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Calorimetric Studies of the Heats of Protonation of the Dangling Phosphorus in η^1-$\mathrm{Ph_2PCH_2PPh_2}$ Complexes of Chromium, Molybdenum, and Tungsten

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Titration calorimetry has been used to determine the heats of protonation (ΔH_{HP}) of $\mathrm{M(CO)_5}(\eta^1\text{-dppm})$ (M = Cr, Mo, W) and *fac*-$\mathrm{M(CO)_3(N^\frown N)}(\eta^1\text{-dppm})$ (M = Mo, $\mathrm{N^\frown N}$ = bipy, phen; M = W, $\mathrm{N^\frown N}$ = bipy) complexes with $\mathrm{CF_3SO_3H}$ in 1,2-dichloroethane solvent at 25.0 °C. Spectroscopic studies show that protonation occurs at the uncoordinated phosphorus atom of the η^1-coordinated dppm ($\mathrm{Ph_2PCH_2PPh_2}$) ligand. For dppm, its monoprotonated form ($\mathrm{dppmH^+}$), and these complexes, the basicity (ΔH_{HP}) of the dangling phosphorus increases from −14.9 kcal/mol to −23.1 kcal/mol in the order: $\mathrm{dppmH^+} < \mathrm{Cr(CO)_5}(\eta^1\text{-dppm}) < \mathrm{Mo(CO)_5}(\eta^1\text{-dppm}) < \mathrm{W(CO)_5}(\eta^1\text{-dppm}) < \mathrm{dppm} \leq$ *fac*-$\mathrm{Mo(CO)_3}(\eta^2\text{-bipy})(\eta^1\text{-dppm}) <$ *fac*-$\mathrm{Mo(CO)_3}(\eta^2\text{-phen})(\eta^1\text{-dppm}) \approx$ *fac*-$\mathrm{W(CO)_3}(\eta^2\text{-bipy})(\eta^1\text{-dppm})$. In this series, $\mathrm{H^+}$ is more electron-withdrawing than $\mathrm{M(CO)_5}$ (M = Cr, Mo, W); $\mathrm{Mo(CO)_3}(\eta^2\text{-phen})$ and $\mathrm{W(CO)_3}(\eta^2\text{-bipy})$ actually enhance the basicity of the dangling phosphorus as compared with dppm itself. The basicity (ΔH_{HM}) of *fac*-$\mathrm{W(CO)_3}(\eta^2\text{-bipy})(\mathrm{PPh_2Me})$, which protonates at the metal center to give a seven-coordinate complex, is −18.8 kcal/mol. Thus, the basicity of the dangling phosphorus atom in *fac*-$\mathrm{W(CO)_3}(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ is approximately 4.3 kcal/mol more basic than the metal center.

Introduction

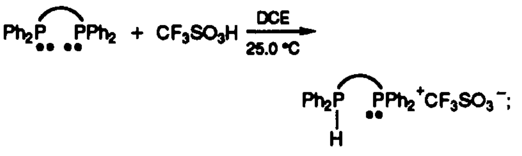
Bidentate phosphine ligands have been widely used in transition metal complexes.[1] In this research group, we have explored the effects of bidentate ligand structure on the basicity of the metal in the complexes $\mathrm{Fe(CO)_3(P^\frown P)}$,[2] $\mathrm{M(CO)_2(P^\frown P)_2}$ (M = Cr, Mo, W),[3] and $\mathrm{CpRu(P^\frown P)H}$ ($\mathrm{Cp = C_5H_5}$)[4] as measured by their heats of protonation with $\mathrm{CF_3SO_3H}$ in 1,2-dichloroethane solvent at 25.0 °C (eq 1). In several of these complexes,[2,3] the chelate ring size dramatically alters the basicity of the metal center.

$$\mathrm{ML}_n + \mathrm{CF_3SO_3H} \xrightarrow[25.0\,^\circ\mathrm{C}]{\mathrm{DCE}} \mathrm{HML}_n{}^+\mathrm{CF_3SO_3}^-;\ \Delta H_{\mathrm{HM}} \quad (1)$$

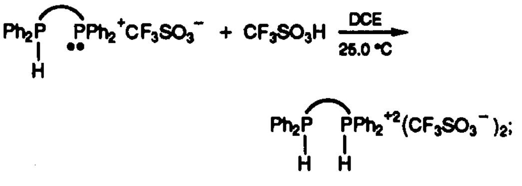
In the present study we sought to understand the effect of a metal complex ML_x on the basicity of the dangling phosphorus of an η^1-coordinated bidentate phosphine ligand by determining heats of protonation (ΔH_{HP}) for reactions of the type in eq 2.

$$\mathrm{L}_x\mathrm{M{-}P^\frown P} + \mathrm{CF_3SO_3H} \xrightarrow[25.0\,^\circ\mathrm{C}]{\mathrm{DCE}} \mathrm{L}_x\mathrm{MP^\frown PH^+CF_3SO_3}^-;\ \Delta H_{\mathrm{HP}} \quad (2)$$

Previously, it was established[5] that free bidentate ligands $\mathrm{Ph_2P(CH_2)}_n\mathrm{PPh_2}$ are protonated in two steps (eqs 3 and 4), and these heats of protonation (ΔH_{HP1} and ΔH_{HP2}) may be substantially different from each other. The largest difference was for dppm ($\mathrm{Ph_2PCH_2PPh_2}$), whose ΔH_{HP1} was −22.0 kcal/mol, but ΔH_{HP2} was only −14.9 kcal/mol. Thus, protonation of one phosphorus decreases the basicity of the other phosphorus by 7.1 kcal/mol, a large change in donor ability.

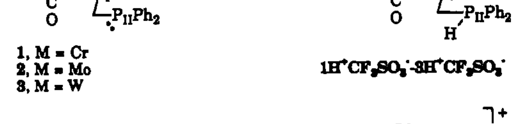


; ΔH_{HP1} (3)



; ΔH_{HP2} (4)

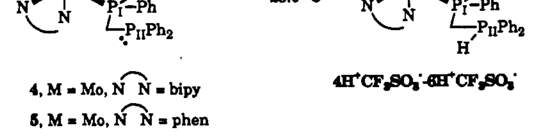
Transition metal complexes, like $\mathrm{H^+}$, would presumably act as Lewis acids when η^1-coordinated to dppm and thereby affect the ΔH_{HP} of the dangling phosphorus. In this investigation, we describe the effects of $\mathrm{M(CO)_5}$ (M = Cr, Mo, W) and the more electron-rich $\mathrm{M(CO)_3(bipy)}$ (M = Mo, W) and $\mathrm{Mo(CO)_3(phen)}$, where bipy is 2,2′-bipyridyl and phen is 1,10-phenanthroline, complexes on the basicity (ΔH_{HP}) of the dangling phosphorus in their η^1-dppm complexes. Thus, ΔH_{HP} values for reactions 5 and 6 were determined under the same conditions as for reactions 3 and 4.



(5)

1, M = Cr
2, M = Mo
3, M = W

$\mathbf{1H^+CF_3SO_3^-}$–$\mathbf{3H^+CF_3SO_3^-}$



(6)

4, M = Mo, $\mathrm{N^\frown N}$ = bipy
5, M = Mo, $\mathrm{N^\frown N}$ = phen
6, M = W, $\mathrm{N^\frown N}$ = bipy

$\mathbf{4H^+CF_3SO_3^-}$–$\mathbf{6H^+CF_3SO_3^-}$

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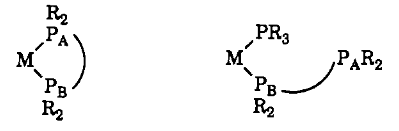
0020-1669/93/1332-2421$04.00/0

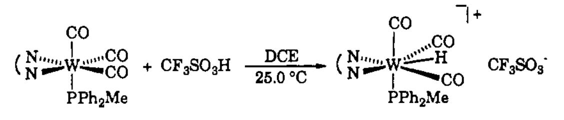
Chart I



(a) (b)

Another reason to measure ΔH_{HP} for reactions 5 and 6 is to estimate the donor ability of the phosphorus atoms in a dppm chelate complex. Previously,[6] we correlated heats of protonation (ΔH_{HM}) of metal complexes with the basicities (ΔH_{HP}) of their phosphine ligands. For chelating ligands such as dppm, one might assume that the measure of donor ability of the P atom to be used in these correlations is ΔH_{HP1}. However, it seems likely that the coordination of one P atom (P_B in Chart Ia) is going to affect the donor ability of the other (P_A) by withdrawing electron density through the CH_2 link. An estimate of this effect is ΔH_{HP} for P_A in a complex of type b in Chart I. Thus, ΔH_{HP} values for reactions 5 and 6 provide an estimate of the effect that coordination through both P atoms in dppm has on the donor ability of each phosphorus. The P-donor ability of chelates with longer hydrocarbon links, e.g., $Ph_2PCH_2CH_2PPh_2$(dppe), will probably be less affected than dppm by coordination of the other end. This is evident from the much smaller difference (2.6 kcal/mol) between ΔH_{HP1} (−22.8 kcal/mol) and ΔH_{HP2} (−20.2 kcal/mol) for dppe (eqs 3 and 4).[5]

In order to compare the basicity of the metal center with that of the dangling phosphorus in eq 6, we also measured the heat of protonation (ΔH_{HM}) of *fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) as shown in eq 7.



(7)

7, N͡N = bipy **7H$^+$CF$_3$SO$_3$$^-$**

Experimental Section

All preparative reactions and solvent purifications were carried out under N_2 atmosphere using standard Schlenk techniques. Hexanes and CH_2Cl_2 were refluxed over CaH_2 and then distilled. Xylenes were deoxygenated with N_2 and then stored over molecular sieves for 12 h before use; the 1,2-dichloroethane (99.8%, HPLC grade, purchased from Aldrich) was distilled under argon from P_4O_{10} immediately prior to use. Deuterated solvents (CD_2Cl_2 and $CDCl_3$) were stored over molecular sieves in air. The CF_3SO_3H was purchased from 3M Co. and purified as previously described.[7] The IR spectra were recorded on a Bio-Rad FTS-7 FTIR spectrometer, ^{1}H NMR spectra were obtained on a Nicolet-NT 300-MHz instrument with TMS (δ = 0.00 ppm) as the internal reference, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer using 85% phosphoric acid (δ = 0.00 ppm) as the external standard.

The complexes W(CO)$_4$(η^2-bipy),[8] Cr(CO)$_5$(η^1-dppm) (**1**),[9] Mo(CO)$_5$(η^1-dppm) (**2**),[9] Mo(CO)$_3$(η^2-bipy)(η^1-dppm) (**4**),[10] Mo(CO)$_3$(η^2-phen)(η^1-dppm) (**5**),[10] and W(CO)$_3$(η^2-bipy)(η^1-dppm) (**6**)[11a] were prepared as previously described. The bipy complexes have also been prepared by a route using Me$_3$NO.[11b] Ligand abbreviations are bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, and dppm = $Ph_2PCH_2PPh_2$.

W(CO)$_5$(η^1-dppm) (3) was prepared in a manner similar to that used by Basolo et al.,[12] by vigorously stirring 250 mg (0.71 mmol) of W(CO)$_6$ and 79 mg (0.71 mmol) of $Me_3NO\cdot 2H_2O$ in 20 mL of CH_2Cl_2 for 15 min. To the yellow solution was added 273 mg (0.71 mmol) of dppm; this solution was stirred at room temperature for 3 days with a slow flow of N_2 through the solution. The air-stable white precipitate was filtered off and washed with MeOH and then recrystallized at −20 °C from a minimal amount of CH_2Cl_2 layered with MeOH. Pure, colorless crystals of W(CO)$_5$(η^1-dppm) were obtained (210 mg) in 42% yield. The spectral data listed below agree with the previously reported literature values.[9]

***fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) (7)** was prepared by refluxing 252 mg (0.56 mmol) of W(CO)$_4$(η^2-bipy)[8] with 0.104 mL (0.56 mmol) of PPh$_2$Me in 20 mL of xylenes for 5 h. The precipitate was filtered from the cooled solution and washed with copious amounts of hexanes. The air-stable fine dark purple crystals of *fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) (194 mg, 56% yield) were collected and dried in vacuo. Spectral data are listed below.

Protonation Reactions. Compounds **1–7** were protonated for spectroscopic characterization by dissolving ~5 mg of the complex in 0.5 mL of CD_2Cl_2 (or $CDCl_3$) in a 5-mm NMR tube under N_2. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe through a rubber septum. Spectroscopic data collected at room temperature are listed below for compounds **1–7** and **1H$^+$–7H$^+$**. Compounds **1–6** have been previously characterized: the spectroscopic data given in the literature are very similar to those listed below.

Cr(CO)$_5$(η^1-dppm) (1): ^{1}H NMR (CD_2Cl_2) δ 7.1–7.3 (m, Ph), 3.28 (dd, $^2J_{PH}$ = 6.9 and 0.6 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 47.2 (d, $^2J_{PP}$ = 94 Hz, Cr-P$_I$), −25.8 (d, $^2J_{PP}$ = 95 Hz, P$_{II}$); IR (CH_2Cl_2) ν(CO) 2067 (w), 1939 (s).

Cr(CO)$_5$[Ph$_2$PCH$_2$P(Ph)$_2$(H)]$^+$CF$_3$SO$_3$$^-$ (1H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR ($CD_2Cl_2$) δ 7.1–7.3 (m, Ph), 4.2 (br s, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 52.3 (s, Cr-P$_I$), 4.2 (br s, P$_{II}$); IR (CD_2Cl_2) ν(CO) 2067 (w), 1939 (s).

Mo(CO)$_5$(η^1-dppm) (2): ^{1}H NMR (CD_2Cl_2) δ 7.1–7.3 (m, Ph), 3.22 (dd, $^2J_{PH}$ = 8.1 and 2.7 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 28.1 (d, $^2J_{PP}$ = 114 Hz, Mo-P$_I$), −24.9 (d, $^2J_{PP}$ = 114 Hz, P$_{II}$); IR (CH_2Cl_2) ν(CO) 2072 (w), 1945 (s).

Mo(CO)$_5$[Ph$_2$PCH$_2$P(Ph)$_2$(H)]$^+$CF$_3$SO$_3$$^-$ (2H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR ($CD_2Cl_2$) δ 7.1–7.3 (m, Ph), 4.2 (br s, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 31.3 (d, $^2J_{PP}$ = 9.2 Hz, Mo-P$_I$), 6.8 (br s, P$_{II}$); IR (CD_2Cl_2) ν(CO) 2072 (w), 1945 (s).

W(CO)$_5$(η^1-dppm) (3): ^{1}H NMR ($CDCl_3$) δ 7.1–7.3 (m, Ph), 3.31 (dd, $^2J_{PH}$ = 8.4 and 2.1 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 10.4 (d, $^2J_{PP}$ = 106 Hz, $^1J_{PW}$ = 246 Hz, W-P$_I$), −24.3 (d, $^2J_{PP}$ = 106 Hz, P$_{II}$); IR (CH_2Cl_2) ν(CO) 2071 (w), 1934 (s).

W(CO)$_5$[Ph$_2$PCH$_2$P(Ph$_2$)(H)]$^+$CF$_3$SO$_3$$^-$ (3H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR ($CDCl_3$) δ 7.2–7.4 (m, Ph), 4.5 (br s, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 11.4 (br s, P$_I$), 7.7 (br s, P$_{II}$); IR ($CDCl_3$) ν(CO) 2071 (w), 1934 (s).

Mo(CO)$_3$(η^2-bipy)(η^1-dppm) (4): ^{1}H NMR (CD_2Cl_2) δ 9.1 (d, $^2J_{HH}$ = 6.5 Hz, 2 H), 8.8 (d, $^2J_{HH}$ = 5.7 Hz, 2 H), 8.1 (d, $^2J_{HH}$ = 8.1 Hz, 2 H), 7.0–7.8 (m, Ph), 2.64 (dd, $^2J_{PH}$ = 4.4 and 2.1 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 47.2 (d, $^2J_{PP}$ = 71 Hz, Mo-P$_I$), −27.9 (d, $^2J_{PP}$ = 71 Hz, P$_{II}$); IR (CH_2Cl_2) ν(CO) 1911 (s), 1824 (m), 1754 (m).

Mo(CO)$_3$(η^2-bipy)[Ph$_2$PCH$_2$P(Ph)$_2$(H)]$^+$CF$_3$SO$_3$$^-$ (4H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR ($CD_2Cl_2$) δ 9.1 (d, $^2J_{HH}$ = 5.9 Hz, 2 H), 8.9 (d, $^2J_{HH}$ = 5.9 Hz, 2 H), 8.1 (d, $^2J_{HH}$ = 8.0 Hz, 2 H), 7.1–7.8 (m, Ph), 4.0 (br s, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 30.2 (d, $^2J_{PP}$ = 17 Hz, Mo-P$_I$), 7.9 (d, $^2J_{PP}$ = 17 Hz, P$_{II}$); IR (CD_2Cl_2) ν(CO) 1911 (s), 1824 (m), 1754 (m).

Mo(CO)$_3$(η^2-phen)(η^1-dppm) (5): ^{1}H NMR (CD_2Cl_2) δ 9.2 (d, $^2J_{HH}$ = 5 Hz, 2 H), 8.0 (d, $^2J_{HH}$ = 8.1 Hz, 2 H), 6.7–7.4 (m, Ph), 2.66 (dd, $^2J_{PH}$ = 4.5 and 2.0 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 28.7 (d, $^2J_{PP}$ = 70 Hz, Mo-P$_I$), −27.6 (d, $^2J_{PP}$ = 7.0 Hz, P$_{II}$); IR (CH_2Cl_2) ν(CO) 1906 (s), 1826 (m), 1781 (m).

Mo(CO)$_3$(η^2-phen)[Ph$_2$PCH$_2$P(Ph)$_2$(H)]$^+$CF$_3$SO$_3$$^-$ (5H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR ($CD_2Cl_2$) δ 9.1 (d, $^2J_{HH}$ = 4.8 Hz, 2 H), 8.9 (d, $^2J_{HH}$ = 4.8 Hz, 2 H), 8.2 (d, $^2J_{HH}$ = 7.5 Hz, 2 H), 6.9–7.8 (m, Ph), 4.2 (br s, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 32.1 (d, $^2J_{PP}$ = 17 Hz, Mo-P$_I$), 8.0 (d, $^2J_{PP}$ = 17 Hz, P$_{II}$); IR (CD_2Cl_2) ν(CO) 1906 (s), 1826 (m), 1781 (m).

W(CO)$_3$(η^2-bipy)(η^1-dppm) (6): ^{1}H NMR (CD_2Cl_2) δ 9.2 (d, $^2J_{HH}$ = 5.7 Hz, 2 H), 8.9 (d, $^2J_{HH}$ = 5.4 Hz, 2 H), 8.1 (d, $^2J_{HH}$ = 8.4 Hz, 2 H), 7.9 (t, $^2J_{HH}$ = 7.5 Hz, 2 H), 7.0–7.5 (m, Ph), 2.22 (dd, $^2J_{PH}$ = 4.5 and 2.1 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.0 (d, $^2J_{PP}$ = 66 Hz, W-P$_I$), −27.8 (d, $^2J_{PP}$ = 66 Hz, P$_{II}$); IR (CH_2Cl_2) ν(CO) 1906 (s), 1822 (m), 1774 (m).

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$W(CO)_3(\eta^2\text{-bipy})[Ph_2PCH_2P(Ph)_2(H)]^+CF_3SO_3^-$ ($6H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 9.2 (d, $^2J_{HH}$ = 6.3 Hz, 2 H), 8.8 (d, $^2J_{HH}$ = 5.1 Hz, 2 H), 8.1 (d, $^2J_{HH}$ = 8.1 Hz, 2 H), 7.0–7.9 (m, Ph), 4.2 (br s, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 19.9 (d, $^2J_{PP}$ = 12 Hz, W-P_I), 8.7 (br d, $^2J_{PP}$ = 12 Hz, P_{II}); IR (CD_2Cl_2) ν(CO) 1906 (s), 1822 (m), 1774 (m).

$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$ (7): ^1H NMR (CD_2Cl_2) δ 8.9 (d, $^2J_{HH}$ = 5.7 Hz, 2 H), 7.8 (d, $^2J_{HH}$ = 8.1 Hz, 2 H), 7.2–7.0 (m, Ph), 1.52 (d, $^2J_{PH}$ = 6 Hz, 3 H, CH_3); IR (CH_2Cl_2) ν(CO) 1906 (s), 1810 (m), 1782 (m).

$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)(H)^+CF_3SO_3^-$ ($7H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 8.8 (d, $^2J_{HH}$ = 5:4 Hz, 2 H), 8.4 (d, $^2J_{HH}$ = 8.1 Hz, 2 H), 8.2 (t, $^2J_{HH}$ = 7.8 Hz, 2 H), 7.6 (t, $^2J_{HH}$ = 6.3 Hz, 2 H), 7.43 (t, $^2J_{HH}$ = 7.5 Hz, 2 H), 7.3 (t, $^2J_{HH}$ = 7.5 Hz, 4 H), 7.0 (t, $^2J_{HH}$ = 10.5 Hz, 4 H), 1.65 (d, $^2J_{PH}$ = 7.2 Hz, 3 H, CH_3), –3.0 (d, $^2J_{PH}$ = 30.3 Hz, 1 H, W-H); IR (CD_2Cl_2) ν(CO) 2021 (s), 1935 (s), 1920 (s).

Calorimetric Studies. The heats of protonation of complexes **1–7** were measured under an argon atmosphere using a Tronac Model 458 isoperibol calorimeter as originally described[7] and then modified.[6a] A three-minute titration period was used for all complexes and was preceded and followed by heat capacity calibrations. During the titration period, approximately 1.2 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 2.6 mM solution of the complex (5–10% excess) in DCE at 25.0 °C.

The ΔH_{HM} values were measured using at least two different standardized acid solutions and are reported as the average of at least four titrations and as many as eight. The heat of dilution of the acid in DCE (–0.2 kcal/mol)[6a] was used to correct the reaction enthalpies.

Results

Characterization of Reactants 1–7 and Protonated Products ($1H^+$–$7H^+$). Complexes **1–7** are air-stable in the solid state and in solution. Protonations of **1–6** result in complexes that are stable in solution. Complex **$7H^+$** is air-sensitive in solution, but is stable under a nitrogen atmosphere.

Complexes **1–3** have previously[9] been assigned octahedral geometries with one phosphorus atom (P_I) of the dppm ligand coordinated to the metal (eq 5) on the basis of their ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra. Since the $^{31}P\{^1H\}$ NMR, ^1H NMR, and IR spectra of **1–3** and **$1H^+$–$3H^+$** are very similar, only $Mo(CO)_5(\eta^1\text{-dppm})$ (**2**) and its protonation will be discussed here. The doublet at –24.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **2** was assigned to P_{II} (eq 5) because the chemical shift is so similar to that (–23.4 ppm) of free dppm in CD_2Cl_2; the doublet at 28.1 ppm was therefore assigned to P_I. The doublet of doublets for the methylene protons in the ^1H NMR spectrum also indicates inequivalent phosphorus atoms, which is consistent with η^1-coordination of the dppm ligand. Addition of 1 equiv of CF_3SO_3H to **2** results in protonation of the uncoordinated phosphorus atom (P_{II}) as suggested by the $^{31}P\{^1H\}$ NMR resonance for P_{II} moving downfield from –24.9 ppm to 6.8 ppm (br s); the resonance for P_I shifts only slightly downfield to 31.3 ppm (d, $^2J_{PP}$ = 9.2 Hz). A broad singlet at 4.22 ppm is observed for the methylene protons in the ^1H NMR spectrum of **$2H^+$**. Since protonation of **2** does not occur at the metal, the ν(CO) bands in the IR spectrum of **$2H^+$** are the same as those of **2** within experimental error.

Cano et al.[10,11] used IR spectroscopy to establish the *fac* geometries for complexes **4–6** (eq 6). Since the $^{31}P\{^1H\}$ NMR, ^1H NMR, and IR spectra of **4–6** and **$4H^+$–$6H^+$** are similar, only *fac*-$Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (**4**) and its protonated analog (**$4H^+$**) will be described here. By comparison with the chemical shift in the $^{31}P\{^1H\}$ NMR spectrum of free dppm (–23.4 ppm), the peak for **4** at –27.9 ppm is assigned to the dangling phosphorus atom (P_{II}) (eq 6); therefore, the peak at 47.2 ppm is assigned to P_I (eq 6). The doublet of doublets for the methylene protons in the ^1H NMR spectrum is also consistent with η^1-coordination of dppm. Addition of 1 equiv of CF_3SO_3H to **4** results in protonation of the free phosphorus atom (P_{II}) as suggested by the $^{31}P\{^1H\}$ resonance for P_{II}, which shifts downfield from –27.9 to 7.9 ppm upon protonation; the peak assigned to P_I shifts upfield from 47.2 to 30.2 ppm. A broad singlet at 4.0 ppm is observed for the methylene protons in the ^1H NMR spectrum of **$4H^+$**. Since protonation occurs at P_{II} and not at the metal center, the ν(CO) bands for **4** and **$4H^+$** are the same.

Table I. Heats of Protonation (ΔH_{HP} and ΔH_{HM}) for $M(CO)_5(\eta^1\text{-dppm})$, *fac*-$M(CO)_3(\eta^2\text{-}N\frown N)(\eta^1\text{-dppm})$, and *fac*-$W(CO)_3(bipy)(PPh_2Me)$ Complexes

metal complex[a]	$-\Delta H_{HP}$,[b] kcal/mol
$Cr(CO)_5(\eta^1\text{-dppm})$ (**1**)	17.1 (±0.1)
$Mo(CO)_5(\eta^1\text{-dppm})$ (**2**)	18.6 (±0.1)
$W(CO)_5(\eta^1\text{-dppm})$ (**3**)	19.1 (±0.3)
fac-$Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (**4**)	22.3 (±0.2)
fac-$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ (**5**)	23.0 (±0.1)
fac-$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (**6**)	23.1 (±0.1)
fac-$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$(**7**)	18.8 (±0.2)[c]
$Ph_2PCH_2PPh_2$	22.0 (±0.1)[d]
$(H)Ph_2PCH_2PPh_2^+$	14.9 (±0.2)[e]

[a] Ligand abbreviations: $Ph_2PCH_2PPh_2$ (dppm), 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen). [b] For protonation with CF_3SO_3H (0.1 M) in DCE solvent at 25.0 °C. Errors are given as average deviations from the mean of at least 4 titrations. [c] ΔH_{HM} for protonation at the tungsten with CF_3SO_3H (0.1 M) in DCE solvent at 25.0 °C. [d] ΔH_{HP1} according to eq 3; ref 5. [e] ΔH_{HP2} according to eq 4; ref 5.

The *fac* geometry is assigned to $W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$ (**7**) on the basis of the three strong ν(CO) bands in its IR spectrum; the frequencies of these bands are nearly identical to those previously reported for *fac*-$W(CO)_3(\eta^2\text{-bipy})(PPh_3)$.[13] In the ^1H NMR spectrum of **7**, a doublet is observed at 1.52 ppm for the methyl group; addition of 1 equiv of CF_3SO_3H results in a downfield shift of the methyl resonance to 1.65 ppm and the appearance of a doublet at –3.0 ppm for the hydride. The IR spectrum of **$7H^+$** has three ν(CO) bands of approximately equal intensity. Since the complex $W(H)(CO)_3[CH_3C(CH_2PPh_2)_3]^+$,[14] which must have three mutually *cis*-CO ligands as required by the phosphine ligand, was reported to have three ν(CO) bands of approximately the same intensity, it is likely that **$7H^+$** also has three mutually *cis*-CO ligands as drawn in eq 7; details of the structure, such as the position of the hydride ligand, are not known.

Complexes **$1H^+$–$7H^+$** are deprotonated rapidly and quantitatively with 1 equiv of 1,3-diphenylguanidine in CH_2Cl_2 or DCE solvent to yield the original complexes **1–7**, which are recovered by passing the solution through a short (~5-cm) neutral alumina column using CH_2Cl_2 as the eluent; the complexes are obtained by evaporating the solutions to dryness. Protonations of $Fe(CO)_4(\eta^1\text{-dppm})$[15] and *fac*-$Mo(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$[16] in CD_2Cl_2 with 1 equiv of CF_3SO_3H result in more than one product as indicated by IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR spectroscopy.

Calorimetric Studies. Heats of protonation (ΔH_{HP} and ΔH_{HM}) for complexes **1–7** as determined by titration calorimetry with CF_3SO_3H in 1,2-dichloroethane solution at 25.0 °C are listed in Table I. Plots of temperature vs amount of acid added were linear, which indicates that the complexes are protonated rapidly and quantitatively. There was no decomposition of either the neutral or the protonated species during the titration as evidenced by the normal pre- and posttitration base-line slopes for **1–7**.

The low dielectric constant (ϵ = 10.46)[17] for DCE suggests that the protonated products occur as ion pairs. However, as discussed elsewhere,[3,4,6] there is no evidence that ion-pairing or solvation energies determine trends in ΔH_{HP} or ΔH_{HM}. Thus, we attribute the differences in the ΔH_{HP} (and ΔH_{HM}) values to the properties of the reactant and product complexes.

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Discussion

Effect of the M(CO)$_5$ Group (M = Cr, Mo, W) on the Basicity (ΔH_{HP}, Equation 5) of the Dangling Phosphorus Atom (P$_{II}$) in M(CO)$_5$(η^1-dppm). As noted in the introduction, (H)Ph$_2$PCH$_2$PPh$_2$$^+CF_3SO_3$$^-$ (ΔH_{HP2} = −14.9 kcal/mol, eq 4) is 7.1 kcal/mol less basic than Ph$_2$PCH$_2$PPh$_2$ (ΔH_{HPI} = −22.0 kcal/mol, eq 3), which illustrates the strong electron-withdrawing effect of H$^+$ through the methylene group in dppm on the basicity of the unprotonated phosphorus. The effect of the M(CO)$_5$ groups (M = Cr, Mo, W) is significantly less as determined by ΔH_{HP} (Table I) for the dangling phosphorus (P$_{II}$) in the M(CO)$_5$(η^1-dppm) complexes; these basicities increase in the order: (H)Ph$_2$PCH$_2$PPh$_2$$^+$ (−14.9 kcal/mol) < Cr(CO)$_5$(η^1-dppm) (−17.1 kcal/mol) < Mo(CO)$_5$(η^1-dppm) (−18.6 kcal/mol) < W(CO)$_5$(η^1-dppm) (−19.1 kcal/mol) < Ph$_2$PCH$_2$PPh$_2$ (−22.0 kcal/mol). The order of M(CO)$_5$(η^1-dppm) basicities (ΔH_{HP}) is not consistent with the trend in either Pauling electronegativities [Cr (1.66) < Mo (2.16) < W (2.36)] or Allred-Rochow electronegativities [Cr (1.35) < Mo (1.24) < W (1.13)],[18] nor is it consistent with the electron affinities of the elements: Cr (65 kJ/mol) < Mo (100 kJ/mol) > W (60 kJ/mol).[19] It seems likely that the trend in ΔH_{HP} values for the M(CO)$_5$(η^1-dppm) complexes is a measure of the relative overall electron-withdrawing abilities of the M(CO)$_5$ groups, which are determined by σ- and π-bonding between the metal and P$_I$. This trend suggests that either π-back-bonding from the metal to the phosphorus increases as Cr < Mo < W or that the σ-accepting ability of the metal increases in the reverse order (W < Mo < Cr).

The electron-withdrawing effect of Mo(CO)$_5$ on the dangling phosphorus in Mo(CO)$_5$(η^1-Me$_2$PCH$_2$PMe$_2$) was determined previously by photoelectron spectroscopy.[20] In that study, the valence ionization energy of the dangling phosphorus in Mo(CO)$_5$(η^1-Me$_2$PCH$_2$PMe$_2$) (8.76 eV) was 0.33 eV higher than that of free Me$_2$PCH$_2$PMe$_2$ (8.43 eV).

Effect of the M(CO)$_3$(η^2-N$\frown$N) Group (M = Mo, W) on the Basicity (ΔH_{HP}, Equation 6) of the Dangling Phosphorus Atom (P$_{II}$) in *fac*-M(CO)$_3$(η^2-N$\frown$N)(η^1-dppm). The basicity of P$_{II}$ in W(CO)$_5$(η^1-dppm) (ΔH_{HP} = −19.1 kcal/mol) increases by 4.0 kcal/mol when two of the CO ligands are replaced by a bipy ligand to give *fac*-W(CO)$_3$(η^2-bipy)(η^1-dppm) (ΔH_{HP} = −23.1 kcal/mol). When two CO ligands in Mo(CO)$_5$(η^1-dppm) (ΔH_{HP} = −18.6 kcal/mol) are substituted by bipy (pK_{a1} = 4.44)[21] to give *fac*-Mo(CO)$_3$(η^2-bipy)(η^1-dppm) (ΔH_{HP} = −22.3 kcal/mol) or by the more basic phen ligand (pK_{a1} = 4.84)[21] to give *fac*-Mo(CO)$_3$(η^2-phen)(η^1-dppm) (ΔH_{HP} = −23.0 kcal/mol), the basicity (ΔH_{HP}) of the dangling phosphorus atom (P$_{II}$) increases by 3.7 and 4.4 kcal/mol, respectively. Thus, replacement of two CO ligands in Mo(CO)$_5$(η^1-dppm) (M = Mo, W) by bipy or phen (N$\frown$N) to give *fac*-Mo(CO)$_3$(N$\frown$N)(η^1-dppm) (**4**–**6**) increases the basicity of the dangling phosphorus atom (P$_{II}$) by 3.7–4.4 kcal/mol. As observed for the M(CO)$_5$(η^1-dppm) complexes, the tungsten derivative M(CO)$_3$(η^2-bipy)(η^1-dppm) is more basic (by 0.8 kcal/mol) than the Mo analog. Summarizing results for dppm and its complexes (**1**–**6**), the following order of increasing basicity (ΔH_{HP}) of the dangling phosphorus atom (P$_{II}$) is observed: (H)Ph$_2$PCH$_2$PPh$_2$$^+$ (−14.9 kcal/mol) < Cr(CO)$_5$(η^1-dppm) (−17.1 kcal/mol) < Mo(CO)$_5$(η^2-dppm) (−18.6 kcal/mol) < W(CO)$_5$(η^1-dppm) (−19.1 kcal/mol) < Ph$_2$P(CH$_2$)PPh$_2$ (−22.0 kcal/mol) ≤ *fac*-Mo(CO)$_3$(η^2-bipy)(η^1-dppm) (−22.3 kcal/mol) < *fac*-Mo(CO)$_3$(η^2-phen)(η^1-dppm) (−23.0 kcal/mol) ≈ *fac*-W(CO)$_3$(η^2-bipy)(η^1-dppm) (−23.1 kcal/mol). Of particular interest is the result that *fac*-W(CO)$_3$(η^2-bipy)(η^1-dppm) (ΔH_{HP} = −23.1 kcal/mol) is 1.1 kcal/mol *more* basic than Ph$_2$PCH$_2$PPh$_2$ itself (ΔH_{HPI} = −22.0 kcal/mol). Similarly, *fac*-Mo(CO)$_3$(η^2-phen)(η^1-dppm) (ΔH_{HPI} = −23.0 kcal/mol) is more basic than dppm. A simple Lewis acid–base σ-bond between the metal and phosphorus would require that P$_I$ donate some electron density to the metal which would make P$_{II}$ *less* basic than dppm itself. These results therefore suggest that the M(CO)$_3$(N$\frown$N) groups actually donate electron density *to* the dppm ligand. This donation would presumably occur by π-back-bonding from the metal to P$_I$.

On the basis of these results, the effect of coordinating P$_B$ (Chart I) on the donor ability of P$_A$ in a dppm chelate complex can vary from decreasing the donor ability of P$_A$ by 4.9 kcal/mol (in Cr(CO)$_5$(η^1-dppm)) to actually increasing its donor ability by 1.1 kcal/mol (in *fac*-W(CO)$_3$(η^2-bipy)(η^1-dppm)), depending on the metal and its other ligands.

Comparison of the Basicities (ΔH_{HM} and ΔH_{HP}) of *fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) and *fac*-W(CO)$_3$(η^2-bipy)(η^1-dppm). In order to estimate the basicity of the metal in *fac*-W(CO)$_3$(η^2-bipy)(η^1-dppm) (**6**), the ΔH_{HM} of the analogous complex, *fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) (**7**), without a dangling phosphorus, was determined (eq 7). Its basicity (ΔH_{HM} = −18.8 kcal/mol) is probably somewhat higher than that of tungsten in **6** because PPh$_2$Me (ΔH_{HPI} −24.7 kcal/mol) is a better donor than dppm (ΔH_{HPI} = −22.0 kcal/mol). However, assuming that the ΔH_{HM} of **7** is a high estimate for the basicity of the metal in **6**, the dangling P$_{II}$ in **6** is at least 4.3 kcal/mol more basic than the tungsten atom. This difference in basicities (4.3 kcal/mol) of these two sites can be expressed in the form of the equilibrium constant (K_{eq}) for reaction 8. Assuming that $\Delta S°$ is zero for this

$$\mathbf{7} + \mathbf{6}\mathrm{H}^+ \overset{K_{eq}}{\rightleftharpoons} \mathbf{7}\mathrm{H}^+ + \mathbf{6} \qquad (8)$$

reaction, which means that $\Delta G°$ is 4.3 kcal/mol, K_{eq} is calculated ($\Delta G° = -RT \ln K_{eq}$) to be 1.4×10^3. This large value accounts for the observation that *fac*-W(CO)$_3$(η^2-bipy)(η^1-dppm) is protonated at the dangling phosphorus (P$_{II}$) rather than at the metal.

Comparison of the Basicities (ΔH_{HM}) of *fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) and *fac*-W(CO)$_3$(PPh$_2$Me)$_3$. The substitution of two PPh$_2$Me ligands in *fac*-W(CO)$_3$(PPh$_2$Me)$_3$ (ΔH_{HM} = −15.1 kcal/mol)[22] by a bipy ligand to give *fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) (ΔH_{HM} = −18.8 kcal/mol) results in a 3.7 kcal/mol increase in the basicity of the metal. That the bipy complex **7** is more basic than *fac*-W(CO)$_3$(PPh$_2$Me)$_3$ is somewhat surprising since bipy (pK_a = 4.44)[20] is less basic than PPh$_2$Me (pK_a = 4.59). In previous studies of metal phosphine complexes,[5,6] we have noted linear correlations between metal complex basicity (ΔH_{HM}) and the basicities of the phosphine ligands as measured by ΔH_{HP}. If the pK_a of bipy is converted to ΔH_{HN} for protonation with CF$_3$SO$_3$H in DCE at 25.0 °C using a correlation (eq 9) of pK_a with ΔH_{HN} for other nitrogen bases,[3] bipy (ΔH_{HN} = −28.3

$$-\Delta H_{HN} = 1.64\mathrm{p}K_a + 21.0 \quad \text{(in kcal/mol)} \qquad (9)$$

kcal/mol) is more basic than PPh$_2$Me, whose ΔH_{HP} is −24.7 kcal/mol. Thus, using ΔH_{HN} and ΔH_{HP} as measures of the donor abilities of bipy and PPh$_2$Me allows one to account for the higher basicity of the metal in *fac*-W(CO)$_3$(η^2-bipy)(PPh$_2$Me) as compared with that of *fac*-W(CO)$_3$(PPh$_2$Me)$_3$.

Conclusions

The basicity (ΔH_{HP}) of the dangling phosphorus (P$_{II}$) in Ph$_2$PCH$_2$PPh$_2$ (dppm) and its η^1-coordinated complexes increases in the order: dppmH$^+$ < Cr(CO)$_5$(η^1-dppm) (**1**) < Mo(CO)$_5$(η^1-dppm) (**2**) < W(CO)$_5$(η^1-dppm) (**3**) < dppm ≤ *fac*-Mo(CO)$_3$(η^2-bipy)(η^1-dppm) (**4**) < *fac*-Mo(CO)$_3$(η^2-phen)(η^1-dppm) (**5**) ≈ *fac*-W(CO)$_3$(η^2-bipy)(η^2-dppm) (**6**). The proton (H$^+$) reduces

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the basicity of P_{II} more than any of the metal complexes. In fact, the basicity of the dangling phosphorus in **5** and **6** is actually higher than that of dppm itself, which indicates that the $W(CO)_3(\eta^2$-bipy) group is a net electron donor to the dppm, perhaps via π-back-bonding from the metal to the phosphorus. It is not surprising that **6** is protonated at the dangling phosphorus rather than at the tungsten since the metal, as estimated by the ΔH_{HM} for $W(CO)_3(\eta^2$-bipy)(PPh_2Me) (**7**), is at least 4.3 kcal/mol less basic than the phosphorus in **6**. The basicity of the metal in **7** is higher than that in *fac*-$W(CO)_3(PPh_2Me)_3$, which is consistent with the donor abilities of the bipy and PPh_2Me ligands.

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