

Calorimetric Studies of the Heats of Protonation of the Metal in *cis*-M(CO)₂(bidentate phosphine)₂ Complexes of Chromium, Molybdenum, and Tungsten

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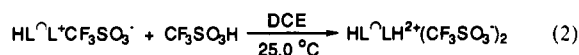
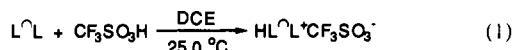
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Titration calorimetry has been used to determine the heats of protonation (ΔH_{HM}) of *cis*-M(CO)₂(L²L)₂ complexes (M = Cr, Mo, W; L²L = dppm, dppe, dppp, arphos, dmpe) with CF₃SO₃H in 1,2-dichloroethane solvent at 25.0 °C. Spectroscopic studies show that protonation occurs at the metal center to form [M(H)(CO)₂(L²L)₂]CF₃SO₃ complexes with trans CO groups. For the M(CO)₂[Ph₂P(CH₂)_nPPh₂]₂ complexes, ΔH_{HM} becomes less exothermic as the chelate size increases from $n = 1$ (-29.7 kcal mol⁻¹) to $n = 3$ (-19.0 kcal mol⁻¹) for Mo and from $n = 1$ (-31.5 kcal mol⁻¹) to $n = 2$ (-25.1 kcal mol⁻¹) for W. The higher basicities of complexes with small chelates are ascribed to distortions imposed on the M(CO)₂(L²L)₂ complexes by the chelate ligand and to reduced steric hindrance in the protonated product. Substituting the dppe chelates in Mo(CO)₂(dppe)₂ ($\Delta H_{HM} = -27.4$ kcal mol⁻¹) with dmpe increases metal basicity ($\Delta H_{HM} = -38.7$ kcal mol⁻¹), and with the arphos ligand metal basicity is decreased ($\Delta H_{HM} = -23.8$ kcal mol⁻¹). In descending group 6, the basicities (ΔH_{HM}) of the M(CO)₂(dppm)₂ complexes increase in the order Cr (-25.5 kcal mol⁻¹) << Mo (-29.7 kcal mol⁻¹) < W (-31.5 kcal mol⁻¹), but for the M(CO)₂(dppe)₂ complexes metal basicity decreases in the order Mo (-27.4 kcal mol⁻¹) > W (-25.1 kcal mol⁻¹). The group 8 complex, (η^5 -C₅Me₅)₂Os ($\Delta H_{HM} = -26.6$ kcal mol⁻¹), is substantially more basic than (η^5 -C₅Me₅)₂Ru ($\Delta H_{HM} = -19.0$ kcal mol⁻¹). The heats of protonation (ΔH_{HN}) of a series of organonitrogen bases have also been determined.

Introduction

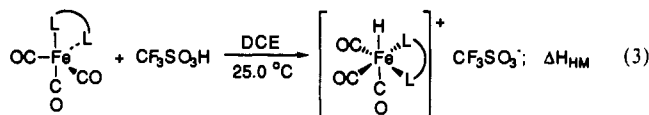
Group 6 *cis*-M(CO)₂(L²L)₂ (L²L = bidentate phosphine or arsine ligand) complexes have been studied extensively for their chemical reactivity^{1-3a} and electrochemical properties.^{2d,3-5} The effects of changing the metal (M = Cr, Mo, W) and the L²L ligands on these properties have been noted.^{1,2a,b,3a,b} There are also several investigations of the protonation chemistry of these molecules.^{1b,2a,6-9} The rates of deprotonation^{6a} of the conjugate acids, [M(H)(CO)₂(L²L)₂]⁺, are kinetically slow as $t_{1/2}$ values with amines are typically days long and are dependent on the size of the amine base. Deprotonation rates^{6a} are greatly enhanced in the presence of halides and acetate anions, which serve as proton carriers. However, no quantitative data concerning the thermodynamic basicities of the neutral *cis*-M(CO)₂(L²L)₂ complexes are available.

Recently we reported¹⁰ the heats of protonation (ΔH_{HP}) of bidentate phosphine compounds (eqs 1 and 2) determined by



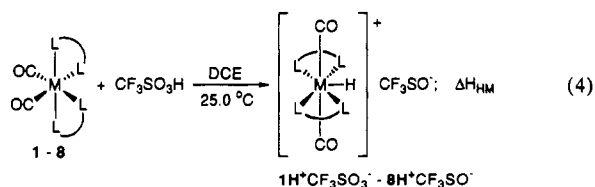
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calorimetric titrations with CF₃SO₃H in 1,2-dichloroethane (DCE) solvent at 25.0 °C. For the series Ph₂P(CH₂)_nPPh₂, $n = 1-6$, the phosphine basicities as measured by ΔH_{HP} increased as the value of n increased. Also the Me₂P(CH₂)_nPMe₂ ligands were shown^{10,11} to be more basic than the corresponding phenyl-substituted bidentate phosphines Ph₂P(CH₂)_nPPh₂. A recent study¹² of the effects of bidentate phosphine ligands on metal basicity showed that the basicities of a series of Fe(CO)₃[Ph₂P(CH₂)_nPPh₂] ($n = 1-4$) complexes as measured by ΔH_{HM} (eq 3) decreased as the



size of the chelate backbone increased from $n = 1$ ($\Delta H_{HM} = -24.0$ kcal mol⁻¹) to $n = 4$ ($\Delta H_{HM} = -20.1$ kcal mol⁻¹). Since ligand basicities (ΔH_{HP})¹⁰ did not explain the effect of chelate size on iron basicity (ΔH_{HM}),¹² the higher basicities of the complexes with small chelate ligands were ascribed to distortions imposed on the Fe(CO)₃(L²L) geometry by the chelate ligand. As for the free ligands, complexes with alkyl-substituted bidentate phosphine ligands such as Fe(CO)₃(Me₂PCH₂PMe₂) ($\Delta H_{HM} = -30.2$ kcal mol⁻¹) were more basic than analogous complexes with phenyl-substituted ligands.¹²

To further understand the effects of chelate size and basicity on the basicities of metal complexes, we report herein our investigations of the heats of protonation (ΔH_{HM}) of *cis*-M(CO)₂(L²L)₂¹³ complexes (eq 4). In addition, we determine the



Cr(CO)₂(dppm)₂ 1

Mo(CO)₂(L²L)₂ (L²L = dppm, 2; dppe, 3; dppp, 4; arphos, 5; dmpe, 6)

W(CO)₂(L²L)₂ (L²L = dppm, 7; dppe, 8)

effect of the group 6 metal on metal basicity as measured by

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- (3) We use the following abbreviations for L²L: Ph₂PCH₂PPh₂ (dppm), Ph₂P(CH₂)₂PPh₂ (dppe), Ph₂P(CH₂)₃PPh₂ (dppp), Ph₂P(CH₂)₂AsPh₂ (arphos), Me₂PCH₂PMe₂ (dmpm), and Me₂P(CH₂)₂PMe₂ (dmpe).

ΔH_{HM} (eq 4). Finally, ΔH_{HM} values for protonations of the decamethyl metallocenes Cp^*_2M ($\text{Cp}^* = \text{C}_5\text{Me}_5$; $\text{M} = \text{Ru}$ (9), Os (10)) and a series of organonitrogen bases with known pK_a values are reported.

Experimental Section

General Methods. All preparative reactions, purifications, and manipulations (except as stated otherwise) were performed under an atmosphere of nitrogen using standard Schlenk techniques. The solvents methylene chloride, hexanes, *n*-decane, and decalin were refluxed over CaH_2 and distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone, and benzene was distilled from LiAlH_4 . Di-*n*-butyl ether and CDCl_3 were stored over molecular sieves (Davison Type 4A, Fisher Scientific). Triflic acid (3M Co.) was distilled under argon, and the 1,2-dichloroethane for the calorimetric titrations was also distilled under argon from P_2O_5 . The Cp^*_2Ru (9) complex was purchased from Strem and used as received, and Cp^*_2Os (10) was prepared from $\text{C}_5\text{Me}_5\text{H}$ and $\text{Na}_2[\text{OsCl}_6]$ as previously reported.¹⁴ The organonitrogen compounds tetramethylguanidine (TMG), morpholine, pyridine, aniline, 2-cyanoaniline, and 3-bromopyridine were purchased from Aldrich as the highest purity grades available and used as received. Triethylamine was predried over molecular sieves and distilled from P_2O_5 under nitrogen. Neutral Al_2O_3 (Brockman, activity 1, ~150 mesh) used for chromatography was deoxygenated at room temperature under vacuum for 9 h, deactivated with 5% (w/w) N_2 -saturated water, and stored under N_2 .

The ^1H NMR spectra of complexes in CDCl_3 were recorded on a Nicolet-NT 300-MHz spectrometer with TMS ($\delta = 0.00$ ppm) as the internal reference. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 4 was recorded in a 10-mm tube on a Bruker WM200-NMR spectrometer in CDCl_3 using 85% H_3PO_4 ($\delta = 0.00$ ppm) as the external reference. Solution infrared spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1-mm spacers.

Preparations of $cis\text{-}M(\text{CO})_2(\text{L}\text{L})_2$ Complexes 1–8. The complexes $cis\text{-Cr}(\text{CO})_2(\text{dppm})_2$ (1) and $cis\text{-Mo}(\text{CO})_2(\text{dppm})_2$ (2) were prepared from $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$) and dppm in refluxing *n*-decane in yields of 48% for 1 and 56% for 2, as previously reported.^{3c} Complex 2 was also prepared in refluxing decalin with the same reaction time in a similar yield. Although the synthesis of $cis\text{-Mo}(\text{CO})_2(\text{dppp})_2$ (4) from $\text{Mo}(\text{CO})_6$ and dppp in refluxing *n*-decane was briefly reported,^{3b} no experimental details were given; thus, this synthesis is presented in detail below. As previously reported, $cis\text{-W}(\text{CO})_2(\text{dppm})_2$ (7) was prepared from $\text{W}(\text{CO})_6$ and dppm in low yield (13%).^{3c} The preparations of $cis\text{-Mo}(\text{CO})_2(\text{L}\text{L})_2$ ($\text{L}\text{L} = \text{dppe}$ (3),^{1a,6,7} arphos (5),^{7a} dmpe (6)^{2b,6,7}) and $cis\text{-W}(\text{CO})_2(\text{dppe})_2$ (8)^{1a} were previously reported, but they were prepared by the methods described below. The $cis\text{-Mo}(\text{CO})_2(\text{NBD})_2$ (NBD = norbornadiene) complex used in the synthesis of 6 was prepared from $\text{Mo}(\text{CO})_6$ and NBD in refluxing di-*n*-butyl ether (reaction time 33 h; yield 50%) instead of petroleum ether (bp 110–140 °C) as described previously.¹⁵ The purities and identities of compounds 1–8 were established by IR and ^1H NMR spectroscopy.

$cis\text{-Mo}(\text{CO})_2(\text{dppe})_2$ (3).^{1a,6,7} A mixture of $\text{Mo}(\text{CO})_6$ (0.42 g, 1.6 mmol) and dppe (1.9 g, 4.7 mmol) was refluxed in *n*-decane (25 mL) for 5 h as a yellow-orange solid precipitated from the solution. The mixture was cooled in an ice bath, and the solid was isolated by filtration and dried under vacuum. The crude solid was recrystallized twice from CH_2Cl_2 /hexanes to give 3 as a fine yellow powder (0.48 g) in 32% yield. ^1H NMR (CDCl_3): δ 1.78 (br s, 2 H, CH_2), 2.05 (m, 2 H, CH_2), 2.25 (br s, 2 H, CH_2), 2.96 (br m, 2 H, CH_2), 6.15–7.82 (m, Ph). IR (CH_2Cl_2): $\nu(\text{CO})$ 1850 (s), 1783 (s) cm^{-1} .

$cis\text{-Mo}(\text{CO})_2(\text{dppp})_2 \cdot 1.8\text{CH}_2\text{Cl}_2$ (4).^{3b,15} A mixture of $\text{Mo}(\text{CO})_6$ (0.47 g, 1.8 mmol) and dppp (1.5 g, 3.6 mmol) in *n*-decane (25 mL) was heated to reflux for 24 h as a red solid precipitated from solution. The reaction mixture was cooled in an ice bath for 1 h, and an orange precipitate was separated by filtration in air on a medium-porosity glass frit and washed with hexanes (20 mL). The filtrate containing the mother liquor was purged with nitrogen and cooled to -10 °C for 12 h to produce 0.4 g of 4 as yellow crystals. The orange solid (above) was dissolved in warm CH_2Cl_2 (60 mL); the solution was filtered and mixed with hexanes (100 mL). After cooling of the mixture in an ice bath, a yellow powder (0.6 g) was isolated by filtration and combined with that isolated from the mother liquor. The combined yellow products were dissolved in CH_2Cl_2 and eluted on a column of neutral alumina (10 \times 2.5 cm) with a 3:1

mixture of CH_2Cl_2 /hexanes. The solvents were removed under vacuum, and the product was recrystallized from CH_2Cl_2 /hexanes at -25.0 °C to give yellow crystals of 4 (0.83 g) in 44% yield. The amount of CH_2Cl_2 contained in the yellow crystals of 4 was determined by ^1H NMR spectroscopy of a solution of 4 in CDCl_3 with Ph_3CH added as an internal standard. ^1H NMR (CDCl_3): δ 1.0–2.7 (m, CH_2), 5.29 (s, CH_2Cl_2), 6.8–7.5 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 17.3 (t, $J_{\text{PP}} = 63$ Hz, P trans to CO), 29.4 (t, P cis to CO). IR (CH_2Cl_2): $\nu(\text{CO})$ 1857 (s), 1790 (m) cm^{-1} .

$cis\text{-Mo}(\text{CO})_2(\text{arphos})_2$ (5).⁷ This compound was prepared in 61% yield from $\text{Mo}(\text{CO})_6$ (0.20 g, 0.76 mmol) and arphos (0.65 g, 1.5 mmol) according to the procedure described above for the preparation of 3. ^1H NMR (CDCl_3): δ 1.55 (m, 2 H, CH_2), 1.75 (m, 2 H, CH_2), 2.2 (br m, 2 H, CH_2), 3.15 (m, 2 H, CH_2), 5.9–7.9 (m, Ph). IR (CH_2Cl_2): $\nu(\text{CO})$ 1848 (s), 1778 (s) cm^{-1} .

$cis\text{-Mo}(\text{CO})_2(\text{dmpe})_2$ (6).^{2b,6,7} To a solution of $cis\text{-Mo}(\text{CO})_2(\text{NBD})_2$ (0.57 g, 1.7 mmol) in benzene (20 mL) was added dmpe (0.60 mL, 3.6 mmol). The mixture was heated to reflux for 9 h until the $\text{Mo}(\text{CO})_2(\text{NBD})_2$ was completely reacted as monitored by IR spectroscopy. The yellow solution was cooled to room temperature, and the solvent was evaporated under vacuum. The oily yellow residue was dissolved in CH_2Cl_2 (5 mL); the resulting solution was filtered, diluted with hexanes (10 mL), and cooled to -78 °C for 12 h. The solution was filtered, and the yellow crystals were washed with cold hexanes (2 \times 2 mL) and dried under vacuum to give 0.46 g of 6 (47% yield). IR (CH_2Cl_2): $\nu(\text{CO})$ 1836 (s), 1766 (s) cm^{-1} .

$cis\text{-W}(\text{CO})_2(\text{dppe})_2$ (8).^{1a} A mixture of $\text{W}(\text{CO})_6$ (1.7 g, 4.7 mmol), dppe (1.8 g, 4.7 mmol), and NaBH_4 (0.5 g, 13 mmol) was refluxed in absolute EtOH (80 mL) for 4 h. After cooling, the yellow solid that formed during reflux was filtered and washed with EtOH (2 \times 5 mL) and hexanes (2 \times 5 mL). More dppe (1.0 g, 2.6 mmol) was added to the crude yellow solid, and the mixture was refluxed in decane (60 mL) for 72 h. After cooling of the reaction mixture in an ice bath, a yellow precipitate was separated by filtration and washed with hexanes. It was then dissolved in CH_2Cl_2 , and the mixture was filtered through a column of alumina (5 \times 2.5 cm). About half of the solvent was evaporated under vacuum, and an equal volume of hexanes was added to give a yellow powder. The precipitate was washed with hexanes and dissolved in benzene. After filtration through a column of alumina (5 \times 2.5 cm) the solution was evaporated to dryness to give 0.38 g of 8 in 16% yield as a yellow powder. ^1H NMR (CDCl_3): δ 1.8 (br s, 2 H, CH_2), 2.1 (m, 2 H, CH_2), 2.3 (br s, 2 H, CH_2), 3.1 (m, 2 H, CH_2), 6.2–7.8 (m, Ph). IR (CH_2Cl_2): $\nu(\text{CO})$ 1851 (s), 1781 (m) cm^{-1} .

Protonation Reactions. Compounds 1–8 were protonated by dissolving approximately 30 mg of each compound in CH_2Cl_2 (3 mL) under nitrogen. To the solution was added 1 equiv of $\text{CF}_3\text{SO}_3\text{H}$ by microliter syringe. The color of the solution changed immediately upon mixing, and the IR spectrum showed the complete disappearance of the $\nu(\text{CO})$ bands corresponding to the starting material and the appearance of new bands at higher frequency for the $[\text{M}(\text{H})(\text{CO})_2(\text{L}\text{L})_2]\text{CF}_3\text{SO}_3$ products. Solutions of the protonated complexes were stable under N_2 . All of the complexes can be isolated as solids by evaporation of their solutions and recrystallization from CH_2Cl_2 /Et₂O at 25.0 °C.

Samples for the ^1H NMR spectra of $1\text{H}^+ \cdot 8\text{H}^+$ and of 9H^+ and 10H^+ were prepared by adding 1 equiv of $\text{CF}_3\text{SO}_3\text{H}$ to solutions of the neutral compounds 1–10 (~20 mg) in CDCl_3 solvent; complete reaction was observed in each case.

The protonated complexes $1\text{H}^+\text{ClO}_4^-$,^{3a} $2\text{H}^+\text{ClO}_4^-$,^{3a} $3\text{H}^+\text{X}^-$ ($\text{X}^- = \text{AlCl}_4^-$,^{6b} BF_4^- ,^{6a,7} SO_3F^-), $5\text{H}^+\text{SO}_3\text{F}^-$,^{7a} $6\text{H}^+\text{X}^-$ ($\text{X}^- = \text{PF}_6^-$,^{2a} HCl_2^- ,^{2a} SO_3F^- ,^{2a,7} BF_4^- ,^{2a,7}), $7\text{H}^+\text{ClO}_4^-$,^{3a} and $8\text{H}^+\text{CF}_3\text{SO}_3^-$ ⁹ have been isolated and characterized previously. Protonations of 9 and 10 with CF_3COOH and HPF_6 to give $9\text{H}^+\text{X}^-$ and $10\text{H}^+\text{X}^-$ ($\text{X}^- = \text{CF}_3\text{COO}^-$, PF_6^-) were previously reported;¹⁴ the products were characterized spectroscopically. No attempts were made to isolate $9\text{H}^+\text{CF}_3\text{SO}_3^-$ or $10\text{H}^+\text{CF}_3\text{SO}_3^-$. The identities and purities of the protonated complexes in this paper were established by IR and ^1H NMR spectroscopies. The colors of the protonated species (below) are those in the solid state and in solution. The phosphorus atoms labeled P_A and P_B correspond to those approximately cis and trans, respectively, to the hydride ligand assuming a pentagonal bipyramidal geometry for $1\text{H}^+ \cdot 8\text{H}^+$.

$[\text{Cr}(\text{H})(\text{CO})_2(\text{dppm})_2]\text{CF}_3\text{SO}_3$ ($1\text{H}^+\text{CF}_3\text{SO}_3^-$). Color: yellow. ^1H NMR (CDCl_3): δ -7.19 (tt, $J_{\text{PBH}} = 109$ Hz, $J_{\text{PAH}} = 26.7$ Hz, 1 H, CrH), 4.83 (br s, 4 H, CH_2), 7.26–7.46 (m, 20 H, Ph). IR (CH_2Cl_2): $\nu(\text{CO})$ 1976 (vw), 1885 (s) cm^{-1} .

$[\text{Mo}(\text{H})(\text{CO})_2(\text{dppm})_2]\text{CF}_3\text{SO}_3$ ($2\text{H}^+\text{CF}_3\text{SO}_3^-$). Color: yellow. ^1H NMR (CDCl_3): δ -3.63 (tt, $J_{\text{PBH}} = 65.7$ Hz, $J_{\text{PAH}} = 15.0$ Hz, 1 H, MoH), 4.70 (br s, 4 H, CH_2), 7.2–7.5 (m, 20 H, Ph). IR (CH_2Cl_2): $\nu(\text{CO})$ 1991 (vw), 1899 (s) cm^{-1} .

$[\text{Mo}(\text{H})(\text{CO})_2(\text{dppe})_2]\text{CF}_3\text{SO}_3$ ($3\text{H}^+\text{CF}_3\text{SO}_3^-$). Color: pink. ^1H NMR (CDCl_3): δ -5.36 (tt, $J_{\text{PBH}} = 69.8$ Hz, $J_{\text{PAH}} = 12.6$ Hz, 1 H, MoH),

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2.61 (br s, 8 H, CH₂), 7.1–7.5 (m, 20 H, Ph). IR (CH₂Cl₂): $\nu(\text{CO})$ 1983 (vw), 1880 (s) cm⁻¹.

[Mo(H)(CO)₂(dppm)₂]CF₃SO₃ (4H⁺CF₃SO₃⁻). Color: orange. ¹H NMR (CDCl₃): -4.52 (tt, $J_{\text{PbH}} = 81.7$ Hz, $J_{\text{PAH}} = 15.8$ Hz, 1 H, MoH), 1.93 (br m, 4 H, 2-CH₂), 2.47 (br s, 8 H, 1,3-CH₂), 7.0–7.5 (m, Ph). IR (CH₂Cl₂): $\nu(\text{CO})$ 1974 (vw), 1869 (s) cm⁻¹. Anal. Calcd for C₂₇H₃₃P₄O₅F₃S: C, 60.75; H, 4.75. Found: C, 60.13; H, 4.91.

[Mo(H)(CO)₂(arphos)₂]CF₃SO₃ (5H⁺CF₃SO₃⁻). Color: pink. ¹H NMR (CDCl₃): δ -4.97 (t, $J_{\text{PbH}} = 68$ Hz, 1 H, MoH), 2.6–2.7 (m, 8 H, CH₂), 7.1–7.5 (m, 20 H, Ph). IR (CH₂Cl₂): $\nu(\text{CO})$ 1984 (vw), 1883 (s) cm⁻¹.

[Mo(H)(CO)₂(dmpe)₂]CF₃SO₃ (6H⁺CF₃SO₃⁻). Color: white. ¹H NMR (CDCl₃): -6.65 (tt, $J_{\text{PbH}} = 69.9$ Hz, $J_{\text{PAH}} = 8.1$ Hz, 1 H, MoH), 1.69 (d, $J_{\text{PH}} = 5.9$ Hz, 12 H, CH₃), 1.76 (d, $J_{\text{PH}} = 9.3$ Hz, 12 H, CH₃), 2.01 (tm, $J_{\text{HH}} = 25$ Hz, 8 H, CH₂). IR (CH₂Cl₂): $\nu(\text{CO})$ 1976 (vw), 1872 (s) cm⁻¹.

[W(H)(CO)₂(dppm)₂]CF₃SO₃ (7H⁺CF₃SO₃⁻). Color: pale yellow. ¹H NMR (CDCl₃): δ -1.51 (tt, $J_{\text{PbH}} = 65.3$ Hz, $J_{\text{PAH}} = 13.8$ Hz, 1 H, WH), 4.91 (t, $J = 7.8$ Hz, 4 H, CH₂), 7.1–7.4 (m, 20 H, Ph). IR (CH₂Cl₂): $\nu(\text{CO})$ 1980 (vw), 1884 (s) cm⁻¹.

[W(H)(CO)₂(dppe)₂]CF₃SO₃ (8H⁺CF₃SO₃⁻). Color: pale yellow. ¹H NMR (CDCl₃): -4.93 (tt, $J_{\text{PbH}} = 73.0$ Hz, $J_{\text{PAH}} = 12.4$ Hz, 1 H, WH), 2.63 (m, 8 H, CH₂), 7.1–7.5 (m, 20 H, Ph). IR (CH₂Cl₂): $\nu(\text{CO})$ 1971 (vw), 1865 (s) cm⁻¹.

[Cp*₂Ru(H)]CF₃SO₃ (9H⁺CF₃SO₃⁻). Color: pink. ¹H NMR (CDCl₃): δ -8.29 (s, 1 H, RuH), 1.87 (s, 30 H, Me).

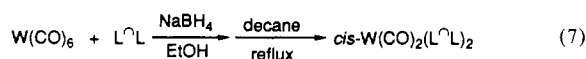
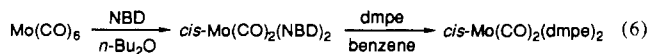
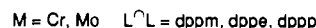
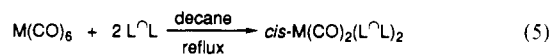
[Cp*₂Os(H)]CF₃SO₃ (10H⁺CF₃SO₃⁻). Color: white. ¹H NMR (CDCl₃): δ -15.5 (s, 1 H, OsH), 2.02 (s, 30 H, Me).

Calorimetry Studies. Determinations of the heats of protonation of the M(CO)₂(L[∧]L)₂ and Cp*₂M complexes and the organonitrogen compounds were performed using a Tronac Model 458 isoperibol calorimeter as previously described.^{16,17} Typically a run consisted of three sections:¹⁸ initial heat capacity calibration, titration (at 25.0 °C), and final heat capacity calibration. Each section was preceded by a baseline acquisition period. The titration period involved the addition of 1.2 mL of a 0.1 M CF₃SO₃H solution (standardized to a precision of ±0.0002 M) in 1,2-dichloroethane (DCE) at a constant rate during a 3-min time period to 50 mL of a 2.6 mM solution of M(CO)₂(L[∧]L)₂ or Cp*₂M (10% excess) in DCE. For compounds **5** and **7**, 2-min titration periods were used. Solutions of the M(CO)₂(L[∧]L)₂ and Cp*₂M complexes were prepared by adding the solid compound to an argon-filled Dewar flask. The flask was then attached to the calorimeter's insert assembly and flushed with argon, and 50 mL of DCE was added by syringe. Stock solutions of the organonitrogen bases were prepared in DCE (13 mM) under argon, and a 10-mL aliquot was added to an argon-filled Dewar flask followed by dilution to 50 mL with DCE. All measured reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (-0.2 kcal mol⁻¹).¹⁶

To ensure reproducibility of the determined ΔH_{HM} values, at least two different standardized acid solutions were used for the titrations of each compound. The ΔH_{HM} values are reported as the average of at least four titrations for each compound. However, only three titrations were performed for **5**. The error is reported as the average deviation from the mean of all the determinations.

Results

Synthesis of *cis*-M(CO)₂(L[∧]L)₂ Complexes. Complexes **1–8** are prepared from M(CO)₆ (M = Cr, Mo, W) using three known methods^{3a,15} (eqs 5–7). We prepared complexes **1**, **2**, and **4** by



direct reaction (eq 5) of M(CO)₆ (M = Cr, Mo) and dppm in refluxing *n*-decane as previously reported.^{3a} This method was also used in the synthesis of **3** (32% yield) and **5** (61% yield). Several

routes are reported for the synthesis of **6** that include direct reaction of Mo(CO)₆ and dmpe in a sealed glass tube,^{2b} reduction of MoCl₃(THF)₃ in the presence of CO(g) and dmpe,⁷ and reaction of Mo(N₂)₂(dmpe)₂ with CO(g),^{6a} however, the preparation (eq 6) of **6** from *cis*-Mo(CO)₂(NBD)₂ (NBD = norbornadiene) in refluxing benzene (eq 6) is the most convenient, and the yield is also reasonable (47%). The *cis*-W(CO)₂(L[∧]L)₂ complexes **7** and **8** were obtained using the two-step procedure in eq 7; however, the yields are low (13–16%).^{3a} Complexes **1–8** were characterized by IR and ¹H NMR spectroscopies.

The structures of **1–8** are well established as having *cis*-carbonyl groups^{1a} as indicated by two $\nu(\text{CO})$ bands in the carbonyl region of the infrared spectrum. Previously these bands were both reported^{1a,3a,15} as strong-intensity bands, but in our hands the intensity of the lower frequency band of **2**, **4**, **7**, and **8** was medium relative to the strong-intensity band at higher frequency. The (OC)–M–(CO) bond angle (θ) can be estimated (eq 8)¹⁹ from

$$I_{\text{sym}}/I_{\text{asym}} = \tan^2(\theta/2) \quad (8)$$

the ratio of intensities of the two $\nu(\text{CO})$ bands, which were determined by measuring their relative areas. The $I_{\text{sym}}/I_{\text{asym}}$ ratio for complex **4** was determined to be 0.78, which corresponds to a (OC)–Mo–(CO) angle (θ) of 83° (eq 8), which is similar to the 81.3 (3)° angle obtained from a single-crystal X-ray structure determination of **4**.¹⁵ The *cis*-octahedral structure of the related *cis*-Cr(CO)₂(dmpe)₂ complex has also been established by X-ray crystallography and IR and ³¹P NMR spectroscopies.²⁰

Except for **6**, the *cis*-M(CO)₂(L[∧]L)₂ complexes **1–5**, **7**, and **8** are stable in air, but as a precaution they were stored under nitrogen in the dark.^{1a} Compound **6** can be weighed in air, otherwise it must be stored under nitrogen as it decomposes rapidly to a pink solid.

Protonation Reactions of *cis*-M(CO)₂(L[∧]L)₂. Complexes **1–8** were protonated with 1 equiv of CF₃SO₃H in CH₂Cl₂ solution, as shown in eq 4. As noted above, all of the protonated complexes except **4H**⁺ have been isolated previously. The IR and ¹H NMR spectra of **4H**⁺ are similar to those of the known derivatives.

The protonation reactions occur immediately, as indicated by the change of the solution color, the disappearance of the starting complex $\nu(\text{CO})$ bands in the infrared spectrum, and the appearance of new $\nu(\text{CO})$ bands at frequencies higher than those of the corresponding neutral starting complexes. These shifts in the $\nu(\text{CO})$ bands are characteristic of protonation at the metal.²¹ Solutions of **1H**⁺–**8H**⁺ are stable for at least 24 h under an atmosphere of nitrogen or argon. Solutions of the protonated complexes also appeared to be fairly air stable as previously indicated by Bond and co-workers for **1H**⁺, **2H**⁺, and **7H**⁺.^{3a} The solid products isolated from the calorimetry experiments were handled in air without apparent decomposition; however, they were stored under nitrogen.

The geometries of the protonated products have been established as having mutually *trans* CO groups.^{2a,3a,6,7} Their infrared spectra show one strong $\nu(\text{CO})$ absorption in the range 1872–1899 cm⁻¹ due to the asymmetric stretching mode of the *trans* CO groups. As previously reported by Darensbourg and Ludvig,^{6a} a very weak $\nu(\text{CO})$ band is detected at higher frequencies in the range 1971–1991 cm⁻¹ that corresponds to a symmetric mode of the mutually *trans* CO groups. These authors^{6a} used the ratio of $\nu(\text{CO})$ intensities (eq 8)¹⁹ to estimate the (OC)–Mo–(CO) bond angle in **3H**⁺ as 169°, which is similar to the value of 175.4 (3)° determined by a single-crystal X-ray diffraction study of **3H**⁺–AlCl₄⁻.^{6b} The crystal structure of the related [Cr(H)(CO)₂(dmpe)₂]PF₆ complex gave a (OC)–Cr–(CO) bond angle of 177.4 (2)°.⁸

The ¹H NMR spectra of **1H**⁺–**8H**⁺ show one resonance in the high-field region that is typical of metal hydrides.²² Except for

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Table I. Heats of Protonation of $cis\text{-M}(\text{CO})_2(\text{L}\text{L})_2$ Complexes (ΔH_{HM}), Bidentate Phosphines (ΔH_{HP1} , ΔH_{HP2}), and Organonitrogen Bases (ΔH_{HN})

compd ^a	$-\Delta H_{\text{prot}}^b$ kcal mol ⁻¹	pK_a
$cis\text{-Cr}(\text{CO})_2(\text{dppm})_2$ (1)	25.5 (± 0.1) ^c	
dppm	22.0, ^d 14.9 ^e	3.81, ^f -2.73 ^g
$cis\text{-Mo}(\text{CO})_2(\text{dppm})_2$ (2)	29.7 (± 0.3) ^c	
$cis\text{-Mo}(\text{CO})_2(\text{dppe})_2$ (3)	27.4 (± 0.2) ^c	
dppe	22.8, ^d 20.2 ^e	3.86, ^f 0.99 ^g
$cis\text{-Mo}(\text{CO})_2(\text{dppp})_2$ (4)	19.0 (± 0.2) ^c	
dppp	23.4, ^d 22.4 ^e	4.50, ^f 2.53 ^g
$cis\text{-Mo}(\text{CO})_2(\text{arphos})_2$ (5)	23.8 (± 0.4) ^c	
arphos	23.2, ^d 8.2 ^e	3.96 ^f
$cis\text{-Mo}(\text{CO})_2(\text{dmpe})_2$ (6)	38.7 (± 0.5) ^c	
$cis\text{-W}(\text{CO})_2(\text{dppm})_2$ (7)	31.5 (± 0.2) ^c	
$cis\text{-W}(\text{CO})_2(\text{dppe})_2$ (8)	25.1 (± 0.2) ^c	
Cp^*_2Ru (9)	19.0 (± 0.1) ^c	
Cp^*_2Os (10)	26.6 (± 0.2) ^c	
3-bromopyridine	25.7 (± 0.1) ^h	2.8 ⁱ
pyridine	29.3 (± 0.1) ^h	5.2 ⁱ
morpholine	35.6 (± 0.4) ^h	8.5 ⁱ
1,3-diphenylguanidine	36.9 (± 0.2) ^{h,j}	10.1 ⁱ
triethylamine	39.3 (± 0.1) ^h	10.8 ⁱ
tetramethylguanidine (TMG)	43.2 (± 0.3) ^h	13.6 ⁱ

^aLigand abbreviations: $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dppe), $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (dppp), $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$ (arphos), $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ (dmpe), and $\eta^5\text{-C}_5\text{Me}_5$ (Cp^*). ^bNumbers in parentheses are average deviations. ^c ΔH_{HM} for protonation with $\text{CF}_3\text{SO}_3\text{H}$ (0.1 M) in DCE solvent at 25.0 °C. ^d ΔH_{HP1} represents the addition of 1 equiv of $\text{CF}_3\text{SO}_3\text{H}$ to 1 equiv of the free phosphine in DCE at 25.0 °C; see ref 10. ^e ΔH_{HP2} represents the addition of a second 1 equiv of $\text{CF}_3\text{SO}_3\text{H}$ to 1 equiv of the free phosphine in DCE at 25.0 °C; see ref 10. ^f pK_a in water; see refs 10 and 11. ^g pK_a in water; see refs 10 and 11. ^h ΔH_{HN} for protonation with $\text{CF}_3\text{SO}_3\text{H}$ (0.1 M) in DCE solvent at 25.0 °C. ⁱ pK_a in water; see ref 36. ^jReference 16.

$5\text{H}^+\text{CF}_3\text{SO}_3^-$ the hydride signal occurs as a triplet of triplets due to coupling of two pairs of inequivalent phosphorus atoms. The J_{PH} coupling constants for the hydride in $4\text{H}^+\text{CF}_3\text{SO}_3^-$ are 15.8 Hz and 81.7 Hz and probably correspond to coupling from the phosphorus atoms that are approximately cis (J_{PAH}) and trans (J_{PBH}),⁸ respectively, assuming the hydride is located in the equatorial plane of a pentagonal bipyramid (eq 4). These data do not eliminate the possibility that the hydride is located in a $\text{P}_A\text{P}_A(\text{CO})$ face of a monocapped octahedron.⁸ For 5H^+ the hydride resonance occurs as a triplet, which is attributed to coupling to equivalent phosphorus atoms that are approximately trans to the hydride ligand as the J_{PBH} value (68 Hz) is close to that of 3H^+ ($J_{\text{PBH}} = 69.7$ Hz). The As atoms in the arphos chelate would then be approximately cis to the hydride ligand in 5H^+ in a pentagonal bipyramidal structure.

The protonations of Cp^*_2M (M = Ru (9), Os (10)) with CF_3COOH and HPF_6 have been previously reported;¹⁴ they are also protonated with 1 equiv of $\text{CF}_3\text{SO}_3\text{H}$ to give $9\text{H}^+\text{CF}_3\text{SO}_3^-$ and $10\text{H}^+\text{CF}_3\text{SO}_3^-$, as indicated by ¹H NMR spectroscopy. Their ¹H NMR spectra show singlet metal hydride resonances at -8.29 ppm for 9H^+ and -15.5 ppm for 10H^+ , indicating that protonation has occurred at the metal. Unfortunately, Cp_2Fe and Cp^*_2Fe decompose to uncharacterized products when reacted with $\text{CF}_3\text{SO}_3\text{H}$ in DCE.

Calorimetric Studies. Heats of protonation determined by calorimetric titration of the $cis\text{-M}(\text{CO})_2(\text{L}\text{L})_2$ and Cp^*_2M complexes (ΔH_{HM}) and the organonitrogen bases (ΔH_{HN}) with $\text{CF}_3\text{SO}_3\text{H}$ in 1,2-dichloroethane (DCE) solvent at 25.0 °C are presented in Table I. The titrations of the organometallic and the organonitrogen compounds proceeded cleanly as evidenced by normal pre- and posttitration baseline slopes. Only the titration curve of **4** exhibited a slight amount of residual heat immediately after the buret was turned off, which abated after ~10 s.

However, the slightly increased slope in the posttitration period was relatively small and the effect on the ΔH_{HM} value is probably within the experimental error. As expected, all of the titrations displayed a linear and immediate increase in temperature with acid addition, indicating the protonation reactions of the compounds occurred rapidly and stoichiometrically.¹⁸ The colors of the final titrant solutions corresponded to those of the respective protonated species; in addition, the IR spectrum of these solutions showed only $\nu(\text{CO})$ bands that were due to the protonated species. The protonated products $1\text{H}^+ - 8\text{H}^+$ could be recovered from the titration solutions by evaporation of the DCE solvent under vacuum and recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. As reported previously, the protonated complexes can be deprotonated with potassium *tert*-butoxide in THF solvent.^{6,7} Complexes 9H^+ and 10H^+ are deprotonated with 1,3-diphenylguanidine in DCE. The final titrant solutions of the organonitrogen bases were colorless; however, those of aniline and 2-cyanoaniline contained precipitates that formed during the titration due to the insolubilities of their conjugate acids; thus, ΔH_{HN} values for these two compounds could not be obtained.

As DCE has a relatively low dielectric constant ($\epsilon = 10.36$),²³ the products formed in all of the titrations probably occur as ion pairs. The contributions of the dissociation of these ion pairs and autoprotolysis and dimerization of the acid to the total ΔH_{HM} or ΔH_{HN} values are presumably negligible as previously discussed.¹⁷ The heats of protonation (ΔH_{HP})^{10,17} of organophosphines and the organonitrogen bases reported herein correlate linearly with their aqueous pK_a values. Because the extent of ion-pairing in DCE and water are much different, the correlations of ΔH values with pK_a indicate that ion-pairing effects do not control trends in basicities measured by heats of protonation in DCE.

Discussion

Dependence of ΔH_{HM} on Chelate Ring Size in $cis\text{-M}(\text{CO})_2\text{-}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$. We have determined ΔH_{HM} values for a series of $cis\text{-M}(\text{CO})_2[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$ complexes (M = Mo, W), **2-4**, **7**, and **8**, where the values of n in the bidentate ligand backbone varies from 1 to 3 for Mo and 1 to 2 for W. The structures of the reactants and products as established by spectroscopic studies and, in a few cases, X-ray diffraction studies, as discussed above, are shown in eq 4.

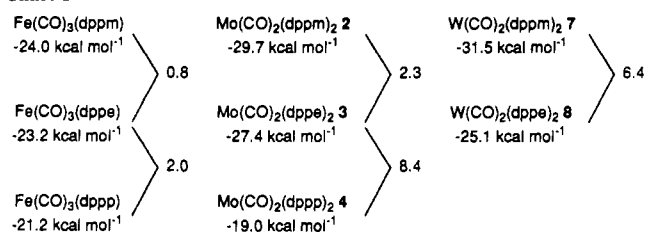
As seen from the data in Table I, the basicity of the metal in the Mo complexes **2-4** is highest ($\Delta H_{\text{HM}} = -29.7$ kcal mol⁻¹) for the smallest chelate ($n = 1$) and lowest (-19.0 kcal mol⁻¹) for the largest chelate ($n = 3$). Also, for the W system, the complex with the smaller chelate ($n = 1$) is more basic (-31.5 kcal mol⁻¹) than that (-25.1 kcal mol⁻¹) with the larger chelate ($n = 2$). In terms of equilibrium constants for protonation, assuming ΔS^\ominus is the same for both reactions, as is nearly true for protonations of other neutral complexes,¹⁶ $\text{Mo}(\text{CO})_2(\text{dppm})_2$ (**2**) is 7×10^7 times more basic than $\text{Mo}(\text{CO})_2(\text{dppp})_2$ (**4**) and $\text{W}(\text{CO})_2(\text{dppm})_2$ (**7**) is 5×10^4 more basic than $\text{W}(\text{CO})_2(\text{dppe})_2$ (**8**). Consideration of the donor abilities of the $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ligands as measured by ΔH_{HP1} ¹⁰ (eq 1, Table I) indicates that these bidentate ligands become better σ -donors as the length of the ligand $-(\text{CH}_2)_n$ backbone increases from that of dppm ($n = 1$, $\Delta H_{\text{HP1}} = -22.0$ kcal mol⁻¹) to that of dppp ($n = 3$, $\Delta H_{\text{HP1}} = -23.4$ kcal mol⁻¹). In contrast, the basicities of the $cis\text{-M}(\text{CO})_2[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$ complexes decrease as the basicities and lengths of the $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ligands increase.

Since ligand basicity does not explain the effect of chelate ring size on metal complex basicity, we suggest that the chelate ligand distorts the geometry of the $cis\text{-M}(\text{CO})_2(\text{L}\text{L})_2$ complexes, which affects their basicities. From X-ray diffraction studies reported in the literature it is evident that the chelate P-Mo-P bond angles change substantially depending on the chelate size. Thus, the average P-Mo-P angle for the dppp chelate in complex **4** is 86.1 (5)°;¹⁵ however, the P-Mo-P angle of the dppe chelate in **3** estimated from that in $3\text{H}^+\text{AlCl}_4^-$ is 78.4°,^{6b} and that in **2** estimated from the $\eta^2\text{-dppm}$ chelate in $\text{MoCl}_2(\text{CO})_2(\eta^2\text{-dppm})(\eta^1\text{-}$

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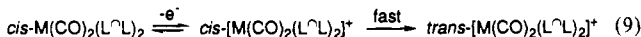
Chart I



dppm) is 63.5° .²⁴ Thus, the P–Mo–P angles of complex **4** are least distorted from the 90° angles of an octahedron. The greatest distortion occurs in **2** with the dppm ligands. The higher basicity of **2** suggests that this distortion makes this complex higher in energy than **3** or **4**, which causes **2** to be more basic than the complexes with larger chelate rings (**3** and **4**). This explanation was used¹² to account for the higher basicity of $\text{Fe}(\text{CO})_3(\text{dppm})$ ($\Delta H_{\text{HM}} = -24.0 \text{ kcal mol}^{-1}$) as compared with $\text{Fe}(\text{CO})_3(\text{dppe})$ ($-23.2 \text{ kcal mol}^{-1}$) and $\text{Fe}(\text{CO})_3(\text{dppp})$ ($-21.2 \text{ kcal mol}^{-1}$).

The same trend is observed in the tungsten complexes where the smaller chelate complex *cis*- $\text{W}(\text{CO})_2(\text{dppm})_2$ (**7**) is more basic than *cis*- $\text{W}(\text{CO})_2(\text{dppe})_2$ (**8**). As for Mo, representative P–W–P angles in chelate complexes selected from the literature decrease on going from dppe ($77.3\text{--}80.0^\circ$)²⁵ to dppm ($64.7\text{--}67.5^\circ$).^{26,27} In addition to the effect of distortion caused by the smaller chelates on *cis*- $\text{M}(\text{CO})_2(\text{L}\text{L})_2$ complex basicity, repulsion between the LL ligands may be a factor. Since protonation gives more sterically crowded seven-coordinate products, the complex with the small dppm ligand will give a less crowded product than that with dppe or dppp; this would favor protonation of the dppm complex.

A comparison (Chart I) of the effects of chelate ring size on the basicities of complexes in the *cis*- $\text{Mo}(\text{CO})_2(\text{L}\text{L})_2$, *cis*- $\text{W}(\text{CO})_2(\text{L}\text{L})_2$, and $\text{Fe}(\text{CO})_3(\text{L}\text{L})$ series shows that substitution of dppe by dppp causes a greater change in the basicities of the $\text{Fe}(\text{CO})_3(\text{L}\text{L})$ ¹² ($2.0 \text{ kcal mol}^{-1}$) and $\text{Mo}(\text{CO})_2(\text{L}\text{L})_2$ ($8.4 \text{ kcal mol}^{-1}$) complexes than substitution of dppm by dppe ($0.8 \text{ kcal mol}^{-1}$ for Fe and $2.3 \text{ kcal mol}^{-1}$ for Mo), which suggests that there is a greater relief of distortion on going from dppe to the largest dppp chelate than from the smallest dppm chelate to dppe. Also, the summary in Chart I shows that chelate effects increase with the number of chelate ligands coordinated to the metal, as illustrated by the larger changes in basicity of the $\text{M}(\text{CO})_2(\text{L}\text{L})_2$ ($\text{M} = \text{Mo}, \text{W}$) complexes as compared with those in $\text{Fe}(\text{CO})_3(\text{L}\text{L})$. These larger differences for the Mo and W complexes may also reflect the steric effects of LL ligand crowding on basicities. In spite of the large effects of chelate ring size on ΔH_{HM} values there is very little influence of chelate ring size on the reported electrochemical potentials ($E_{1/2}$, vs SCE in acetone)^{3c} for the electrode process in eq 9 for **2** (0.30 V) and **3** (0.31 V) or **7** (0.30 V) and **8** (0.31 V).



Effects on ΔH_{HM} of Other Bidentate Ligands in $\text{M}(\text{CO})_2(\text{L}\text{L})_2$. Substitution of the dppe ligand in **3** ($\Delta H_{\text{HM}} = -27.4 \text{ kcal mol}^{-1}$) with dmpe increases its basicity by $11.3 \text{ kcal mol}^{-1}$; ΔH_{HM} of the dmpe complex **6** is $-38.7 \text{ kcal mol}^{-1}$. This increase in ΔH_{HM} is attributed to the greater σ -donor ability of the dmpe chelate ligand. In terms of equilibrium constants K for protonation,

assuming ΔS° is the same for both reactions as is nearly true for protonations of other neutral complexes,¹⁶ $\text{Mo}(\text{CO})_2(\text{dmpe})_2$ (**6**) is 2×10^8 times more basic than $\text{Mo}(\text{CO})_2(\text{dppe})_2$ (**3**). Previously, we reported¹² that $\text{Fe}(\text{CO})_3(\text{dmpm})$ is 3.5×10^4 times (or $6.2 \text{ kcal mol}^{-1}$) more basic than $\text{Fe}(\text{CO})_3(\text{dppm})$. Thus, alkyl-substituted bidentate phosphines strongly enhance the basicities of metal complexes as compared to the phenyl-substituted analogues. As noted by Connor et al.,^{2a} and Darensbourg and Ludvig,^{6a} the $\nu(\text{CO})$ values (see Experimental Section) of **6** and 6H^+ are lower than those of **3** and 3H^+ , respectively; the $\delta(\text{M-H})$ chemical shift of 6H^+ is upfield of that of 3H^+ . These trends are also consistent with dmpe being a stronger donor ligand than dppe. The $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ (depe) ligand in $[\text{Mo}(\text{H})(\text{CO})_2(\text{depe})_2]\text{BF}_4$ is reported^{6a} to be a better donor than the dmpe ligand in 6H^+ as the $\nu(\text{CO})$ values in the depe complex are lower than those in 6H^+ . The electrochemical potential ($E_{1/2}$, vs SCE in CH_2Cl_2) of **3** (-0.02 V)^{2d,3d} is greater than that of **6** (-0.23 V),^{2d} which is probably also due to the better σ -donor ability of the dmpe ligand. The same trend is observed in the ΔH_{HM} values for **3** and **6**.

Replacing the dppe ligand in **3** with arphos makes **5** ($\Delta H_{\text{HM}} = -23.8 \text{ kcal mol}^{-1}$) $3.6 \text{ kcal mol}^{-1}$ less basic than **3** ($\Delta H_{\text{HM}} = -27.4 \text{ kcal mol}^{-1}$). This is presumably due to the weaker donor ability of arsines as compared to that of phosphines.^{10,12}

Effect of Cr, Mo, and W on ΔH_{HM} in $\text{M}(\text{CO})_2(\text{L}\text{L})_2$. In the series of *cis*- $\text{M}(\text{CO})_2(\text{dppm})_2$ complexes **1**, **2**, and **7**, metal basicity (ΔH_{HM}) increases in the order Cr ($-25.5 \text{ kcal mol}^{-1}$) < Mo ($-29.7 \text{ kcal mol}^{-1}$) < W ($-31.5 \text{ kcal mol}^{-1}$) as one goes down the group. This effect has been observed previously,²⁸ as the $\text{p}K_a$ values of the conjugate acids of the $[\text{CpM}(\text{CO})_3]^-$ complexes determined in CH_3CN increase in the order Cr (13.3) < Mo (13.9) < W (16.1).²⁹ This trend also follows the tendency of third-row elements to form stronger M–H bonds than first-row elements.^{29a,30} The M–H bond dissociation energies of $\text{CpCr}(\text{H})(\text{CO})_3$ (54 kcal mol^{-1}) and $\text{CpW}(\text{H})(\text{CO})_3$ (65 kcal mol^{-1}) in CH_3CN solution were estimated recently.^{30a} Although the difference in basicity between $\text{CpCr}(\text{CO})_3^-$ ($\text{p}K_a = 13.3$) and $\text{CpMo}(\text{CO})_3^-$ ($\text{p}K_a = 13.9$) is small, that between the Cr complex **1** ($\Delta H_{\text{HM}} = -25.5 \text{ kcal mol}^{-1}$) and Mo complex **2** ($\Delta H_{\text{HM}} = -29.7 \text{ kcal mol}^{-1}$) is large and the difference in basicities of **2** and W complex **7** ($\Delta H_{\text{HM}} = -31.5 \text{ kcal mol}^{-1}$) is small. The trend of increasing basicity in the $\text{M}(\text{CO})_2(\text{dppm})_2$ complexes with increasing size of the group 6 metal atom may be related to the observation that the P–M–P bond angles for dppm complexes of Mo (63.5°)²⁴ and W ($64.7\text{--}67.5^\circ$)^{26,27} are smaller than those of Cr (69.8° in *mer*- $[\text{Cr}(\text{NO})(\text{CNCMe})_3(\text{dppm})]\text{PF}_6$).³¹ As discussed above, smaller chelates have a destabilizing effect on the *cis*- $\text{M}(\text{CO})_2(\text{L}\text{L})_2$ complexes that increases their basicity; therefore, the smaller bite of the dppm chelate in **2** and **7** may be part of the reason why the basicities of the *cis*- $\text{M}(\text{CO})_2(\text{dppm})_2$ complexes increase in the order Cr < Mo < W. In spite of the trend in ΔH_{HM} values, the reported $E_{1/2}$ values (eq 9, vs SCE in acetone) of **1** (0.01 V), **2** (0.30 V), and **7** (0.30 V) increase as one goes down the group.^{3c}

For the $\text{M}(\text{CO})_2(\text{dppe})_2$ ($\text{M} = \text{Mo}, \text{W}$) complexes a reversal in the periodic trend is observed as the Mo complex **3** ($\Delta H_{\text{HM}} = -27.4 \text{ kcal mol}^{-1}$) is $2.3 \text{ kcal mol}^{-1}$ more basic than the W complex **8** ($\Delta H_{\text{HM}} = -25.1 \text{ kcal mol}^{-1}$). Reversals in the order of basicities for isostructural complexes of first- and second-row transition metals have been observed in $\text{p}K_a$ values of $\text{HM}[\text{P}(\text{OMe})_3]_4^+$

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complexes: Pd (1.0) < Ni (1.7) < Pt (10.2), determined in methanol.^{29a} Qualitative studies of the acidities of group 9 complexes give the following order of decreasing acidities: HRhL₄ > HCoL₄ > HIrL₄ (L = CO, PF₃, respectively).³⁴ Recently, Morris and co-workers³⁵ reported increasing pK_a values of *trans*-[MH(η²-H₂)(PR₂CH₂CH₂PR₂)₂]⁺ (R = Ph, *p*-CF₃C₆H₄) complexes in the order Fe < Os < Ru. This latter example and that of **3** and **8** (Table I) are the first reported examples of a reversal between complexes of second- and third-row metals.

ΔH_{HM} of Cp*₂M, Where M = Ru, Os. The basicities of the Cp*₂M complexes, **9** and **10**, also increase on going down the column from Ru (ΔH_{HM} = -19.0 kcal mol⁻¹) to Os (ΔH_{HM} = -26.6 kcal mol⁻¹). In terms of equilibrium constants for protonation, **10** is 4 × 10⁵ times more basic than **9** assuming ΔS^o is the same for both reactions. Qualitative studies of the basicities of Cp₂Fe and Cp₂Ru reported previously^{29b,32} indicate that the Ru complex is more basic than the Fe complex. This suggests that Cp*₂Fe will also be less basic than Cp*₂Ru (**9**) although we were unable to obtain a ΔH_{HM} value for Cp*₂Fe. In contrast to those of complexes **1**, **2**, and **7** above, the electrochemical potentials (vs SCE in CH₂Cl₂)³³ of **9** (E_{1/2} = 0.55 V) and **10** (E_{1/2} = 0.46 V) decrease as one goes down the group.

Basicities of Organonitrogen Complexes, ΔH_{HN}. The wide range of ΔH_{HM} values from -19.0 kcal mol⁻¹ for complex **4** to -38.7 kcal mol⁻¹ for complex **6** demonstrates that substantial changes in metal basicity occur upon changing the metal and/or the chelate ligand. A comparable range of ΔH_{HN} values was

obtained for the six organonitrogen bases in Table I. The variation from the weakly basic 3-bromopyridine to the strongly basic tetramethylguanidine is 17.6 kcal mol⁻¹. The ΔH_{HN} values for these organonitrogen bases correlate linearly (r = 0.997) with their pK_a values³⁶ in water (eq 10). A similar correlation (eq 11) of

$$-\Delta H_{HN} = 1.64 \text{ p}K_a + 21.0; \text{ in kcal mol}^{-1} \quad (10)$$

$$-\Delta H_{HP} = 1.82 \text{ p}K_a + 16.3; \text{ in kcal mol}^{-1} \quad (11)$$

the heats of protonation (ΔH_{HP}) of a series of phosphines with their pK_a values was previously reported.^{10,17} It is evident, that while the correlations in eq 10 and 11 are similar, they are distinctly different for these two different families of compounds. Arnett and Scorrano³⁷ previously reported correlations of the heats of protonation in FSO₃H with pK_a values for various organic bases; these correlations were also different for different families of compounds.

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Registry No. **1**, 53092-55-0; **2**, 53152-36-6; **3**, 17523-42-1; **4**, 66633-00-9; **5**, 41367-49-1; **6**, 51005-80-2; **7**, 53092-56-1; **8**, 17523-43-2; **9**, 84821-53-4; **10**, 100603-32-5; TMG, 80-70-6; dppm, 2071-20-7; dppe, 1663-45-2; dppp, 6737-42-4; arphos, 23582-06-1; 3-bromopyridine, 626-55-1; pyridine, 110-86-1; morpholine, 110-91-8; triethylamine, 121-44-8.

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Redox and Spectral Properties of the Four-Electron Oxidant *trans*-[Ru(tpy)(O)₂(H₂O)](ClO₄)₂

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The complex *trans*-[Ru(tpy)(O)₂(H₂O)](ClO₄)₂ (**1**) (tpy is 2,2':6',2''-terpyridine) has been prepared and characterized by UV-visible, FTIR, resonance Raman, and ¹H NMR spectroscopies and earlier by X-ray crystallography. Its redox properties were investigated by electrochemical techniques over the pH range 0-9 in water. The couples Ru(VI/IV), Ru(IV/III), and Ru(III/II) appear and are pH dependent. At pH = 1.0, E_{1/2} values for *trans*-[Ru^{VI}(tpy)(O)₂(H₂O)]²⁺/[Ru^{IV}(tpy)(O)(H₂O)₂]²⁺, [Ru^{IV}(tpy)(O)(H₂O)₂]²⁺/[Ru^{III}(tpy)(H₂O)₃]³⁺, and [Ru^{III}(tpy)(H₂O)₃]³⁺/[Ru^{II}(tpy)(H₂O)₃]²⁺ are 1.27, 1.11, and 0.71 V vs NHE. Plots of E_{1/2} vs pH are revealing in defining regions of stability for the various oxidation states and in defining the pK_a values of their aqua and hydroxo forms. An intense band appears in the infrared spectrum of **1** at 841 cm⁻¹ in KBr, and an intense Raman band, at 834 cm⁻¹ in the solid state. These have been assigned to ν_{as}(O=Ru=O) and ν_{sym}(O=Ru=O), respectively. From the results of an X-ray crystallographic study, reported previously, the average Ru=O bond length is 1.661 Å and the O=Ru=O angle of the *trans*-dioxo group is 171.3° with the bending occurring away from the tpy ligand. Addition of **1** to CH₃CN led to *trans*-[Ru^{VI}(tpy)(O)₂(CH₃CN)]²⁺ (k₁ = 4.9 ± 0.2 s⁻¹, 19.5 °C), and addition of H₂O to the CH₃CN solution, to the reappearance of **1** (k₋₁ = 35.3 ± 0.1 M⁻¹ s⁻¹). The value of the equilibrium constant, K (=k₁/k₋₁) = 0.15 ± 0.01 M, was determined independently from ¹H NMR studies in D₂O/CD₃CN mixtures. Comparisons with redox potentials for related couples and a thermodynamic analysis based on related ruthenium and structurally equivalent complexes of osmium reveal a number of features that may bear on the reactivity of **1** in solution.

Introduction

Oxo and dioxo complexes of the higher oxidation states of Ru(IV), Ru(V), and Ru(VI), have proven to be useful stoichiometric and catalytic oxidants.¹⁻⁴ An extensive chemistry of

trans-dioxo complexes of Ru(VI) and Os(VI) is emerging based on porphyrins,⁴ macrocycles,⁵ polypyridyl complexes,^{6,7} and py-

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