Steric and Electronic Effects of Mono- and Tridentate Phosphine Ligands on the Basicities of the Metal in Tungsten Tris(phosphine) Tricarbonyl Complexes

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Titration calorimetry has been used to determine the heats of protonation (ΔH_{HM}) of the *fac*-$W(CO)_3(PR_3)_3$ (PR_3 = $PMePh_2$ (**1**), $PEtPh_2$ (**2**), PMe_2Ph (**3**), PEt_2Ph (**4**), PMe_3 (**5**), PEt_3 (**6**)) and *fac*-$W(CO)_3(L_3)$ (L_3 = $PhP(CH_2CH_2PPh_2)_2$ (**7**), $MeC(CH_2PPh_2)_3$ (**8**)) complexes with CF_3SO_3H in 1,2-dichloroethane solvent at 25.0 °C. The $W(CO)_3(PR_3)_3$ and $W(CO)_3(L_3)$ complexes undergo protonation at the tungsten with 1 equiv of CF_3SO_3H to form $[W(H)(CO)_3(PR_3)_3]CF_3SO_3$ (**1H$^+$–6H$^+$**) and $[W(H)(CO)_3(L_3)]CF_3SO_3$ (**7H$^+$**,**8H$^+$**), respectively. For the $W(CO)_3(PR_3)_3$ (**1–6**) complexes, the metal basicity ($-\Delta H_{HM}$) generally increases as phosphine basicity ($-\Delta H_{HP}$) increases; the ΔH_{HM} values range from −15.1 kcal mol^{-1} (PR_3 = $PMePh_2$) to −25.0 kcal mol^{-1} (PR_3 = PEt_3). However, the trend in the ΔH_{HM} values is also influenced by the steric bulk of the phosphine ligand. Steric crowding in the *fac*-$W(CO)_3(PR_3)_3$ complexes is relieved when the complexes are protonated and the phosphine ligands adopt a less crowded arrangement in which they are approximately coplanar with the metal; metal basicity increases as the cone angle (θ) of the phosphine increases. ΔH_{HM} of the tridentate phosphine complex **8** (−10.5 kcal mol^{-1}) with the facially coordinating $MeC(CH_2PPh_2)_3$ ligand is 6.2 kcal mol^{-1} less exothermic than that of **7** (−16.7 kcal mol^{-1}) with the flexible $PhP(CH_2CH_2PPh_2)_2$ ligand. The lower basicity of **8** is attributed to a destabilization of the **8H$^+$** product, which is forced by the $MeC(CH_2PPh_2)_3$ ligand to adopt a structure less favorable than that of **7H$^+$**. The ΔH_{HM} values (−18.3 and −20.1 kcal mol^{-1}, respectively) of the $Cp^*Re(CO)_2(PR_3)$ (PR_3 = PMe_2Ph (**9**), PMe_3 (**10**)) complexes have also been determined.

Introduction

Recently we reported[1] the effects of phosphine donor ability, as measured by ΔH_{HP} (eq 1),[2] on the basicity (ΔH_{HM}) of the

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HPR_3^+CF_3SO_3^- \quad \Delta H_{HP} \qquad (1)$$

$$ML_x + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HML_x^+CF_3SO_3^- \quad \Delta H_{HM} \qquad (2)$$

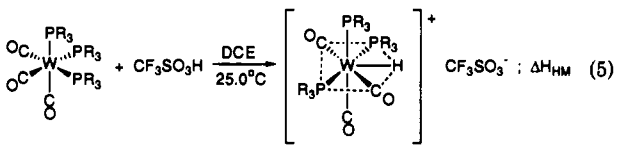
metal in $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes (eq 2); both ΔH_{HP} and ΔH_{HM} were determined by calorimetric titration with CF_3SO_3H in 1,2-dichloroethane solvent (DCE) at 25.0 °C. Linear correlations between metal basicity and phosphine basicity were obtained for Ir (eq 3) and Fe (eq 4), for these relatively

$$-\Delta H_{HM} = -0.298(\Delta H_{HP}) + 23.9 \quad \text{(for Ir)} \qquad (3)$$

$$-\Delta H_{HM} = -0.916(\Delta H_{HP}) - 5.36 \quad \text{(for Fe)} \qquad (4)$$

uncrowded complexes; no steric size effect of the phosphines on ΔH_{HM} was detected. It is possible, however, with complexes that are more crowded that metal basicity will be affected by the steric bulk of the phosphine ligand. In this paper we report the basicities as determined by ΔH_{HM} of a series of *fac*-$W(CO)_3(PR_3)_3$ complexes (eq 5) where the *fac* arrangement of the phosphine ligands is likely to cause steric crowding in these octahedral complexes. Their protonations give seven-coordinate products that are probably also sterically crowded. It is these steric effects that we sought to understand in the study reported herein.

Previously,[3] protonations of complexes **1**, **3**, **5**, and **6** were described, and the products were proposed to have the pentagonal structure shown in eq 5, on the basis of infrared and ^1H and ^{31}P NMR spectroscopic studies. For comparison with ΔH_{HM} values for the tris(monodentate) phosphine complexes (eq 5), we also include ΔH_{HM} values for the tridentate chelate complexes $W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**7**) and $W(CO)_3[MeC(CH_2PPh_2)_3]$ (**8**); some of the results describing the effects of tridentate ligand structure on metal basicity were communicated previously.[4]



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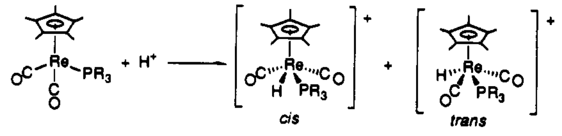
1-6 **1H$^+$CF$_3$SO$_3^-$ - 6H$^+$CF$_3$SO$_3^-$**

PR_3: $PMePh_2$ (**1**, **1H$^+$**), $PEtPh_2$ (**2**, **2H$^+$**), PMe_2Ph (**3**, **3H$^+$**), PEt_2Ph (**4**, **4H$^+$**), PMe_3 (**5**, **5H$^+$**), PEt_3 (**6**, **6H$^+$**)

Finally, we include in this paper studies of the basicities of $Cp^*Re(CO)_2(PR_3)$ (PR_3 = PMe_2Ph (**9**), PMe_3 (**10**)) complexes (eq 6) for comparison with the tungsten complexes as well as other related systems.



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Experimental Section

The titrations were performed with use of a Tronac Model 458 titration calorimeter as previously described.[2,5] Typically a 2.6 mM solution of the organometallic complex (**1–10**) or PEt_2Ph in 1,2-dichloroethane (DCE)

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was titrated under an argon atmosphere with 0.1 M CF_3SO_3H (standardized to a precision of ±0.0002 M) at a constant buret delivery rate (0.3962 mL min^{-1}) during a 3-min time period. The heats of reaction were corrected for the heat of dilution of 0.1 M CF_3SO_3H ($\Delta H_{dil} = -0.2$ kcal mol^{-1}).

All preparative reactions, manipulations, and purifications (except as stated otherwise) were performed under an atmosphere of nitrogen. Hexanes and CH_2Cl_2 were refluxed over CaH_2 and then distilled. Tetrahydrofuran (THF) was distilled from sodium benzophenone, and 1,2-dichloroethane was distilled under argon from P_4O_{10}. Triflic acid (CF_3SO_3H) was distilled under an argon atmosphere. The phosphine ligands, PEt_2Ph (Fluka) and $PEtPh_2$ (Aldrich), were used as received. Infrared spectra were recorded on a Bio-Rad FTS-7 FT-IR spectrometer, and the ^1H NMR spectra were obtained on a Nicolet-NT 300 MHz instrument with TMS (δ = 0.00 ppm) as the internal reference.

The complexes $W(CO)_3(PMePh_2)_3$ (**1**), $W(CO)_3(PMe_2Ph)_3$ (**3**), $W(CO)_3(PMe_3)_3$ (**5**), $W(CO)_3(PEt_3)_3$ (**6**), $W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**7**), and $W(CO)_3[MeC(CH_2PPh_2)_3]$ (**8**) were prepared from $W(CO)_3[MeN(CH_2CH_2NMe_2)_2]$ as previously described.[3] The $Cp^*Re(CO)_2(PR_3)$ ($PR_3 = PMe_2Ph$ (**9**), PMe_3 (**10**)) complexes were prepared from $Cp^*Re(CO)_3$ by UV photolysis as previously reported.[6]

Preparation of *fac*-$W(CO)_3(PEtPh_2)_3$ (2). To a stirred suspension of $W(CO)_3[MeN(CH_2CH_2NMe_2)_2]$ (0.77 g, 1.7 mmol)[3] in THF (30 mL) was added $PEtPh_2$ (1.1 mL, 5.4 mmol), and the mixture was heated at reflux for 3.5 h. After the solution was cooled to room temperature, the solvent was removed under vacuum and the residue was washed with 3 × 10 mL of hexanes. The residue was then dissolved in CH_2Cl_2, and the solution was placed on a column of neutral alumina (10 × 1.5 cm) and eluted with a mixture of hexanes/CH_2Cl_2/Et_2O (8:4:1). The solvent mixture was evaporated and the product was recrystallized from CH_2Cl_2/hexanes (3:1) at –25 °C to give 1.05 g of **2** as an air-stable pale yellow powder in 66% yield. Anal. Calcd for $C_{45}H_{45}O_3P_3W$: C, 59.35; H, 4.98. Found: C, 59.60; H, 5.04. ^1H NMR ($CDCl_3$): δ 0.708 (pentet, $J_{PH} = J_{HH} = 7.2$ Hz, 9H, CH_3), 2.20 (m, 6H, CH_2), 6.91 (m, 12H, *m*-Ph), 7.07 (t, $J = 7.4$ Hz, 12H, *o*-Ph), 7.25 (t, $J = 7.2$ Hz, 6H, *p*-Ph). IR (CH_2Cl_2): ν(CO) 1926 (s), 1823 (s) cm^{-1}.

Preparation of $W(CO)_3(PEt_2Ph)_3$ (4). This compound was prepared in 67% yield as an air-stable white powder from $W(CO)_3[MeN(CH_2CH_2NMe_2)_2]$ (0.75 g, 1.7 mmol) and PEt_2Ph (0.90 mL, 5.2 mmol) in refluxing THF for 4.5 h as described above for the synthesis of complex **2**. Anal. Calcd for $C_{33}H_{45}O_3P_3W$: C, 51.71; H, 5.92. Found: C, 52.05; H, 6.02. ^1H NMR ($CDCl_3$): δ 0.874 (m, 18H, CH_3), 1.93 (m, 12H, CH_2), 6.60 (br s, 6H, Ph), 7.15–7.30 (m, 9H, Ph). IR (CH_2Cl_2): ν(CO) 1922 (s), 1815 (s) cm^{-1}.

Protonation Reactions. The protonations of complexes **1**, **3**, and **5–8** with CF_3SO_3H (1 equiv) in CH_2Cl_2 or $CDCl_3$ solvent were previously reported.[3] The protonations of **2**, **4**, **9**, and **10** were carried out in a similar way by dissolving ~30 mg of each compound in CH_2Cl_2 (3 mL) under nitrogen and adding 1 equiv of CF_3SO_3H. Infrared spectra of these solutions showed new bands corresponding to the protonated complexes $\mathbf{2H^+}CF_3SO_3^-$, $\mathbf{4H^+}CF_3SO_3^-$, $\mathbf{9H^+}CF_3SO_3^-$, and $\mathbf{10H^+}CF_3SO_3^-$, respectively, and the disappearance of the bands corresponding to the neutral complexes. Samples (~20 mg) for ^1H NMR spectra were dissolved in $CDCl_3$ (~0.6 mL) under nitrogen; after the addition of 1 equiv of CF_3SO_3H, quantitative formation of the protonated products was observed.

$[W(H)(CO)_3(PEtPh_2)_3]CF_3SO_3$ ($\mathbf{2H^+}CF_3SO_3^-$). ^1H NMR ($CDCl_3$): δ –2.13 (multiplet with 4 peaks,[3] 1H, W–H), 0.81 (br m, 9H, CH_3), 2.56 (br s, 6H, CH_2), 7.19–7.49 (m, Ph). IR (CH_2Cl_2): ν(CO) 2032 (m), 1953 (m, sh), 1918 (s) cm^{-1}.

$[W(H)(CO)_3(PEt_2Ph)_3]CF_3SO_3$ ($\mathbf{4H^+}CF_3SO_3^-$). ^1H NMR ($CDCl_3$): δ –3.03 (multiplet with 4 peaks,[3] 1H, W–H), 0.97 (br m, 18H, CH_3), 2.12 (br m, 12H, CH_2), 7.1–7.4 (m, Ph). IR (CH_2Cl_2): ν(CO) 2028 (m), 1957 (m, sh), 1907 (s) cm^{-1}.

$[Cp^*Re(H)(CO)_2(PMe_2Ph)]CF_3SO_3$ ($\mathbf{9H^+}CF_3SO_3^-$). ^1H NMR ($CDCl_3$): δ –8.09 (d, $J_{PH} = 44.9$ Hz, Re–H, cis isomer, relative intensity = 2), –9.07 (br s, Re–H, trans isomer, relative intensity = 1), 2.10–2.16 (m, PMe_2Ph + Cp*), 7.6 (br m, Ph). IR (CH_2Cl_2): ν(CO) 2031 (s), 1961 (s) cm^{-1}, ν(Re–H) 1986 (w) cm^{-1}.

$[Cp^*Re(H)(CO)_2(PMe_3)]CF_3SO_3$ ($\mathbf{10H^+}CF_3SO_3^-$). ^1H NMR ($CDCl_3$): δ –8.46 (d, $J_{PH} = 47.0$ Hz, Re–H, cis isomer, relative intensity = 2), –9.43 (br s, Re–H, trans isomer, relative intensity = 1), 1.94–2.29 (m, PMe_3 + Cp*). IR (CH_2Cl_2): ν(CO) 2031 (s), 1961 (s) cm^{-1}, ν(Re–H) 1982 (m, sh) cm^{-1}.

Isolation of $\mathbf{6H^+}CF_3SO_3^-$.[3] To a solution of **6** (0.11 g, 0.17 mmol) in Et_2O (20 mL) at 0 °C was added an excess of CF_3SO_3H (30.5 μL, 0.34 mmol); a cloudy pale yellow solution immediately developed upon mixing. The solution was cooled to –25 °C for 18 h, and the solid that precipitated from the solution was filtered out, washed with hexanes (2 × 2.5 mL), and dried under vacuum to give 0.095 g of $\mathbf{6H^+}CF_3SO_3^-$ as an air-sensitive, pale yellow, microcrystalline solid in 72% yield. Anal. Calcd for $C_{22}H_{46}F_3O_6P_3SW$: C, 34.21; H, 6.00. Found: C, 33.81; H, 6.14. IR(CH_2Cl_2): ν(CO) 2024 (w), 1945 (m, sh), 1910 (s).

Isolation of $\mathbf{5H^+}CF_3SO_3^-$.[3] This complex was isolated as an air-sensitive, bright yellow, microcrystalline solid as described above for $\mathbf{6H^+}CF_3SO_3^-$. Yield of $\mathbf{5H^+}CF_3SO_3^-$: 0.080 g, 55%. IR (CH_2Cl_2): ν(CO) 2033 (w), 1944 (m, sh), 1922 (s).

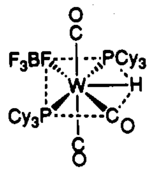
Results

Compound Characterization. The *fac*-$W(CO)_3(L_3)$ (L_3 = 3 PR_3, tridentate phosphine) complexes **1–8** including the new compounds **2** and **4** were prepared from $W(CO)_3[MeN(CH_2CH_2NMe_2)_2]$ in refluxing THF as previously reported (eq 7).[3] The identity and purity of complexes **1–8** were established

$$\mathrm{W(CO)_3[MeN(CH_2CH_2NMe_2)_2] + L_3 \xrightarrow[\text{reflux}]{\text{THF}}} \underset{\mathbf{1\text{–}8}}{\textit{fac}\text{-}\mathrm{W(CO)_3(L_3)}} \quad (7)$$

by IR and ^1H NMR spectroscopy. The *fac* structure of **7** was reported recently.[7] Complexes **1**, **3**, and **5–8** are quantitatively protonated at the tungsten (eq 5) with 1 equiv of CF_3SO_3H, as previously[3] determined by IR and ^1H and ^{31}P NMR spectroscopy. New complexes **2** and **4** also protonate at the tungsten (eq 5) with 1 equiv of CF_3SO_3H to give $\mathbf{2H^+}CF_3SO_3^-$ and $\mathbf{4H^+}CF_3SO_3^-$, respectively. The similarity of their IR and ^1H NMR spectra to those of the known $[W(H)(CO)_3(PR_3)_3]CF_3SO_3$ complexes[3] indicates that they have the same structures. As previously discussed,[3] infrared and ^1H and ^{31}P NMR studies indicate that the $PhP(CH_2CH_2PPh_2)_2$ complex, $\mathbf{7H^+}$, has a structure similar to that proposed for $\mathbf{1H^+}$–$\mathbf{6H^+}$; however, as a result of the constraint imposed by the $MeC(CH_2PPh_2)_3$ ligand, complex $\mathbf{8H^+}$,[3] has a different geometry in which the phosphorus donors remain mutually cis.

Complexes $\mathbf{5H^+}CF_3SO_3^-$ and $\mathbf{6H^+}CF_3SO_3^-$ are isolated by protonation of the respective neutral complexes in Et_2O; however, attempts to grow crystals suitable for X-ray diffraction studies have been unsuccessful thus far. We were unable to isolate any of the other protonated tungsten complexes. Spectroscopic studies[3] of the seven-coordinate complexes $\mathbf{1H^+}$–$\mathbf{7H^+}$ suggest a geometry in which two CO groups are approximately trans to each other while the three phosphorus ligands are approximately coplanar as shown for the products in eq 5. Recently, a single-crystal X-ray diffraction study[8] showed that $W(H)(CO)_3(PCy_3)_2(BF_4)$ (**A**) has a geometry similar to that proposed above for the $[W(H)(CO)_3(PR_3)_3]^+$ complexes and $\mathbf{7H^+}$, although the hydride ligand was not located. Complex **A** is related to



A

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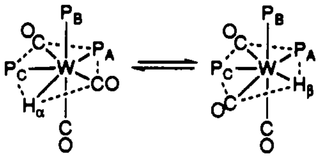
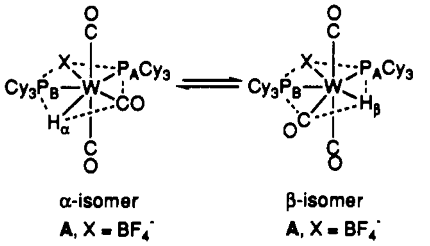
$[W(H)(CO)_3(PR_3)_3]^+$ if an axial CO in **A** is substituted with a phosphine ligand and the BF_4^- is replaced by a CO ligand. The IR spectra of **A** and $[W(H)(CO)_3(PR_3)_3]^+$ both show three ν(CO) bands,[3,8] but the relative intensities of the bands are different.

Previously[3] the variable-temperature ^1H and ^{31}P NMR spectra of **7H**$^+$ were extensively investigated. At low temperature (−35 °C) the ^1H NMR resonance (−3.78 ppm) of the hydride ligand was a doublet of doublets which was attributed to the α- and β-isomers, where $J_{P_AH_\alpha} = J_{P_CH_\beta}$ = 46 Hz and $J_{P_CH_\alpha} = J_{P_AH_\beta}$ = 18 Hz.[3] At higher temperatures (37 °C) hydride migration is fast and the hydride resonance appears as a triplet as P_A and P_C become equivalent on the NMR time scale and an averaged value of the coupling constant is obtained where $^1/_2[J_{P_AH_\alpha} + J_{P_CH_\alpha}] = {}^1/_2[J_{P_CH_\beta} + J_{P_AH_\beta}]$ = 32 Hz.[3] Further coupling of the hydride ligand with the axial phosphorus (P_B) is not observed as P_B is cis to the equatorial hydride ligands and J_{P_BH} is approximately zero. Also at low temperature (−40 °C) three signals were observed for P_A, P_B, and P_C in the $^{31}P\{^1H\}$ NMR spectrum, but at higher temperatures (25 °C) the resonances of P_A and P_C severely broaden indicating that they are becoming equivalent.[3] As for **7H**$^+$, the low-temperature (−9 °C) ^1H NMR resonance of the hydride ligand (−5.78 ppm) in **A** occurs as a doublet of doublets that becomes a triplet at high temperatures (55 °C).[7] Also in the ^{31}P NMR spectrum, the PCy_3 ligands are inequivalent at low temperature (−35 °C) and broaden at higher temperature (25 °C). The similarity of the variable-temperature ^1H and ^{31}P NMR spectra of **7H**$^+$ and **A** thus indicate that these compounds share similar structures.[3,8] Although it was not previously discussed,[8] on the basis of the comparison of the variable-temperature of **A** and **7H**$^+$, the presence of two isomers (α and β) that interconvert on the NMR time scale would explain the temperature dependence of the ^1H and ^{31}P NMR spectra of **A**. Since the ^1H NMR spectra of $W(H)(CO)_3(PCy_3)_2(OSO_2CF_3)$ (**B**), which has a structure similar to that of **A**, were published[8] in greater detail, we can assign the J_{PH} coupling constants to the α- and β-isomers of **B** on the basis of the similarity of its spectra to those[3] of **7H**$^+$. Thus, the doublet of doublets at −5.71 ppm reported for **B** at −46 °C results from a large J_{PH} value of 57.0 Hz that corresponds to $J_{P_AH_\alpha} = J_{P_BH_\beta}$ and a small J_{PH} value of 16.8 Hz that corresponds to $J_{P_BH_\alpha} = J_{P_A}H_\beta$. At high temperature there is rapid exchange between the α- and β-isomers of **B**; thus, an averaged J_{PH} value (37.4 Hz) is obtained which corresponds to $^1/_2[J_{P_AH_\alpha} + J_{P_BH_\alpha}] = {}^1/_2[J_{P_BH_\beta} + J_{P_AH_\beta}]$.



α-isomer (**7H**$^+$) β-isomer (**7H**$^+$)



α-isomer
A, X = BF_4^-
B, X = $CF_3SO_3^-$

β-isomer
A, X = BF_4^-
B, X = $CF_3SO_3^-$

Complexes **1H**$^+$–**8H**$^+$ are deprotonated, rapidly and quantitatively, with 1 equiv of 1,3-diphenylguanidine base in CH_2Cl_2 or DCE solvent. This deprotonation gives back **1**–**8** as their *fac* isomers, which are recovered by chromatography on alumina by elution with CH_2Cl_2 and recrystallization from CH_2Cl_2/hexanes.

Table I. Heats of Protonation (ΔH_{HM}) of *fac*-$W(CO)_3(PR_3)_3$, *fac*-$W(CO)_3(L_3)$ (L_3 = Tridentate Phosphine), and $Cp^*Re(CO)_2(PR_3)$ Complexes[a]

compd	θ[b]	$-\Delta H_{HM}$, kcal mol^{-1}	$-\Delta H_{HP}$,[c] kcal mol^{-1}
$W(CO)_3(PMePh_2)_3$ (**1**)	136	15.1 (±0.3)[d]	24.7 (±0.0)[d]
$W(CO)_3(PEtPh_2)_3$ (**2**)	140	16.9 (±0.3)	25.2[e]
$W(CO)_3(PMe_2Ph)_3$ (**3**)	122	17.5 (±0.2)	28.4 (±0.2)
$W(CO)_3(PEt_2Ph)_3$ (**4**)	136	18.3 (±0.1)	27.8 (±0.4)
$W(CO)_3(PMe_3)_3$ (**5**)	118	19.5 (±0.3)	31.6 (±0.2)
$W(CO)_3(PEt_3)_3$ (**6**)	132	25.0 (±0.3)	33.7 (±0.3)
$W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**7**)	130[f]	16.7 (±0.1)	26.4[f]
$W(CO)_3[MeC(CH_2PPh_2)_3]$ (**8**)		10.5 (±0.1)	
$Cp^*Re(CO)_2(PMe_2Ph)$ (**9**)	122	18.3 (±0.4)	28.4 (±0.2)
$Cp^*Re(CO)_2(PMe_3)$ (**10**)	118	20.1 (±0.3)	31.6 (±0.2)

[a] For protonation with CF_3SO_3H (0.1 M) in DCE at 25.0 °C. [b] Cone angle (deg) of the phosphine ligand.[11,18] [c] Reference 2. [d] Numbers in parentheses are average deviations. [e] Calculated from eq 8. [f] See text.

Infrared and ^1H NMR spectroscopic studies also establish that the $Cp^*Re(CO)_2(PR_3)$ complexes (PR_3 = PMe_2Ph (**9**), PMe_3(**10**)) are rapidly and quantitatively protonated at the rhenium with 1 equiv of CF_3SO_3H to give **9H**$^+CF_3SO_3^-$ and **10H**$^+CF_3SO_3^-$ as a mixture of cis and trans isomers (eq 6). Attempts to isolate these complexes by protonation in Et_2O with CF_3SO_3H were unsuccessful. Two resonances are observed in the hydride region for **9H**$^+$ at −8.09 ppm (doublet, J_{PH} = 44.9 Hz) and −9.07 ppm (broad singlet) which are assigned as the cis and trans isomers. The ratio of the cis to trans Re–H resonances found by integration is about 2:1 indicating a preference for the cis isomer at room temperature. The assignment of the resonance with the larger J_{PH} value to the cis isomer is based on the assignments made for cis- and trans-$[CpRe(H)(CO)_2(PPh_3)]^+$; Panosyan and coworkers[9] previously reported that protonation of $CpRe(CO)_2(PPh_3)$ in a mixture of $CHCl_3/CF_3COOH/BF_3{\cdot}H_2O$ (1:1:0.5) affords $[CpRe(H)(CO)_2(PPh_3)]^+$ as a mixture of the cis and trans isomers in a 1:4 ratio. In their study,[9] the Re–H ^1H NMR resonance at −8.70 ppm (d, J_{PH} = 15 Hz) was assigned to the trans isomer based on the smaller J_{PH} value[10] as compared to that at −7.54 ppm (d, J_{PH} = 39 Hz) which was assigned to the cis isomer. As for **9H**$^+$, the cis isomer of **10H**$^+$, which is assigned to the doublet resonance at −8.46 ppm (J_{PH} = 47.0 Hz), is favored by approximately a 2:1 ratio over the trans isomer (−9.43 ppm, br s). We were unable to resolve Cp* and PR_3 resonances for the cis and trans isomers of **9H**$^+$ and **10H**$^+$ as they overlap each other. In the infrared spectrum, two strong bands for **9H**$^+$ (2031, 1961 cm^{-1}) are assigned to both the cis and trans isomers;[10] the weak band at 1986 cm^{-1} is probably due to the Re–H stretch as this band was not present when the protonation was performed with CF_3SO_3D. For **10H**$^+$, two strong bands, which happen to have the same value as those of **9H**$^+$, are assigned to the cis and trans isomers[10] and the band at 1982 (m, sh) is probably from the Re–H stretch as this band was also not present when the protonation was performed with CF_3SO_3D. The protonated complexes **9H**$^+$ and **10H**$^+$ are rapidly and quantitatively deprotonated by 1,3-diphenylguanidine base in CH_2Cl_2 solvent as monitored by IR spectroscopy.

Calorimetry Studies. Heats of protonation determined by calorimetric titration of the tungsten complexes **1**–**8**, the rhenium complexes **9** and **10**, and PEt_2Ph with CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C are presented in Table I. Plots of temperature vs amount of acid added were linear indicating the complexes are protonated rapidly and quantitatively with 1 equiv of CF_3SO_3H as established for the organometallic complexes by the spectroscopic methods described above. There

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(9) Panosyan, G. A.; Petrovskii, P. V.; Pyshnograyeva, N. I.; Kolobova, N. E.; Setkina, U. N.; Fedin, E. I. *J. Organomet. Chem.* **1976**, *108*, 209.

(10) The cis and trans isomers of $CpMo(CO)_2(PR_3)(R)$ complexes also show superimposable ν(CO) bands: Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

was no decomposition of either the neutral or protonated tungsten complexes or PEt_2Ph during the titration experiment as evidenced by normal pre- and posttitration baseline slopes. The posttitration periods for **9** and **10** exhibited slightly increased baseline slopes; however, as this was relatively small, the effect on the ΔH_{HM} value is probably within the experimental error. Infrared spectra of the titrated solutions in DCE indicated the presence of the protonated species; however, since **1H**$^+$–**10H**$^+$ are very acidic, they were usually partially deprotonated by adventitious water or the NaCl windows in the IR cell.

Due to significant amounts of decomposition in the posttitration period we were unable to obtain reproducible ΔH_{HM} values for $Cp^*Re(CO)_2(PMePh_2)$[6] and $W(CO)_3[MeN(CH_2CH_2NMe_2)_2]$.[3] The protonation of $W(CO)_3(PPh_3)_3$ was not studied as this complex was insoluble in DCE.

On the basis of a previous correlation[2] (eq 8) of ΔH_{HP} and pK_a for protonated phosphines, the pK_a of protonated PEt_2Ph is

$$-\Delta H_{HP} = 1.82(pK_a) + 16.3 \qquad (8)$$

calculated to be 6.32 using the experimentally determined ΔH_{HP} value of -27.8 ± 0.4 kcal mol^{-1}; this pK_a value agrees within experimental error with the previous[11] value of 6.25, which was determined by a completely different method.[11] Previously the heats of reaction of monodentate phosphine ligands with (toluene)$Mo(CO)_3$ which yield *fac*-$Mo(CO)_3(PR_3)_3$ products were correlated with the pK_a values and cone angles of the phosphines.[12a] Assuming the $PhP(CH_2CH_2PPh_2)_2$ ligand behaves as three monodentate phosphines, an average "effective" pK_a (5.53) (for the protonated phosphine) and cone angle (130°) were previously[13] estimated from the infrared data and the heat of reaction of $PhP(CH_2CH_2PPh_2)_2$ with (toluene)$Mo(CO)_3$ using the QALE approach to the *q*uantitative *a*nalysis of *l*igand *e*ffects.[12,14] Thus, using eq 8 and the 5.53 pK_a value, we estimate the average effective ΔH_{HP} value of $PhP(CH_2CH_2PPh_2)_2$ as -26.4 kcal mol^{-1}.

As DCE has a relatively low dielectric constant ($\epsilon = 10.36$), the products formed in all of the titrations probably occur as ion pairs.[15] Contributions of ion-pair dissociation and autoprotolysis and dimerization of the acid to the heats of protonation values are presumably negligible as previously discussed.[2] The measured ΔH values undoubtedly include some contribution due to ion pairing. However, these ion-pairing energies appear to be relatively constant from one complex to another. If trends in the ΔH_{HM} values were affected by differences in ion pairing energies, it would be expected that the protonated complexes $HML_x{}^+CF_3SO_3{}^-$ with smaller phosphine ligands would form a tighter ion pair and would yield more exothermic ΔH_{HM} values than those with larger phosphine ligands. However, this is not observed as $W(CO)_3(PEt_3)_3$ (**6**), which has larger phosphine ligands, is considerably more basic than $W(CO)_3(PMe_3)_3$ with smaller phosphine ligands. Also, we have shown previously that heats of protonations of organophosphine[2,16] and organonitrogen[17] bases correlate linearly with their respective aqueous pK_a values; since there must be substantially different ion pairing in DCE and water, these results indicate that ion pairing does not play a major role in determining trends in ΔH values measured in DCE. Therefore, we attribute trends and differences in ΔH values to properties of the reactant and product complexes.

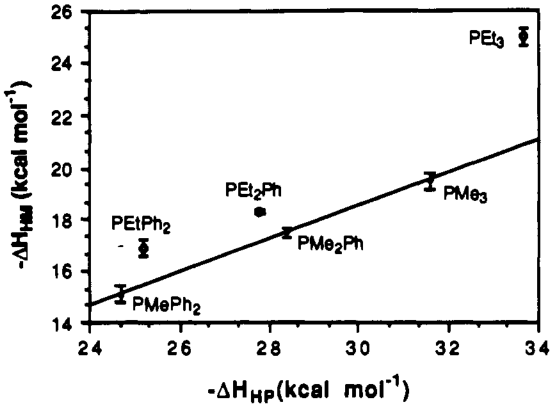

Figure 1. Correlation of the basicities (ΔH_{HM}) of the *fac*-$W(CO)_3(PR_3)_3$ complexes **1**–**6** with phosphine basicities (ΔH_{HP}). The line correlates ΔH_{HM} values of the $W(CO)_3(PMe_xPh_{3-x})_3$ complexes.

Discussion

Basicities (ΔH_{HM}) of *fac*-$W(CO)_3(PR_3)_3$ Complexes. We have determined ΔH_{HM} for protonation reactions (eq 5) of the series of *fac*-$W(CO)_3(PR_3)_3$ complexes (**1**–**6**) where the basicity and cone angle of the PR_3 ligand[11,18] are varied (Table I). Structures of the reactants and products as established by studies discussed above are shown in eq 5.[3] As seen from the data in Table I, the basicity of the metal in these complexes is greatest ($\Delta H_{HM} = -25.0$ kcal mol^{-1}) for the complex which contains the most basic PEt_3 ligands and is lowest ($\Delta H_{HM} = -15.1$ kcal mol^{-1}) for **1** with the least basic $PMePh_2$ ligands. While there is generally an increase in ΔH_{HM} with an increase in the basicity (ΔH_{HP}) of the ligand, an equation ($-\Delta H_{HM} = -0.887(\Delta H_{HP}) - 6.56$; in kcal mol^{-1}) that attempts to correlate linearly these quantities gives a low correlation coefficient ($r = 0.917$); this poor correlation can also be seen in Figure 1. However, if one considers only the complexes **1**, **3**, and **5** with methylphenylphosphine ligands (PMe_xPh_{3-x}, $x = 1$–3), an excellent correlation ($r = 1.00$) with ΔH_{HP} is observed (eq 9). The 0.638 coefficient in this equation

$$-\Delta H_{HM} = -0.638(\Delta H_{HP}) - 0.645 \qquad (9)$$

indicates that an increase of 1.0 kcal mol^{-1} in $-\Delta H_{HP}$ of the phosphine increases $-\Delta H_{HM}$ by 0.638 kcal mol^{-1}. Since three phosphine ligands contribute to this increase, each phosphine contributes 0.213 kcal mol^{-1} (0.638/3). Thus, $-\Delta H_{HM}$ changes only 0.213 kcal mol^{-1} when $-\Delta H_{HP}$ of one phosphine ligand changes 1.0 kcal mol^{-1}. This change is small as compared with corresponding changes of 0.298 kcal mol^{-1} for $CpIr(CO)(PR_3)$ and 0.458 kcal mol^{-1} for $Fe(CO)_3(PR_3)_2$.[1] A possible reason for this small change in the tungsten system is that the more sterically crowded complexes in the $W(CO)_3[PMe_xPh_{3-x}]_3$ series have a higher basicity than expected from the ΔH_{HP} values of their phosphines. That is, steric crowding in *fac*-$W(CO)_3(PMePh_2)_3$ may be relieved as the *fac* complex is protonated (eq 5) and rearranges to the less crowded structure of $[W(H)(CO)_3(PMePh_2)_3]^+$ in which the phosphines are no longer mutually cis. On the other hand, *fac*-$W(CO)_3(PMe_3)_3$ is much less crowded, so its protonation is less favored by relief of phosphine ligand crowding.

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[11] Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758 and references cited therein.

[12] (a) Rahman, M. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650. (b) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.

[13] See footnote 20 in ref 12a.

[14] (a) Prock, A.; Giering, W. P.; Greene, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. C.; Wilson, M.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* **1991**, *10*, 3479. (b) Poë, A. J. *Pure Appl. Chem.* **1988**, *60*, 1209 and references cited therein.

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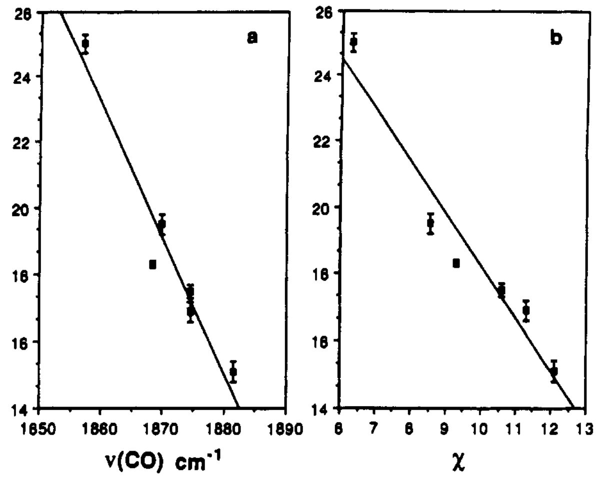


Figure 2. Correlation of *fac*-W(CO)$_3$(PR$_3$)$_3$ basicity (ΔH_{HM}) (a) vs the average value of the ν(CO) bands of the *fac*-W(CO)$_3$(PR$_3$)$_3$ complexes (eq 11) and (b) vs the χ value (eq 12) of the PR$_3$ ligands taken from ref 11.

Further evidence that phosphine ligand bulkiness enhances the basicities of these complexes can be noted in ΔH_{HM} values for the W(CO)$_3$(PEt$_x$Ph$_{3-x}$)$_3$ complexes. In Figure 1, it is evident that the PEt$_x$Ph$_{3-x}$ complexes are more basic than their PMe$_x$Ph$_{3-x}$ analogs by 0.8–5.5 kcal mol^{-1}. Part of the reason for this is that PEt$_3$ and PEtPh$_2$ are more basic (Table I) than PMe$_3$ and PMePh$_2$, respectively. (Rather surprisingly, PEt$_2$Ph is less basic than PMe$_2$Ph; this is true whether the basicity is measured by ΔH_{HP} (Table I) or pK_a values (pK_a = 6.25 and 6.50, respectively).[11]) However, the deviation of ΔH_{HM} values for the W(CO)$_3$(PEt$_x$Ph$_{3-x}$)$_3$ complexes from the line for the PMe$_x$Ph$_{3-x}$ complexes in Figure 1 indicates that another factor is involved. Given the expected crowding in the *fac*-W(CO)$_3$(PR$_3$)$_3$ complexes and the discussion of crowding in the PMe$_x$Ph$_{3-x}$ complexes, it seems likely that large phosphines will enhance the basicities of the PEt$_x$Ph$_{3-x}$ complexes. One might use the following cone angles (θ)[11,18] to estimate the bulkiness of these ligands: PMePh$_2$ (136°), PEtPh$_2$ (140°); PMe$_2$Ph (122°), PEt$_2$Ph (136°); PMe$_3$ (118°), PEt$_3$ (132°). In fact, if one corporates a cone angle term into eq 9 to give eq 10, where θ_{Et} and θ_{Me} are the cone angles of the

$$-\Delta H_{HM} = -0.638(\Delta H_{HP}) - 0.645 + 0.253(\theta_{Et} - \theta_{Me}) \quad (10)$$

PEt$_x$Ph$_{3-x}$ and PMe$_x$Ph$_{3-x}$ phosphines, ΔH_{HM} values for all six of the W(CO)$_3$(PR$_3$)$_3$ complexes can be calculated within a 3% error, except for W(CO)$_3$(PEt$_2$Ph)$_3$ (**4**), for which the calculated ΔH_{HM} (−20.6 kcal mol^{-1}) is significantly higher than the experimental value (−18.3 kcal mol^{-1}). The reason for this discrepancy is not clear but could be related to the anomalously low basicity of PEt$_2$Ph relative to PMe$_2$Ph. It is also possible that the cone angle (θ_{Et}) of PEt$_2$Ph in complex **4** is overestimated, as a value of 127° for θ_{Et} gives a more suitable calculated ΔH_{HM} value of −18.4 kcal mol^{-1} according to eq 10. Nevertheless, the useful inclusion of the cone angle term in eq 10 suggests that steric crowding in the *fac*-W(CO)$_3$(PR$_3$)$_3$ complexes does indeed enhance the basicity of the metal. This is presumably due to a relief of crowding during the formation of the [W(H)(CO)$_3$(PR$_3$)$_3$]$^+$ product.

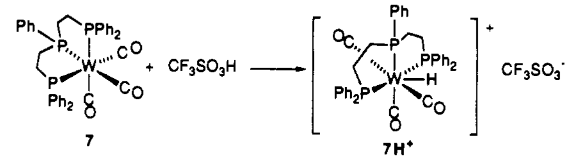
The $-\Delta H_{HM}$ values of complexes **1**–**6** increase as their ν(CO) values[3] decrease. This correlation (r = −0.973) is expressed in eq 11 and is shown in Figure 2a; it indicates that as tungsten to

$$-\Delta H_{HM} = 0.403[1917.4 - \nu(\mathrm{CO})] \quad (\text{in kcal mol}^{-1}) \quad (11)$$

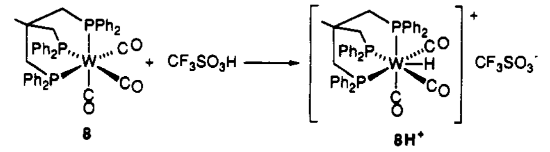
$$-\Delta H_{HM} = -1.57\chi + 33.9 \quad (\text{in kcal mol}^{-1}) \quad (12)$$

CO d$\pi \rightarrow$ pπ^* back-bonding increases, the basicity of the tungsten metal increases.[1] Also, $-\Delta H_{HM}$ correlates (eq 12 and Figure 2b; r = −0.969) with phosphine χ values,[11] which are derived from ν(CO) values of Ni(CO)$_3$(PR$_3$) complexes[18a] and are considered measures of the σ-donor abilities[11] of alkyl-, aryl- and mixed alkylarylphosphines. However, since χ does not correlate well with ΔH_{HP} or pK_a, it appears that χ is not the same measure of donor ability as ΔH_{HP}[2] or pK_a.[12b] Equations 11 and 12 may be used to estimate basicities of other W(CO)$_3$(PR$_3$)$_3$ complexes.

Basicities of W(CO)$_3$(tridentate phosphine) Complexes. As previously reported,[4] *fac*-W(CO)$_3$[PhP(CH$_2$CH$_2$PPh$_2$)$_2$] (**7**) protonates at the tungsten (eq 13) to form {W(H)(CO)$_3$[PhP(CH$_2$CH$_2$PPh$_2$)$_2$]}CF$_3$SO$_3$ (**7H**$^+$CF$_3$SO$_3^-$), whose structure is similar to that of complexes **1H**$^+$–**6H**$^+$ as indicated by their similar ν(CO) patterns in the infrared spectrum.[3]



(13)



(14)

That the ΔH_{HM} value of **7** (−16.7 kcal mol^{-1})[4] is between that of W(CO)$_3$(PMePh$_2$)$_3$ (−15.1 kcal mol^{-1}) and W(CO)$_3$(PMe$_2$Ph)$_3$ (−17.5 kcal mol^{-1}) indicates the PhP(CH$_2$CH$_2$PPh$_2$)$_2$ ligand contributes to the basicity of the metal to approximately the same extent as a combination of one PMe$_2$Ph and two PMePh$_2$ ligands. The previously reported[13] "effective" pK_a value (5.53) and cone angle (θ = 130°) as discussed above support this comparison since the average pK_a (5.21) and cone angle (131°) values for the (PMePh$_2$)$_2$(PMe$_2$Ph) ligand combination which are calculated from a 2:1 weighted average of the individual pK_a and cone angle values,[11] respectively, are similar. Using the effective ΔH_{HP} value of −26.4 kcal mol^{-1} and cone angle of PhP(CH$_2$CH$_2$PPh$_2$)$_2$ discussed above gives according to eq 10 an estimated ΔH_{HM} value for **7** of −16.1 kcal mol^{-1}, which is in reasonable agreement with the experimentally determined value of −16.7 kcal mol^{-1}.

A related comparison[19] of PhP(CH$_2$CH$_2$PPh$_2$)$_2$ and the (PMePh$_2$)$_2$(PMe$_2$Ph) combination shows that the heat of reaction (ΔH_{rx}) for the displacement of toluene from (η^6-toluene)Mo(CO)$_3$ and PhP(CH$_2$CH$_2$PPh$_2$)$_2$ (ΔH_{rx} = −41.0 kcal mol^{-1}) is within experimental error of that estimated (ΔH_{rx} = −39.4 kcal mol^{-1}) for the toluene displacement reaction with the (PMePh$_2$)$_2$(PMe$_2$Ph) ligand combination. These data suggest that the σ-donor and steric properties of the PhP(CH$_2$CH$_2$PPh$_2$)$_2$ ligand and the (PMePh$_2$)$_2$(PMe$_2$Ph) ligand combination are similar. Some steric repulsion is likely to be involved in both of these combinations as suggested for **1** above and for **7** in other studies.[20]

Protonation of *fac*-W(CO)$_3$[MeC(CH$_2$PPh$_2$)$_3$] (**8**) with CF$_3$SO$_3$H gives {W(H)(CO)$_3$[MeC(CH$_2$PPh$_2$)$_3$]}CF$_3$SO$_3$ (**8H**$^+$CF$_3$SO$_3^-$), which adopts a structure different from that of **7H**$^+$ as a result of the MeC(CH$_2$PPh$_2$)$_3$ chelate design which forces the phosphorus donors to remain mutually cis (eq 14).[3] Complex **8** (ΔH_{HM} = −10.1 kcal mol^{-1})[4] is also substantially less basic than **7** (ΔH_{HM} = −16.7 kcal mol^{-1}). The origin of this effect is most likely caused by a difference in energies between the protonated products **7H**$^+$ and **8H**$^+$ since the neutral complexes

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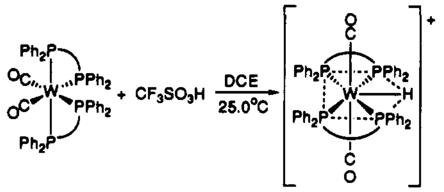
7 and **8** both have *fac* geometries and therefore probably similar energies.[4] The $PhP(CH_2CH_2PPh_2)_2$ chelate in **7** is sufficiently flexible to permit **7H**$^+$ to adopt the more stable geometry of the complexes with monodentate ligands (eq 5). Since **8H**$^+$ is forced to adopt a different geometry because of the restrictive $MeC(CH_2PPh_2)_3$ ligand, the lower basicity of **8** is attributed to the relatively high energy of the **8H**$^+$ structure. The 6.2 kcal mol^{-1} lower basicity for **8** means that the equilibrium constant for the protonation of **8** is 3.5×10^4 times smaller than that of **7**, assuming $\Delta S°$ values for both protonations to be the same.

Recently[17] we reported the basicities of *cis*-$W(CO)_2[Ph_2PCH_2PPh_2]_2$ ($\Delta H_{HM} = -31.5$ kcal mol^{-1}) and *cis*-$W(CO)_2[Ph_2P(CH_2)_2PPh_2]_2$ ($\Delta H_{HM} = -25.1$ kcal mol^{-1}), which protonate at the tungsten to give the protonated complexes with mutually trans-CO groups (eq 15). Both of these complexes are substantially more basic than the tris(phosphine) complexes $W(CO)_3(PMePh_2)_3$ (−15.1 kcal mol^{-1}) and $W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (−16.7 kcal mol^{-1}). Previously[1] we estimated that replacement of a CO in $CpIr(CO)_2$ with a PPh_3 group to give $CpIr(CO)(PPh_3)$ increases the Ir basicity by 14.4 kcal mol^{-1}. Similarly, the greater basicity of the $W(CO)_2$(bidentate phosphine)$_2$ complexes can be attributed to the replacement of the π-accepting CO ligand in $W(CO)_3(L_3)$ with a σ-donating phosphine group.



$CF_3SO_3^-$; ΔH_{HM} (15)

Basicities of Cp*Re(CO)$_2$(PR$_3$) Complexes. The protonation of $Cp^*Re(CO)_2(PR_3)$ (**9**, **10**) with CF_3SO_3H gives a mixture of *cis*- and *trans*-$[Cp^*Re(H)(CO)_2(PR_3)]CF_3SO_3$ in an approximately 2:1 ratio in favor of the cis isomer (eq 6). These isomers are probably in rapid equilibrium as was previously shown for $[CpRe(H)(CO)_2(PPh_3)]^+$.[9] Substituting the phosphine ligand in $Cp^*Re(CO)_2(PMe_2Ph)$ (**9**, $\Delta H_{HM} = -18.3$ kcal mol^{-1}) with PMe_3 to give **10** ($\Delta H_{HM} = -20.1$ kcal mol^{-1}) causes a 1.8 kcal mol^{-1} increase in metal basicity, which is consistent with the trend in increasing σ-donor ability of the phosphine ligands. Previously[1] we reported that substitution of PMe_2Ph with PMe_3 increases metal basicity by 0.8 kcal mol^{-1} in $CpIr(CO)(PR_3)$ and 1.0 kcal mol^{-1} (per phosphine ligand) in $Fe(CO)_3(PR_3)_2$. In the cases of Ir and Fe, steric effects of the phosphine ligands on ΔH_{HM} were ruled out because of the relatively uncrowded reactants and products. The greater change in Re basicity as compared to Ir or Fe suggests that substituting the more bulky PMe_2Ph ligand ($\theta = 122°$) in **9** with the less bulky PMe_3 ($\theta = 118°$) ligand in **10** reduces steric crowding in the seven-coordinate $[Cp^*Re(H)(CO)_2(PR_3)]CF_3SO_3$ product; both this steric effect and the greater basicity of PMe_3 probably contribute to making ΔH_{HM} more exothermic for **10**.

Acknowledgment. We thank Giacomo Facchin for preparations and initial protonation studies of **9** and **10**. We are also grateful to the National Science Foundation (Grants CHE-8719744 and CHE-9103948) for supporting this work.