh_3)_2X$ complexes is quite sensitive to the particular halide ion, changes in ΔH_{HM} for the ruthenium complexes $CpRu(PMe_3)_2X$ are much smaller: I^- (−20.6 kcal/mol) < Br^- (−20.9 kcal/mol) < Cl^- (−21.2 kcal/mol). Although the same trend is observed, the ΔH_{HM} values are nearly the same within experimental error.

In earlier studies,[36] equilibrium constants (K_{H^+}) for the reaction of CF_3SO_3H or $RC(O)OH$ with $Ir(CO)(PR_3)_2(X)$ ($PR_3 = PPh_3$, $PPhMe_2$; X = Cl, Br, I) to give $Ir(CO)(PR_3)_2(X)(H)(sol)$ (eq 8) were determined. Equilibrium constants for the PPh_3 complexes increase in the following order: Cl^- ($1.14 \times 10^2\ M^{-1}$) < Br^- ($4.16 \times 10^2\ M^{-1}$) < I^- (7.04×10^2). For the $PPhMe_2$ complexes they increase in the same order: Cl^- (0.60 M^{-1}) < Br^- (4.0 M^{-1}) < I^- (6.2 M^{-1}). It is not suprising that these reactions follow a different trend than we observe for simple protonation since the K_{H^+} values include not only protonation of the metal but also coordination of a sixth ligand (sol = either a solvent molecule or the anion of the acid). The energetics of protonation and of ligand coordination probably follow trends that are opposite, as the halide (X) is changed. In these reactions (eq 8), it is not possible to determine whether it is the protonation or coordination of the sixth ligand that determines the overall trend.



(8)

Hydride compounds $CpOs(PPh_3)_2H$ (**4**) and $CpOs(PPh_2Me)_2H$ (**6**) (ΔH_{HM} = −37.3 and −39.2 kcal/mol, respectively) are dramatically more basic than the analogous halide compounds. For example, they are 21.0 and 19.2 kcal/mol more basic than the bromo complexes **2** and **5** (ΔH_{HM} = −16.3 and −20.0 kcal/mol, respectively). The magnitude of these differences is illustrated by the estimated equilibrium constants (*K*) for the bromide–hydride pairs of complexes. They can be estimated if $\Delta S°$ is assumed to be the same for the protonation of both $CpOs(PR_3)_2H$ and $CpOs(PR_3)_2Br$. This assumption is supported by the $\Delta\Delta S°$ value (−1.0 (±1.0) eu) for reaction 4, which means that $T\Delta\Delta S°$ (−0.30 kcal/mol) is small compared to $\Delta\Delta H_{HM}$ (−1.9 ± 0.3 kcal/mol); thus, $\Delta\Delta G° \approx \Delta\Delta H_{HM}$ and $\Delta\Delta H_{HM} \approx -RT \ln K_{eq}$. Assuming that $\Delta\Delta S°$ is also small for the equilibrium constant comparisons of **2** vs **4** and **5** vs **6**, $CpOs(PPh_3)_2H$ is 2.5×10^{15} times (i.e., $\Delta\Delta H_{HM}$ = 21.0 kcal/mol) more basic than $CpOs(PPh_3)_2Br$, and $CpOs(PPh_2Me)_2H$ is 1.2×10^{14} times (i.e., 19.2 kcal/mol) more basic than $CpOs(PPh_2Me)_2Br$. While these comparisons are approximate, they do demonstrate that the hydride complexes are remarkably more basic than the bromide and other halide analogs of $CpOs(PR_3)_2X$ (Table III). The largest difference in basicity (23.2 kcal/mol) is between $CpOs(PPh_3)_2H$ and $CpOs(PPh_3)_2I$; this difference means that the hydride complex is approximately 1.1×10^{17} times more basic than the iodide complex.

Tilset et al.[6b] determined that a $1e^-$ oxidation of $CpM(CO)_3H$ (M = Cr, Mo, W) produces the 17-electron radical cation $CpM(CO)_3H^+$, which is up to 22.8 pK_a units more acidic than the corresponding neutral $CpM(CO)_3H$ complex. For example, $CpW(CO)_3H^+$ (pK_a = −3.0) is 19.1 pK_a units more acidic than $CpW(CO)_3H$ (pK_a = 16.1); at 25.0 °C the 19.1 pK_a units translate into 26.0 kcal/mol when the equation $\Delta\Delta G° = -RT \ln K_{eq}$ is used. The increase of 19.1 pK_a units ($\Delta\Delta G°$ = 26.0 kcal/mol) caused by a one-electron oxidation is only slightly larger than the 23.2-kcal/mol increase in basicity ($\Delta\Delta H_{HM}$) that results from substitution of an I^- ligand by a hydride ligand. Thus, the replacement of I^- by H^- has nearly the same effect as reducing the metal by one unit (+3 to +2 for the $CpW(CO)_3H$ system). Thus, if Os has a +2 oxidation state in $CpOs(PPh_3)_2I$, $CpOs(PPh_3)_2H$ behaves in its protonation reaction as if its oxidation state is approximately +1, i.e., the hydride ligand behaves as an H atom. Support for this view is found in molecular orbital calculations of Low and Goddard,[37] who concluded that the addition of H_2 to $Pt(PH_3)_2$ is not oxidative, since covalent bonds are formed. They suggested that formal oxidation numbers denote the maximum covalency of the metal not its oxidation state.

The trend in ΔH_{HM} values ($I^- < Br^- < Cl^- \ll H^-$) for the $CpOs(PPh_3)_2X$ complexes can be understood in terms of the basicity of the X^- ligand, as measured by the proton affinity (PA) of $X^-(g)$. These PA values increase in the same order, I^- (314.3 kcal/mol) < Br^- (323.6 kcal/mol) < Cl^- (333.3 kcal/mol) < H^- (400.4 kcal/mol),[35] as the ΔH_{HM} values of their $CpOs(PPh_3)_2X$ complexes. As the strongest X donor to the Os in the $CpOs(PR_3)_2X$ complexes, the hydride ligand should make **4** and **6** the most basic complexes in the series, as is observed (Table III). In fact, there is an excellent correlation (r = 0.9995 for eq 9) between

$$-\Delta H_{HM}\ (\text{kcal/mol}) = 0.2698(\text{PA}) - 70.64 \quad (9)$$

the donor ability of the halide or hydride ligand as measured by the PA of $X^-(g)$ and ΔH_{HM} for complexes **1**–**4** (Figure 2). Since PA values of a variety of anions (A^-) (e.g., F^-, CN^-, $CH_3CO_2^-$, $C{\equiv}CH^-$, and CH_3^-) are known,[35] eq 9 allows one to estimate basicities for a range of $CpOs(PPh_3)_2(A)$ complexes.[38]

Phosphine Effect on Metal Basicity (ΔH_{HM}) in $CpOs(PR_3)_2Br$. The basicities (ΔH_{HM}) of the $CpOs(PR_3)_2Br$ complexes increase in the following order: PPh_3 (−16.3 kcal/mol) < PPh_2Me (−20.0 kcal/mol) < $PPhMe_2$ (−26.2 kcal/mol) < PMe_3 (−29.4 kcal/mol). The basicities (ΔH_{HM}) of the free phosphines in DCE[8] [PPh_3 (−21.0 kcal/mol) < PPh_2Me (−24.7 kcal/mol) < $PPhMe_2$ (−28.4 kcal/mol) < PMe_3 (−31.6 kcal/mol)] increase in the same order. A plot of $-\Delta H_{HM}$ vs $-\Delta H_{HP}$ (Figure 3) is fit by eq 10a

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[37] Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 6928.

[38] It is also possible that the increasing π-donor ability of the halide ligands ($I^- < Br^- < Cl^-$) accounts for the halide complex basicity trend (Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190). However, it does not explain the high basicities of the H^- compounds.

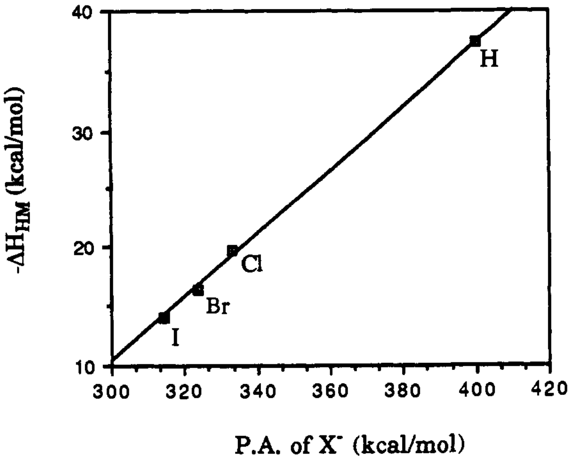

Figure 2. Correlation of metal basicities (ΔH_{HM}) of $CpOs(PPh_3)_2X$ with gas-phase proton affinities (PA) of $X^-(g)$.

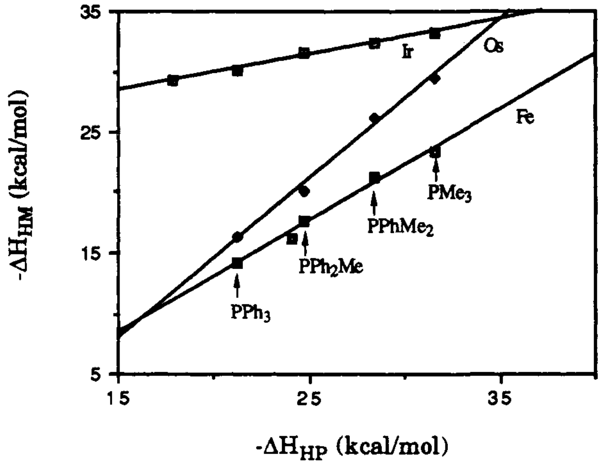

Figure 3. Correlations of metal basicity (ΔH_{HM}) with phosphine basicity (ΔH_{HP}) in DCE for $CpIr(CO)(PR_3)$ (top line), $CpOs(PR_3)_2Br$ (middle line), and $Fe(CO)_3(PR_3)_2$ (lower line).

$$-\Delta H_{HM} = -1.31\Delta H_{HP} - 11.6 \qquad (10a)$$

$$-\Delta H_{HM} = 2.30pK_a + 10.1 \qquad (10b)$$

with a correlation coefficient of 0.995. Equation 10a indicates that for the osmium series a 1.0 kcal/mol increase in the basicity of the phosphine ligands increases the basicity of the complex by 1.31 kcal/mol. Since there are two phosphine ligands, each contributes an average of 0.655 kcal/mol toward the basicity of the compound.

It is of particular interest to note that the basicity (ΔH_{HM}) of the mixed phosphine ligand complex $CpOs(PPh_3)(PMe_3)Br$ (**9**) (−25.6 kcal/mol) is not intermediate between that of $CpOs(PPh_3)_2Br$ (**2**) (−16.3 kcal/mol) and that of $CpOs(PMe_3)_2Br$ (−29.4 kcal/mol). Complex **9** is only 3.8 kcal/mol less basic than $CpOs(PMe_3)_2Br$ (**8**), but it is 9.3 kcal/mol more basic than $CpOs(PPh_3)_2Br$ (**2**). Steric or electronic factors could be responsible for **9** having a basicity closer to **8** than to **2**. The 9.3-kcal/mol increase in the ΔH_{HM} caused by substituting one PPh_3 ligand in **2** with PMe_3 is similar to the 10.4-kcal/mol increase in basicity (ΔH_{HP}) of the free phosphines in DCE ($\Delta H_{HP} = -21.2$ kcal/mol for PPh_3 and −31.6 kcal/mol for PMe_3).[8] Since such a large change in ΔH_{HM} upon PPh_3 replacement by PMe_3 has not been observed in any other metal complex system (*vide infra*), it seems unlikely that it can be caused by an electronic effect only. On the other hand, steric repulsion among the ligands around Os increases when the metal is protonated. Thus, protonation will be sterically disfavored by bulky ligands such as PPh_3. For this reason, the basicity of $CpOs(PPh_3)_2Br$ may be unusually low. Replacement of one PPh_3 group in **2** by PMe_3 to form $CpOs(PPh_3)(PMe_3)Br$ (**9**) would reduce ligand repulsion and make **9** more basic than would be expected from the electronic effect of PMe_3 alone. Replacement of the second PPh_3 would result in less steric reduction and less change in basicity, as is observed.

Substitution of one PPh_3 ligand in $CpOs(PPh_3)_2H$ (**4**) (ΔH_{HM} = −37.3 kcal/mol) with $P(OEt)_3$ results in a decrease of 3.7 kcal/mol in the basicity of $CpOs(PPh_3)[P(OEt)_3]H$ (**11**) (ΔH_{HM} = −33.6 kcal/mol). Since $CpOs(PPh_3)[P(OEt)_3]Br$ is not protonated by CF_3SO_3H, it was not possible to measure its ΔH_{HM}. However, in order to compare the effect of $P(OEt)_3$ on the basicity of $CpOs(PPh_3)(L)Br$ complexes, one can estimate that $CpOs(PPh_3)[P(OEt)_3]Br$ would be ~21 kcal/mol less basic than $CpOs(PPh_3)[P(OEt)_3]H$, which is based on $CpOs(PPh_3)_2Br$ being 21.0 kcal/mol less basic than $CpOs(PPh_3)_2H$. With this assumption, ΔH_{HM} for $CpOs(PPh_3)[P(OEt)_3]Br$ would be −12.6 kcal/mol. Therefore, the basicities (ΔH_{HM}) of the $CpOs(PPh_3)(L)Br$ complexes increase in the following order: L = $P(OEt)_3$ (−12.6 kcal/mol, estimated) < PPh_3 (−16.3 kcal/mol) < PMe_3 (−25.6 kcal/mol). Thus, $P(OEt)_3$ is the weakest donor ligand in this series.

The influence of phosphine ligand basicity (ΔH_{HP}) on metal complex basicity (ΔH_{HM}) has previously been observed in the $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ series of complexes (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$, and PMe_3),[9] which were also studied by titration calorimetry under the same conditions as in this present study. Plotting $-\Delta H_{HM}$ of these complexes vs $-\Delta H_{HP}$ of the free phosphine results in linear correlations for Ir (eq 11) and Fe (eq 12) (Figure 3). In the Ir series, the phosphine causes a 0.298-kcal/mol change in the Ir basicity per 1.00-kcal/mol change in PR_3 basicity (ΔH_{HP}); in the Fe series each phosphine causes an average 0.458-kcal/mol (0.916/2) change in Fe basicity (ΔH_{HM}) as the basicity of the phosphine (ΔH_{HP}) changes by 1.00 kcal/mol. Thus, the average change in ΔH_{HM} per PR_3 ligand per 1.00-kcal/mol change in ΔH_{HP} increases in the following order: $CpIr(CO)(PR_3)$, 0.298 < $Fe(CO)_3(PR_3)_2$, 0.458 < $CpOs(PR_3)_2Br$, 0.655. A possible reason why the basicity of the Os compounds is the most sensitive to the phosphine is that the higher coordination number (6) of the Os complexes causes more crowding in complexes which contain bulky PR_3 ligands, e.g., PPh_3, as noted above. These steric effects should be less important in the less crowded $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes. Another reason for the greater sensitivity of the Os complexes is the absence of CO ligands which could absorb some of the electron density donated to the metal by basic PR_3 ligands. The π-accepting CO ligands in the Fe and Ir complexes would make the metals in these systems less sensitive to the donor ability of the PR_3 ligands.

$$-\Delta H_{HM}\ (\text{kcal/mol}) = -0.298(\Delta H_{HP}) + 23.9 \qquad (\text{for } CpIr(CO)(PR_3)) \quad (11)$$

$$-\Delta H_{HM}\ (\text{kcal/mol}) = -0.916(\Delta H_{HP}) = 5.36 \qquad (\text{for } Fe(CO)_3(PR_3)_2) \quad (12)$$

With three π-accepting CO ligands in $Fe(CO)_3(PR_3)_2$, as compared with only one in $CpIr(CO)(PR_3)$, the Fe complexes are expected to be less sensitive to PR_3 basicity than the Ir complexes; however, as noted above, the reverse is true. The lower sensitivity of the Ir series could be due to the Cp ligand acting as a substantial π-accepting ligand. This is supported by MO calculations and ESCA studies of $CpRh(CO)_2$ that show the Cp π* and filled metal orbitals have similar energies which allows substantial π-bonding from the metal to the Cp ligand.[39]

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[39] Lichtenberger, D. L.; Calabro, D. C.; Kellogg, G. E. *Organometallics* **1984**, *3*, 1623.

Effect of Chelating Phosphines on Metal Basicity (ΔH_{HM}). The ΔH_{HM} of $CpOs(PPh_2Me)_2Br$ (**5**) is -20.0 kcal/mol, while the ΔH_{HM} of the chelated complex CpOs(dppp)Br (**13**) is the same within experimental error at -20.1 kcal/mol; both complexes give *trans* protonated products (eq 3). Since the free phosphines (ΔH_{HP} = -24.7 kcal/mol for PPh_2Me[8] and ΔH_{HP1} = -23.4 kcal/mol for dppp[40]) have nearly the same basicity, it is not surprising that **5** and **13** have the same basicity. The basicity (-17.5 kcal/mol) of CpOs(dppm)Br (**12**) is less than those of **5** and **13**, which is explained in part by the poorer σ-donor ability of the dppm ligand (ΔH_{HP1} = -22.0 kcal/mol).[40] In addition, the dppm ligand constrains the product $CpOs(dppm)(Br)(H)^+$ (**12H$^+$**) to adopt a *cis* structure; since the monodentate phosphine complex **5H$^+$** could adopt either the *cis* or *trans* structure and it is observed to form only the *trans* isomer, the *cis* isomer must be of higher energy. The *cis* structure of $CpOs(dppm)(Br)(H)^+$ (**12H$^+$**) is therefore of relatively high energy which makes the protonation of **12** less favorable than that of **5** or **13**. Thus, the basicity of the metal is decreased as a result of dppm constraining the complex to the less stable *cis* structure.

A decrease in basicity of the metal complex also occurs when dppp is replaced by the shorter chelates dppe and dppm that give the *cis* isomers in the $CpRu(\overset{\frown}{PP})H$ series [$\overset{\frown}{PP}$ = dppp (**22**, ΔH_{HM} = -29.6 kcal/mol), dppe (**21**, ΔH_{HM} = -29.0), dppm (**20**, ΔH_{HM} = -28.9)], although the effects are less dramatic. The dppp product **22H$^+$** is completely *trans*, the dppe derivative **21H$^+$** is a mixture of *cis* and *trans* isomers, and the dppm isomer is completely *cis* with the η^2-H_2 structure $CpRu(dppm)(\eta^2\text{-}H_2)^+$.[7,30] In this series, it was not possible to study the monodentate analog $CpRu(PPh_2Me)_2H$ due to its partial decomposition in the calorimeter. However, comparison of **20**–**22** with $CpRu(PPh_3)_2H$ (**17**, ΔH_{HM} = -29.7 kcal/mol) indicates that the basicities of the $CpRu(P)_2X$ complexes depend little on the monodentate or bidentate nature of the phosphine ligands. Morris and Jia[7] determined pK_a values in CH_2Cl_2 solvent for the same complexes **20H$^+$**–**22H$^+$** and observed the same trend of decreasing basicity as the product adopts the *cis* structure: *trans*-$CpRu(dppp)(H)_2^+$ (pK_a = 8.4) > *trans*-$CpRu(PPh_3)_2(H)_2^+$ (8.3) > *trans*-$CpRu(dppe)(H)_2^+$ (7.3) > *cis*-$CpRu(dppm)(H_2)^+$ (7.1) > *cis*-$CpRu(dppe)(H_2)^+$ (7.0). For $CpRu(dppe)H_2^+$, where they were able to determine pK_a values for both the *cis* and *trans* isomers, the *cis* isomer was less basic than the *trans*.

Those complexes that are constrained by the chelate to form the less stable *cis*-$CpRu(\overset{\frown}{PP})(H_2)^+$ products are the least basic. This effect was also observed in $W(CO)_3$(tridentate phosphine)[10] complexes in which the less flexible $MeC(CH_2PPh_2)_3$ ligand forces the tungsten in the protonated product into a higher energy structure thereby decreasing the basicity of the metal by 6.2 kcal/mol compared to the basicity of the complex with the flexible $PhP(CH_2CH_2PPh_2)_2$ ligand. The opposite effect is observed when a small dppm chelate in $Fe(CO)_3$(dppm) distorts the geometry from the favored diaxial structure of $Fe(CO)_3(PPh_2Me)_2$ to a higher energy structure.[41] This distortion causes the Fe to be 6.4 kcal/mol more basic in $Fe(CO)_3$(dppm) than in $Fe(CO)_3(PPh_2Me)_2$. Similarly, small-ring chelating ligands increase the basicities of the metal in the $M(CO)_2(\overset{\frown}{PP})_2$ (M = Cr, Mo, W) complexes.[42]

Effect of Cp and Cp* on Metal Basicity (ΔH_{HM}). The data in Table III show that the basicity of $Cp^*Ru(PMe_3)_2Cl$ is 9.0 kcal/mol greater than that of $CpRu(PMe_3)_2Cl$, $Cp^*Ru(PPh_3)_2H$ is 5.5 kcal/mol more basic than $CpRu(PPh_3)_2H$, and $Cp^*Ir(COD)$ is 5.7 kcal/mol more basic than CpIr(COD).[11] Converting the K_{eq} values for the protonation of various anions in acetonitrile to $\Delta G°$ values, $Cp^*Mo(CO)_3^-$ is 4.5 kcal/mol (3.2 pK_a units)[4] more basic than $CpMo(CO)_3^-$, and $Cp^*Cr(CO)_3^-$ is more basic[6a] than $CpCr(CO)_3^-$ by 3.8 kcal/mol (2.8 pK units)[4]; while $Cp^*Fe(CO)_2^-$ is 9.4 kcal/mol (6.9 pK_a units) more basic than $CpFe(CO)_2^-$.[4] Thus, the basicity enhancement (3.8–9.4 kcal/mol) caused by the replacement of Cp by Cp* depends on the metal and the ligands in the complex.

Effect of the Metal (Ru vs Os) on Metal Basicity (ΔH_{HM}). It has previously been reported by this group[42] that the third row metal complex Cp^*_2Os (ΔH_{HM} = -26.6 kcal/mol) is 7.6 kcal/mol more basic than the second row metal analog Cp^*_2Ru (ΔH_{HM} = -19.0 kcal/mol). We expand this comparison (Table III) by showing that $CpOs(PPh_3)_2H$ (**4**) is 7.6 kcal/mol more basic than $CpRu(PPh_3)_2H$ (**17**), $CpOs(PMe_3)_2Br$ (**8**) is 8.5 kcal/mol more basic than $CpRu(PMe_3)_2Br$ (**15**), and $CpOs(PMe_3)_2I$ (**10**) is 6.0 kcal/mol more basic than $CpRu(PMe_3)_2I$ (**16**); Norton and coworkers determined that $HOs(CO)_4^-$ is 2.9 kcal/mol (2.1 pK_a units) more basic (in CH_3CN) than $HRu(CO)_4^-$.[43] These comparisons illustrate that the magnitude of the increase in basicity when Ru is substituted by Os depends on the ligands in the complex.

Conclusions

Systematically changing the ligands and/or the metal in $Cp'M(PR_3)(PR'_3)X$ complexes yields metal basicities (ΔH_{HM} in DCE) that range from -14.1 to -39.2 kcal/mol. We have demonstrated that the basicities of the $CpOs(PPh_3)_2X$ complexes increase with the halide or hydride ligand in the following order: $I^- < Br^- < Cl^- \ll H^-$. In fact, the substitution of a halide (X^-) ligand by a hydride (H^-) causes the basicity of the metal to increase by as much as 23.2 kcal/mol. A linear correlation between the ΔH_{HM} of these complexes and the gas-phase proton affinities of the anions X^- is observed. Studies of the $CpOs(PR_3)_2Br$ complexes show that there is a linear correlation between the basicity (ΔH_{HM}) of the metal center and the basicity of the phosphine (pK_a or ΔH_{HP}), which increases in the order $PPh_3 < PPh_2Me < PPhMe_2 < PMe_3$ (Figure 3). However, since the basicity (ΔH_{HM}) of the mixed phosphine complex $CpOs(PPh_3)(PMe_3)Br$ does not lie midway between those of $CpOs(PPh_3)_2Br$ and $CpOs(PMe_3)_2Br$ as one might expect, the basicities of the $CpOs(PR_3)_2Br$ complexes are probably determined not only by the basicities of the phosphines but also by their steric properties. In the $CpM(\overset{\frown}{PP})X$ compounds with chelating phosphines, there was little difference in the basicity (ΔH_{HM}) of the metal when compared to complexes of monodentate phosphines; however, the basicities (ΔH_{HM}) of the *cis* complexes are less than those of the *trans* complexes. These titration studies show that complexes with the Cp* ligand are 5.5–9.0 kcal/mol more basic than those with the Cp ligand, and Os complexes are 6.0–8.5 kcal/mol more basic than the analogous Ru complexes.

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Supplementary Material Available: Tables of bond distances and angles, displacement parameters, and least-squares planes for **4H$^+$CF$_3$SO$_3^-$** (24 pages); a table of observed and calculated structure factors for **4H$^+$CF$_3$SO$_3^-$** (32 pages). Ordering information is given on any current masthead page.

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