Heats of Protonation of Transition-Metal Complexes: The Effect of Phosphine Basicity on Metal Basicity in $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$

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Abstract: Titration calorimetry has been used to determine the effects of phosphine ligand basicity on the heats of protonation (ΔH_{HM}) of the metal in the CpIr(CO)(PR₃) and Fe(CO)₃(PR₃)₂ complexes (PR₃ = P(p-ClC₆H₄)₃, PPh₃, P(p-MeOC₆H₄)₃, PMePh₂, PMe₂Ph, PMe₃) with CF₃SO₃H at 25.0 °C in 1,2-dichloroethane solvent. The ΔH_{HM} values of the CpIr(CO)(PR₃) compounds range from -29.2 (PR₃ = P(p-ClC₆H₄)₃) to -33.2 kcal mol⁻¹ (PR₃ = PMe₃), and those of the Fe(CO)₃(PR₃)₂ compounds range from -14.1 (PR₃ = PPh₃) to -23.3 kcal mol⁻¹ (PR₃ = PMe₃). Linear correlations of metal basicity (ΔH_{HM}) with phosphine basicity ($\Delta H_{\rm HP}$ or pK_a) show that increasing the phosphine basicity by 1.0 kcal mol⁻¹ increases the CpIr(CO)(PR₃) basicity by 0.298 kcal mol⁻¹ and the $Fe(CO)_3(PR_3)_2$ basicity by 0.458 kcal mol⁻¹ per PR₃ ligand. For both the Ir and Fe complexes, the $\Delta H_{\rm HM}$ values correlate linearly with the respective $\nu(\rm CO)$ values. The effect of the indenyl, CS, and CO ligands on the basicities ($\Delta H_{\rm HM}$) of (indenyl)lr(CO)(PPh₃), CpIr(CS)(PPh₃), and Cp*Ir(CO)₂ are also discussed.

Introduction

There is considerable interest in the basicities of metals in transition-metal complexes¹⁻³ because these basicities are indicators of other types of reactivity that depend upon electron-richness at the metal center.⁴ It is widely recognized that metal basicity is influenced by the basicity (e.g., pK_a)⁵⁻⁷ of phosphine ligands bound to the metal. Numerous metal-phosphine complexes undergo protonation at the metal center,8 however, few quantitative data^{2b,1,9-11} are available concerning the relationship between

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phosphine basicity and metal basicity. Recently, we⁷ reported heats of protonation ($\Delta H_{\rm HP}$ in eq 1) of phosphines in 1,2-di-

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

chloroethane (DCE) solvent as a measure of phosphine basicity. Heats of protonation (ΔH_{HM}) have also been used as a measure of the basicities of transition-metal complexes; this method has been shown^{3,7} to be capable of measuring basicities of compounds that are either weakly or strongly basic. Calorimetric titrations are performed with 0.1 M triflic acid (CF₃SO₃H) in 1,2-dichloroethane (DCE) solution (eq 2), the same conditions that were

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

used to determine the heats of protonation (ΔH_{HP}) of phosphines (eq 1). Previously, it was established that the basicity (ΔH_{HM}) of the iridium in Cp'Ir(1,5-COD) complexes (Cp' = η^5 -C₅Me_xH_{5-x}, x = 0, 1, 3-5) increases linearly as the number of methyl groups in the cyclopentadienyl ring increases.³

In this paper, we report studies of the basicities (ΔH_{HM}) of two series of complexes, $CpIr(CO)(PR_3)$ (eq 3) and $Fe(CO)_3(PR_3)_2$ (eq 4), in which the basicity of the phosphine ligand is systematically varied. In addition, we include protonation studies of (indenyl)Ir(CO)(PPh₃) (11), CpIr(CS)(PPh₃) (12), Cp*Ir(CO)₂ (13), and $(1,2,3-C_5Me_3H_2)Ir(CO)(PPh_3)$ (14).

Experimental Section

General Methods. All preparative reactions, chromatography, and manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The solvents were purified under nitrogen as described below using the methods in Perrin et al.¹² Hexanes and CH₂Cl₂ were refluxed over CaH₂ and then distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Benzene was distilled from LiAlH₄ and toluene from sodium metal. Deuteriochloroform (Aldrich) was stored over molecular sieves in air or distilled from P2O5 under nitrogen. Anhydrous ethanol was obtained by distillation of absolute ethanol from Mg(OEt)₂ under nitrogen. Neutral Al₂O₃ (Brockmann, activity I) used for chromatography was deoxygen-

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PR3: P(p-ClC6H4)3 (1, 1H⁺), PPh3 (2, 2H⁺), PMePh2 (3, 3H⁺), PMe₂Ph (4, 4H⁺), PMe₃ (5, 5H⁺)

 $\begin{array}{c} PR_{3} \\ OC - Fe \\ PR_{3} \\ OC \\ PR_{3} \\ PR_{3} \end{array} + CF_{3}SO_{3}H \xrightarrow{DCE} OC \\ 25.0 \ ^{\circ}C \\ R_{3}P \end{array} \xrightarrow{PR_{3}} CF_{3}SO_{3}; \ \Delta H_{HM}$ (4) 6 - 10 6H*CF3SO3 - 10H*CF3SO3

PR3: PPh3(6, 6H⁺), P(p-MeOC₆H₄)₃ (7, 7H⁺), PMePh₂ (8, 8H⁺), PMe2Ph (9, 9H*), PMe3 (10, 10H*)

ated at room temperature under high vacuum (10⁻⁵ mm Hg) for 9 h. deactivated with 5% (w/w) N_2 -saturated water, and stored under N_2

The ¹H NMR spectra were recorded in CDCl₃ on a Nicolet-NT 300 MHz spectrometer using TMS ($\delta = 0.00$ ppm) as the internal reference. Varian VXR-300 MHz instrument was used to obtain the ¹³C{H} NMR spectra in CDCl₃ solvent (internal reference, CDCl₃, $\delta = 77.0$ ppm). Infrared spectra of the neutral complexes 1-14 were recorded on a Digilab FTS-7 FT-IR spectrometer. Spectra of the protonated products were obtained either on the Digilab (1H⁺, 3H⁺, 4H⁺, 7H⁺, 11H⁺, 13H⁺) or on a Nicolet 710 FT-IR spectrometer for the remaining compounds. Sodium chloride cells with 0.1-mm spacers were used to record all FT-IR spectra. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN

The phosphine compounds $P(p-C|C_6H_4)_3$ and $P(p-MeOC_6H_4)_3$ were purchased from Strem while PPh₃, PMePh₂, PMe₂Ph, and PMe₃ (1.0 M in toluene) were purchased from Aldrich. Vaska's complex, IrCl-(CO)(PPh₃)₂, used in the preparations of 2, 11, and 14 was synthesized according to an updated procedure.13 The iridium complexes 2,14 12,15 and 13^{16} were prepared as previously reported. The compounds $[CpIrI_2]_n$ and $CpIr(I)_2(PMe_3)$ used for the preparations of 1 and 5, respectively, were prepared as reported by Heinekey et al.¹⁷ The starting material for 6-10, Fe(CO)₃(bda) (bda = benzylideneacetone), was prepared according to Brookhart and co-workers.^{18a} Preparations of compounds 6,¹⁹⁻²¹ 8,^{19,20,21} 9,²¹ and 10^{19a,22} by other methods have been previously reported.

Preparation of Iridium Complexes, Cp'Ir(L)(L'), 1-5 and 11-14. $CpIr(CO)[P(p-ClC_6H_4)_3]$ (1). The starting material, $CpIr(I)_2[P(p-ClC_6H_4)_3]$ $ClC_6H_4)_3$ - CH_2Cl_2 , was prepared using the same procedure described for the synthesis of $CpIr(I)_2(PMe_3)$.¹⁷ It coprecipitated with 1 equiv of

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 CH_2Cl_2 as a deep red powder in 92% yield [¹H NMR δ 5.44 (d, J_{PH} = 1.3 Hz, 5 H, Cp), 7.42 (m, 6 H, Ph), 7.51 (m, 6 H, Ph)]. A mixture of $CpIr(I)_2[P(p-ClC_6H_4)_3] \cdot CH_2Cl_2$ (908 mg, 0.944 mmol), Na₂CO₃ (830 mg, 7.83 mmol), and anhydrous EtOH (30 mL) was heated to reflux under a slow stream of carbon monoxide (1 atm) for 24 h. The color of the mixture gradually turned from red to clear yellow. When monitoring the reaction by 'H NMR spectroscopy we observed a yellow intermediate $[\delta 5.35 \text{ (d, } J_{PH} = 1.3 \text{ Hz}, 5 \text{ H}, \text{ Cp}), 7.3-7.5 \text{ (m, } 12 \text{ H}, \text{ Ph})]$ which transformed to the desired yellow product 1. The EtOH solvent was removed under vacuum, and the residue was extracted with CH2Cl2 (3 \times 5 mL). The extract solution was reduced to \sim 5 mL under vacuum and diluted with 5 mL of hexanes. This solution was chromatographed on a neutral alumina column (15×1.5 cm): elution with Et₂O/hexanes (1:5) gave a yellow band containing 1. After evaporation of the solvents, the resulting solid was recrystallized from CH₂Cl₂/hexanes at -40 °C to give 390 mg of 1 as a yellow-orange powder in 63% yield [1H NMR δ 5.13 (s, 5 H, Cp), 7.36 (m, 6 H, Ph), 7.48 (m, 6 H, Ph); IR (CH₂Cl₂) ν (CO) 1929 cm⁻¹]. The similarity of its spectra to those of the other CpIr(CO)(PR₃) complexes established its identity as 1.

CpIr(CO)(PPh₃) (2). This compound was prepared in 56% yield from KCp^3 and $IrCl(CO)(PPh_3)_2^{13}$ according to the previously reported procedure:¹⁴ ¹H NMR δ 5.14 (d, J_{PH} = 1.0 Hz, 5 H, Cp), 7.34–7.61 (m, 15 H, Ph); IR (CH₂Cl₂) ν (CO) 1923 cm⁻¹.

 $CpIr(CO)(PMePh_2)$ (3). To a solution of 2 (150 mg, 0.27 mmol) in 20 mL of toluene was added PMePh₂ (0.27 mL, 1.45 mmol). The mixture was refluxed for 5 h when the starting material (2) was observed by ¹H NMR spectroscopy to be completely reacted. The solvent was removed under vacuum, and the oily residue dissolved in hexanes was added to a chromatography column of neutral alumina (10×1.5 cm). Elution with Et₂O/hexanes (1:10) gave a yellow band which was collected. The solvent was slowly evaporated under vacuum until a precipitate began to form. Cooling the solution to -20 °C gave yellow crystals of 3 (108 mg, 82% yield): ¹H NMR δ 2.30 (d, $J_{PH} = 9.9$ Hz, 3 H, Me), 5.13 (s, 5 H, Cp), 7.4–7.6 (m, 10 H, Ph); IR $(CH_2Cl_2) \nu(CO)$ 1922 cm⁻

CpIr(CO)(PMe₂Ph) (4). To a solution of 2 (403 mg, 0.735 mmol) in benzene (20 mL) was added PMe₂Ph (0.53 mL, 3.7 mmol). The mixture was refluxed for 2 h as the solution developed a yellow-red hue. The ¹H NMR spectrum showed that 2 was completely reacted. After cooling to room temperature the solvent was removed under vacuum. The oily residue was then dissolved in hexanes and chromatographed on a column of neutral alumina (10 \times 1.5 cm) with a mixture of Et₂O/ hexanes (1:5). A yellow band was collected, and the solvent was evaporated under vacuum affording yellow needles. They were dissolved in a 1:3 mixture of Et₂O/hexanes and filtered through a 2×3 cm column of alumina. Recrystallization from Et₂O/hexanes at -20 °C gave yellow crystals of 4 (178 mg, 56% yield): ¹H NMR δ 2.02 (d, J_{PH} = 10.2 Hz, 6 H, Me), 5.24 (s, 5 H, Cp), 7.40–7.80 (m, 5 H, Ph); $IR (CH_2Cl_2) \nu(CO)$ 1917 cm⁻¹. Anal. Calcd for C₁₄H₁₆IrOP: C, 39.71; H, 3.81. Found: C, 39.61; H, 3.88.

CpIr(CO)(PMe₃) (5). A mixture of CpIr(I)₂(PMe₃)¹⁷ (435 mg, 0.741 mmol) and Na₂CO₃ (600 mg, 5.66 mmol) in anhydrous EtOH (30 mL) was heated to reflux under a slow stream of carbon monoxide for 16 h. During this time the red suspension turned to a milky orange-yellow suspension. The mixture was then allowed to cool slowly to room temperature while maintaining the CO atmosphere. After removing the solvent under vacuum, the residue was extracted with 30 mL of hexanes. The hexanes solution was added to a neutral alumina column (15×1.5 cm), and a yellow band was eluted with Et₂O/hexanes (1:5). After evaporation of the solvents under vacuum, the yellow solid was dissolved in 10 mL of hexanes; the solution was filtered and cooled to -20 °C to obtain 145 mg of 5 (54%) as yellow needles. Yields of 5 were variable and ranged from 27 to 54%: ¹H NMR δ 1.77 (d, J_{PH} = 10.5 Hz, 9 H, Me), 5.30 (s, 5 H, Cp); IR (CH₂Cl₂) ν (CO) 1914 cm⁻¹; IR (hexanes) ν (CO) 1937 cm⁻¹. Anal. Calcd for C₉H₁₄IrOP: C, 29.91; H, 3.90. Found: C, 30.19; H, 3.95.

(Indenyl)Ir(CO)(PPh₃) (11). This compound was prepared in 63% yield from K(indenide)³ (0.16 g, 4.1 mmol) and IrCl(CO)(PPh₃)₂ (0.83 g, 1.1 mmol) according to the procedure reported for the synthesis of **2**.¹⁴ ¹⁴ H NMR δ 5.18 (br s, 2 H, H1, H3), 6.25 (m, 1 H, H2), 6.81 (m, 4 H, H4-H7), η^5 -indenyl;²³ 7.0-7.4 (m, 15 H, Ph); IR (CH₂Cl₂) ν (CO) 1934 cm⁻¹. Anal. Calcd for C₂₈H₂₂IrOP: C, 56.27; H, 3.71. Found: C, 55.92; H, 3.69

Cplr(CS)(PPh₃) (12). This complex was prepared from KCp³ and IrCl(CS)(PPh₃)₂²⁴ according to the previously reported procedure:¹⁵ yield

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45%; ¹H NMR δ 5.06 (s, 5 H, Cp), 7.39-7.70 (m, 15 H, Ph); IR (Nujol mull) ν (CS) 1291 cm⁻¹

 $Cp^{*}Ir(CO)_{2}$ (13). This complex was synthesized from $[Cp^{*}IrCl_{2}]_{2}^{16b}$ and $Fe_3(CO)_{12}^{25}$ as previously reported:¹⁶⁸ yield 64%; ¹H NMR δ 2.19 (s, 15 H, Cp*); IR (CH₂Cl₂) ν (CO) 2010 (s), 1938 (s) cm⁻¹.

(1,2,3-C₅Me₃H₂)Ir(CO)(PPh₃) (14). Compound 14 was prepared using K(1,2,3-C,Me₁H₂)³ (0.39 g, 2.7 mmol) and IrCl(CO)(PPh₁)₂ (0.32 g, 0.41 mmol) in the same manner as previously described for the synthesis of $2^{.14}$ yield of 14 45%; ¹H NMR δ 1.85 (d, $J_{PH} = 1.9$ Hz, 6 H, 1,3-Me₂Cp), 2.06 (d, $J_{PH} = 1.1$ Hz, 3 H, 2-MeCp), 4.77 (s, 2 H, Cp), 7.3-7.6 (m, 15 H, Ph); IR (CH₂Cl₂) ν (CO) 1914 cm⁻¹. Anal. Calcd for C₂₇H₂₆IrOP: C, 54.99; H, 4.44. Found: C, 54.60; H, 4.61.

Preparation of Iron Complexes, Fe(CO)₃(PR₃)₂. Method A. To a solution of $Fe(CO)_3(bda)^{18s}$ (280 mg, 1.0 mmol) in THF (20 mL) was added the triarylphosphine (2.2 equiv). The mixture was stirred at room temperature for the length of time indicated below. During this time much of the $Fe(CO)_3(PR_3)_2$ complex precipitated from solution. After reducing the solution to ~ 10 mL under vacuum, it was diluted with hexanes (20 mL). The resulting precipitate was filtered and washed with hexanes $(3 \times 3 \text{ mL})$. Recrystallization by dissolution of the golden yellow solid in a minimum of CH₂Cl₂, layering this solution with Et₂O (10 × volume of CH_2Cl_2), and cooling to -20 °C gave the desired product.

Method B. A solution of Fe(CO)₃(bda)^{18a} (420 mg, 1.5 mmol) in THF (30 mL) was mixed with the phosphine (3.3 equiv). The mixture was stirred for the time indicated below. Evaporation of the solution under vacuum gave an oily residue. The residue was dissolved in a minimum of CH_2Cl_2 and added to a neutral alumina column (20 × 1.5 cm). Elution with CH₂Cl₂ gave a very pale yellow band. Evaporation of the eluent to dryness and recrystallization from CH2Cl2/hexanes (1:10) at -20 °C gave the desired product.

 $Fe(CO)_3(PPh_3)_2$ (6). Method A: reaction time 20 h; yield 82%; ¹H NMR δ 7.40–7.60 (m, Ph); IR (CH₂Cl₂) ν (CO) 1965 (w), 1881 (s) cm⁻¹.

 $Fe(CO)_{3}[P(p-MeOC_{6}H_{4})_{3}]_{2}$ (7). Method A: reaction time 15 h; yield 78%; ¹H NMR δ 3.82 (s, 18 H, Me), 6.91–7.51 (m, 24 H, Ph); IR (CH₂Cl₂) ν (CO) 1964 (w), 1875 (s) cm⁻¹.

Fe(CO)₃(PMePh₂)₂ (8). Method B: reaction time 15 h; yield 87%; ¹H NMR δ 2.18 (d, J_{PH} = 6.8 Hz, 6 H, Me), 7.39–7.67 (m, 20 H, Ph); IR (CH₂Cl₂) ν (CO) 1965 (w), 1876 (s) cm⁻¹.

Fe(CO)₃(PMe₂Ph)₂ (9). Method B: reaction time 24 h; yield 72%; ¹H NMR δ 1.88 (s, 12 H, Me), 7.42-7.78 (m, 10 H, Ph); IR (CH₂Cl₂) v(CO) 1965 (w), 1870 (s) cm⁻¹

Fe(CO)₃(PMe₃)₂ (10). Method B: reaction time 96 h; yield 74%; ¹H NMR δ 1.59 (d, J_{PH} = 8.3 Hz, Me); IR (CH₂Cl₂) ν (CO) 1963 (w), 1864 (s) cm⁻¹.

Protonation Reactions of Iridium Complexes 1-5 and 11-14. Compounds 1-5 and 11-14 were protonated by dissolving \sim 30 mg of each compound in 3 mL of CH₂Cl₂ under N₂. To the solution was added 1 equiv of CF₃SO₃H by microliter syringe. Immediately, the color of the solution was bleached. The IR spectra showed new $\nu(CO)$ bands at higher frequency (\sim 140 cm⁻¹, see below) and the complete disappearance of the bands corresponding to the neutral starting material (see above). Solutions of the protonated complexes are stable as long as they are kept under nitrogen or argon. By adding 1 equiv of 1,3-diphenylguanidine base (except for 5H⁺ which requires excess base) the original color reappeared as did the IR bands corresponding to the unprotonated starting material. The protonated complexes $2H^+X^-$ (X = BPh₄⁻, BF₄⁻), ¹⁴a^{,17} 12H⁺Cl⁻, ¹⁵ and 13H⁺BF₄⁻, ²⁶ have been isolated and characterized previously

Samples of 1H⁺-5H⁺ and 11H⁺-14H⁺ for ¹H NMR spectroscopy were prepared by adding 1 equiv of CF3SO3H to solutions of the neutral complex (~10 mg) in $CDCl_3$ (~0.5 mL). The yields as determined by ¹H NMR spectroscopy are also quantitative.

Compounds 11H+CF₃SO₃⁻ and 14H+CF₃SO₃⁻ were isolated as white solid precipitates by protonation of 11 (20.7 mg, 0.0346 mmol) and 14 (39.0 mg, 0.0661 mmol), respectively, with CF₃SO₃H (1 equiv) in Et₂O (5 mL) solution. After filtration, $11H^+CF_3SO_3^-$ (18.1 mg, 0.0242 mmol) was obtained in 70% yield, and $14H^+CF_3SO_3^-$ (36.8 mg, 0.0497 mmol) was obtained in 75% yield. They were characterized by their spectra as compared with those of 2H⁺, 12H⁺, and 13H⁺ which were previously reported.148,15,17,26

Spectroscopic data for 1H+CF3SO3-5H+CF3SO3 and 11H+-CF₃SO₃-14H+CF₃SO₃ are presented below.

{CpIr(H)(CO)[P(p-ClC₆H₄)₃]}CF₃SO₃ (1H⁺CF₃SO₃⁻): ¹H NMR δ 5.94 (s, 5 H, Cp), 7.35 (d, J_{HH} = 9.0 Hz, 6 H, meta Ph protons), 7.57 (dd, $J_{PH} = 12.3$ Hz, 6 H, ortho Ph protons), -14.45 (d, $J_{PH} = 24.41$ Hz, 1 H, Ir-H); IR (CH₂Cl₂) v(CO) 2063 cm⁻¹.

[CpIr(H)(CO)(PPh₃)]CF₃SO₃ (2H⁺CF₃SO₃⁻): ¹H NMR δ 5.88 (s, 5 H, Cp), 7.56–7.40 (m, 15 H, Ph), -14.44 (d, $J_{PH} = 24.10$ Hz, 1 H, Ir-H); IR (CH₂Cl₂) v(CO) 2063 cm⁻¹

[CpIr(H)(CO)(PMePh₂))CF₃SO₃ (3H⁺CF₃SO₃⁻): ¹H NMR & 5.90 (s, 5 H, Cp), 2.70 (d, $J_{PH} = 12.3$ Hz, 3 H, Me), 7.5 (m, 10 H, Ph), -14.66 (d, $J_{PH} = 23.21$ Hz, 1 H, Ir-H); IR (CH₂Cl₂) ν (CO) 2061 cm⁻¹

[CpIr(H)(CO)(PMe2Ph)]CF3SO3 (4H+CF3SO3-): 1H NMR 8 5.89 (s, 5 H, Cp), 2.36 (d, J_{PH} = 11.6 Hz, 3 H, Me), 2.39 (d, J_{PH} = 11.4 Hz, 3 H, Me), 7.27-7.62 (m, 5 H, Ph), -15.03 (d, $J_{PH} = 25.11$ Hz, 1 H, Ir-H); IR (CH₂Cl₂) v(CO) 2057 cm⁻¹

 $[CpIr(H)(CO)(PMe_3)]CF_3SO_3^{-}(5H^+CF_3SO_3^{-}): {}^{1}H NMR \delta 6.01 (s, s)$ 5 H, Cp), 2.12 (d, J_{PH} = 12.1 Hz, 9 H, Me), -15.32 (d, J_{PH} = 25.33 Hz, 1 H, Ir-H); IR (CH₂Cl₂) ν (CO) 2052 cm⁻¹.

[(Indenyl)Ir(H)(\tilde{CO})(PPh₃)] \tilde{CF}_3SO_3 (11H⁺ CF_3SO_3 ⁻): ¹H NMR δ 6.63 (br s, 2 H, H1, H3), 7.19 (t, $J_{1,3-2} = 7.6$ Hz, 1 H, H2), 7.84 (d, $J_{5,6-4,7} = 8.4$ Hz, 2 H, H4, H7), 6.32 (d, 2 H, H5, H6) η^5 -indenyl;²³ 7.00 (m, 6 H, ortho Ph protons), 7.51 (m, 9 H, meta and para Ph protons),

-17.14 (d, $J_{PH} = 21.6$ Hz, 2 H, Ir-H); IR (CH₂Cl₂) ν (CO) 2058 cm⁻¹. [CpIr(H)(CS)(PPh₃)]CF₃SO₃ (12H⁺CF₃SO₃⁻): ¹H NMR δ 5.85 (s, 5 H, Cp), 7.44-7.56 (m, 15 H, Ph), -13.72 (d, $J_{PH} = 24.32$ Hz, 1 H, Ir-H); IR (CH₂Cl₂) ν (CS) 1372 cm⁻¹.

 $[(C_5Me_5)Ir(H)(CO)_2]CF_3SO_3 (13H^+CF_3SO_3^-): ^1H NMR \delta 2.43 (s,$ 15 H, Me), -13.80 (br s, 1 H, Ir-H); IR (CH₂Cl₂) ν (CO) 2119 (s), 2080 (s) cm⁻¹

 $[(1,2,3-C_5Me_3H_2)Ir(H)(CO)(PPh_3)]CF_3SO_3 (14H^+CF_3SO_3^-): {}^{1}H$ NMR δ 1.93 (s, 3 H, 2-Me), 2.13 (s, 3 H, 1,3-Me₂), 2.22 (s, 3 H, $1,3-Me_2$, 5.59 (s, 2 H, Cp), 7.56-7.38 (m, 15 H, Ph), -14.43 (d, $J_{PH} =$ 25.5 Hz, 1 H, Ir-H); IR (CH₂Cl₂) ν(CO) 2045 cm⁻¹.

Protonation Reactions of Iron Complexes 6-10. These complexes were protonated using the same procedure described above for the iridium complexes. However, we found that filtration of solutions of 6-10 in air-free CDCl₃ through a short column of Celite (2×0.5 cm), under N₂, resulted in better quality ¹H NMR spectra of the protonated products 6H⁺CF₃SO₃⁻-10H⁺CF₃SO₃⁻. Yields of the protonated products as determined by IR and ¹H NMR spectroscopy are quantitative. Only the protonation of 6 in H₂SO₄ solution was reported previously.²⁷ Attempts to isolate the protonated complexes as solids were unsuccessful; however, solutions are stable if kept under N2 or Ar. The spectroscopic data for 6H+CF₃SO₃-10H+CF₃SO₃ are given below.

 $[Fe(H)(CO)_{3}(PPh_{3})_{2}]CF_{3}SO_{3}(6H^{+}CF_{3}SO_{3}^{-}): ^{1}H NMR \delta 7.45-7.61$ (m, 30 H, Ph), -7.90 (t, $J_{PH} = 30.7$ Hz, 1 H, Fe-H); IR (CH₂Cl₂) ν (CO) 2088 (w), 2039 (m, sh), 2026 (s) cm⁻¹

 ${Fe(H)(CO)_{3}[P(p-MeOC_{6}H_{4})_{3}]_{2}}CF_{3}SO_{3}(7H^{+}CF_{3}SO_{3}^{-}): {}^{1}H NMR$ δ 3.88 (s, 18 H, Me), 7.06–7.33 (m, 24 H, Ph), -7.89 (t, J_{PH} = 29.9 Hz, 1 H, Fe-H); IR (CH₂Cl₂) ν (CO) 2080 (vw), 2032 (m, sh), 2020 (s) cm⁻¹.

 $[Fe(H)(CO)_3(PMePh_2)_2]CF_3SO_3 (8H^+CF_3SO_3^-): ^1H NMR \delta 2.42 (s,)$ 6 H, Me), 7.6 (m, 20 H, Ph), -8.27 (t, $J_{PH} = 34.2$ Hz, 1 H, Fe-H); IR $(CH_2Cl_2) \nu(CO) 2092$ (w), 2027 (s) cm⁻¹

[Fe(H)(CO)₃(PMe₂Ph)₂)CF₃SO₃ (9H⁺CF₃SO₃⁻): ¹H NMR δ 2.07 (br, s, 12 H, Me), 7.5 (m, 10 H, Ph), -8.92 (t, $J_{PH} = 36.7$ Hz, 1 H, Fe-H); IR (CH₂Cl₂) v(CO) 2090 (w), 2023 (s) cm

 $[Fe(H)(CO)_3(PMe_3)_2]CF_3SO_3$ (10H+CF_3SO_3-): ¹H NMR δ 1.76 (d, $J_{PH} = 8.5$ Hz, 18 H, Me), -9.49 (t, $J_{PH} = 36.6$ Hz, 1 H, Fe-H); IR $(CH_2Cl_2) \nu(CO) 2090 (w), 2023 (s) cm^{-1}$

Calorimetric Titrations. The calorimetric titration procedure was similar to that previously described.^{3,7} Typically a run consisted of three sections: 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 DCE under an argon atmosphere at a constant rate during 3 min time to 50 mL of a \sim 2.6 mM solution of the metal complex $(\sim 10\%$ excess) in DCE. In order to reduce the amounts of the iridium complexes (3, 4, and 12) required, 2-min titration periods were used. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (-0.2 kcal mol⁻¹).3

The enthalpy values are reported as the average of usually four titrations and as many as eight. However, only three titrations were performed with 12. At least two different standardized acid solutions were used for the titrations of each compound. The error is reported as the average deviation from the mean.

Results

Synthesis of Iridium Complexes 1-5, 11, 12, and 14. In spite of the well-developed syntheses of $CpM(CO)(PR_3)$ complexes

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Table I. Heats of Protonation (ΔH_{HM}) of Cp'Ir(L)(L') and Fe(CO)₃(PR₃)₂ Complexes

metal complex	$-\Delta H_{\rm HP}$, ^{<i>a,b</i>} kcal mol ⁻¹	$-\Delta H_{\rm HM}$, ^{<i>a,c</i>} kcal mol ⁻¹
$CpIr(CO)(P(p-C C_{2}H_{2})) = 1$	$17.9(\pm 0.2)$	$29.2 (\pm 0.2)$
$CpIr(CO)(PPh_{3}), 2$	$21.2 (\pm 0.1)$	$30.1 (\pm 0.2)$
Cplr(CO)(PMePh ₂), 3	24.7 (±0.0)	31.5 (±0.1)
Cplr(CO)(PMe2Ph), 4	28.4 (±0.2)	32.4 (±0.3)
$CpIr(CO)(PMe_3), 5$	31.6 (±0.2)	33.2 (±0.5)
(indenyl)Ir(CO)(PPh ₃), 11	21.2 (±0.1)	29.8 (±0.3)
$CpIr(CS)(PPh_3), 12$	21.2 (±0.1)	26.51 (±0.01)
$Cp^{*}Ir(CO)_{2}, 13$		21.4 (±0.1)
$CpIr(1,5-COD)^d$		22.8 (±0.2)
$Cp*Ir(1,5-COD)^d$		28.5 (±0.2)
$Fe(CO)_3(PPh_3)_2$, 6	21.2 (±0.1)	14.1 (±0.1)
$Fe(CO)_{3}[P(p-MeOC_{6}H_{4})_{3}]_{2}, 7$	24.1 (±0.2)	16.2 (±0.3)
$Fe(CO)_3(PMePh_2)_2, 8$	24.7 (±0.0)	17.6 (±0.4)
$Fe(CO)_3(PMe_2Ph)_2, 9$	28.4 (±0.2)	21.2 (±0.3)
$Fe(CO)_{3}(PMe_{3})_{2}, 10$	31.6 (±0.2)	23.3 (±0.3)

^a For protonation with CF₃SO₃H in DCE solvent at 25.0 °C. ^bReference 7. ^cNumbers in parentheses are average deviations. ^dReference 3.

where $M = Co, Rh,^{4a,9b}$ only the preparations of Ir complexes 2^{14} and 4²⁸ have been reported previously. However, 5 was recently identified spectroscopically in a solid CO matrix as a product from the photolysis of $CpIr(C_2H_4)(PMe_3)$.²⁹ Compounds 1-5 and 11-14 have the half-sandwich geometry shown in eq 3 as confirmed for 2 by an X-ray crystallographic determination.³⁰ The compounds were characterized by ¹H NMR and IR spectroscopy (see Experimental Section). Only 5 is air-sensitive in the solid state; even so, it can be handled in air for brief periods. As a precaution all compounds were stored under N_2 , and solutions were prepared using dry deaerated solvents. Compound 5, however, is best stored for long periods under vacuum in a sealed glass ampoule.

We have found potassium cyclopentadienide (KCp)³ more convenient to prepare than NaCp. Thus, known complexes 2^{14} and 12^{15} were prepared from KCp and IrCl(CO)(PPh₃)₂ or IrCl(CS)(PPh₃)₂, respectively. Similarly, the previously unreported complexes 11 and 14 were prepared from KCp' (Cp' = indenyl, $1,2,3-C_5Me_3H_2$ ³ and $IrCl(CO)(PPh_3)_2$ (eq 5).

$$KCp' + IrCl(CO)(PPh_{3})_{2} \xrightarrow{\text{Denzene}} Cp'Ir(CO)(PPh_{3})$$
(5)

$$Cp' = indenyl, 11, 40\%$$
(5)

$$Cp' = 1,2,3-C_{5}Me_{3}H_{2}, 14, 45\%$$

Attempts to prepare 3 and 4 from KCp and $IrCl(CO)(PR_3)_2$ $(PR_3 = PMePh_2, PMe_2Ph)^{31}$ resulted only in low yields of the desired products. But starting from 2, the PPh₃ ligand was completely replaced with $PMePh_2$ or PMe_2Ph (eq 6) under reflux.

$$\frac{\text{CpIr(CO)(PPh_3)}}{2} \xrightarrow{\text{xs PMerh_2, toluene reflux}} \text{CpIr(CO)PR_3} (6)$$

$$\frac{\text{PR}_3 = \text{PMePh_2, 3, 60\%}}{\text{PR}_3 = \text{PMe2Ph, 4, 82\%}}$$

Unfortunately, the reaction conditions used to prepare 3 and 4 (eq 6) were not successful for the synthesis of the PMe₃ derivative 5 as only decomposition of the starting material 2 was observed. However, reduction of $CpIr(I)_2(PMe_3)^{17}$ in slightly basic alcoholic solution³² under an atmosphere of carbon monoxide gave 5 (eq

(32) See, for example: Booth, B. L.; Haszeldine, R. N.; Hill, M. J. Organomet. Chem. 1969, 16, 491-496.

7) in variable yields (27-54%)

$$CpIr(I)_{2}(PR_{3}) + CO (1 \text{ atm}) \xrightarrow{EtOH, reflux} Optimizer (CO)(PR_{3}) = (7)$$

$$PR_{3} = P(p-ClC_{6}H_{4})_{3}, 1, 60\%$$

$$PR_{3} = PMe_{3}, 5, 27-54\%$$

which tended to be lower for prolonged reaction times. The $P(p-ClC_6H_4)_3$ derivative 1 was prepared similarly. The syntheses of 1 and 5 are best followed by ¹H NMR spectroscopy. An intermediate, which is observed in each reaction (see Experimental Section), is tentatively assumed to be CpIr(H)(OEt)(PR₃).³³ Carbon monoxide-induced reductive elimination of EtOH then produces the CpIr(CO)(PR₃) product.

Protonation Reactions of the Iridium Complexes. The protonated complexes $2H^+X^-$ (X = BPh₄⁻, BF₄⁻), 14a,17 12H⁺Cl⁻, 15 and $13H^+BF_4^{-26}$ have been isolated and characterized previously. It was established that protonation occurred at the iridium metal center. We observed that the addition of 1 equiv of CF₃SO₃H to solutions of the neutral metal complexes (1-5 and 11-14) in CH₂Cl₂ results in quantitative formation of 1H⁺CF₃SO₃^{--5H⁺-} CF₃SO₃⁻ and 11H⁺CF₃SO₃⁻-14H⁺CF₃SO₃⁻ as indicated by IR spectroscopy. The $\nu(CO)$ band moves by ~140 cm⁻¹ (or 81 cm⁻¹ for the $\nu(CS)$ band of 12) to higher frequency (see Experimental Section). Quantitative formation of 1H⁺-5H⁺ and 11H⁺-14H⁺ in CDCl₂ solution is also observed by ¹H NMR spectroscopy. Hydride resonances for 1H⁺-5H⁺ occur as doublets between -14.45 (1H⁺) and -15.32 ppm (5H⁺) with ${}^{2}J_{PH} = 24-25$ Hz due to coupling with the phosphine phosphorus. The Ir-H resonances for 11H⁺-14H⁺ are found in a wider range, -13.72 for 12H⁺ to -17.14 ppm for 11H⁺. Complexes 11H⁺CF₃SO₃⁻ and 14H⁺- $CF_3SO_3^-$ were isolated as white solids in yields of 70% and 75%, respectively, from reactions of 11 and 14 with CF₃SO₃H in Et₂O solution.

In $4H^+CF_3SO_3^-$ the Me groups in the PMe₂Ph ligand are diastereotopic;¹⁷ thus, they are observed as two sets of doublets centered at 2.32 (${}^{2}J_{PH} = 11.6 \text{ Hz}$) and 2.39 ppm (${}^{2}J_{PH} = 11.4$ Hz) in the ¹H NMR spectrum. Also, the 1,3-Me groups in the 1,2,3-C₅Me₃H ligand of $14H^+CF_3SO_3^-$ are diastereotopic which gives rise to separate signals for these Me groups at 2.13 and 2.22 ppm. The resonance at 1.93 ppm because it is the most different from the other two was assigned to the 2-Me group. The chemical shifts of the 4,5-Cp' ring protons are indistinguishable, but in principle they could also give two distinct ¹H NMR resonances.

The protonated complexes are stable in solution as long as they are kept under an atmosphere of N₂ or Ar. However, solutions of $5H^+CF_3SO_3^-$ decompose readily upon exposure to air. The isolated complexes 11H⁺CF₃SO₃⁻ and 14H⁺CF₃SO₃⁻ are stable in air long enough to be weighed out. Also, 11H⁺CF₃SO₃⁻ did not isomerize (vide infra) or decompose after 24 h in refluxing DCE (bp 83 °C) under N₂. The protonated compounds can be deprotonated with 1,3-diphenylguanidine base and recovered by chromatography.

Syntheses of Iron Complexes, Fe(CO)₃(bda). The use of Fe- $(CO)_3(bda)$ (bda = benzylideneacetone) as a source of the Fe- $(CO)_3$ moiety in the preparation of $Fe(CO)_3(\eta^4$ -diene) complexes has been described.^{18,34} Except for brief reports of the synthesis of Fe(CO)₃(PPh₃)₂ (6),^{19c-e} Fe(CO)₃(bda) has not been widely used as a precursor to other $Fe(CO)_3(PR_3)_2$ complexes. We used $Fe(CO)_3(bda)$ to prepare all of the $Fe(CO)_3(PR_3)_2$ compounds, 6-10 (eq 8). The generality of this reaction and the ability to store Fe(CO)₃(bda) (under N₂) makes this an excellent synthetic method for these complexes.^{19f} Complexes 6,¹⁹⁻²¹ 8,^{19b,20,21} 9,²¹ and 10^{19a,22} were characterized

by comparison of their ¹H NMR and IR spectra with those re-

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⁽³³⁾ The reaction of Cp*Ir(Cl)₂(PPh₃) with NaOEt in EtOH solution gives Cp*Ir(OEt)(H)(PPh₃) which eliminates EtOH in the presence of L (CO, PPh₃, C₂H₄) to give Cp*Ir(L)(PPh₃). (a) Newman, L. J.; Bergman, R. G. J. Am. Chem. Soc. 1985, 107, 5314-5315. (b) Newman, L. J. Ph.D. Thesis, University of California at Berkeley, 1986.

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$$Ph \longrightarrow_{Fe} O + 2PR_3 \xrightarrow{THF} Fe(CO)_3(PR_3)_2$$
(8)

ported in the literature for these compounds. Spectroscopic studies, 22,35a,38b,c X-ray diffraction determinations, 35b,c and theoretical calculations 35d indicate that the Fe(CO)₃(PR₃)₂ complexes prefer to adopt the trigonal-bipyramidal geometry shown in eq 4 with the phosphines in the axial positions. Complexes **6-9** are air-stable as solids but were normally stored under N₂ at 0 °C. Complex 10 is only moderately air-stable. However, solutions of **6-10** were handled under nitrogen or argon using Schlenk techniques.

Protonation of Fe(CO)₃(PR₃)₂ Complexes. It has been shown previously by ¹H NMR and IR spectroscopy that 6 protonates at the metal center in concentrated H₂SO₄ solution.²⁷ With 1 equiv of CF₃SO₃H we observe quantitative protonation of 6 to give 6H⁺CF₃SO₃⁻ (eq 4). Three ν (CO) infrared bands (2088 (w), 2039 (m, sh), 2026 (s) cm⁻¹) in CH₂Cl₂ solution are observed for 6H⁺CF₃SO₃⁻ shifted by greater than 100 cm⁻¹ from the unprotonated 6 values (1965 (w), 1881 (s) cm⁻¹). A trace of unprotonated 6 is also detected in the spectrum. This is probably due to deprotonation of 6H⁺CF₃SO₃⁻ by adventitious water or even Cl⁻ in the NaCl IR cells since titration calorimetry, vide infra, establishes that protonation of 6 with CF₃SO₃⁻ in CDCl₃ shows a high field triplet hydride resonance at -7.90 ppm (²J_{PH} = 30.7 Hz) which is coupled to two equivalent phosphine ligands.

Compounds 7-10 are also quantitatively protonated at the metal center as determined by IR and ¹H NMR spectroscopy with 1 equiv of CF₃SO₃H. The two ν (CO) bands of weak and strong intensity in 7H⁺CF₃SO₃⁻-10H⁺CF₃SO₃⁻ are more than 100 cm⁻¹ higher than those of their neutral precursors. The ¹H NMR spectra of 7H⁺-10H⁺ show characteristic high field triplets (-7.89 ppm, $J_{PH} = 29.9$ Hz, for 7H⁺ to -9.49, $J_{PH} = 36.6$ Hz, for 10H⁺) for the hydride ligand. The proton resonances of the PR₃ ligands are shifted downfield from those in the unprotonated complexes. The protonated complexes 6H⁺CF₃SO₃⁻-10H⁺CF₃SO₃⁻ are stable in solution as long as they are kept under nitrogen or argon. Also, the solution (CH₂Cl₂) IR spectra of 6H⁺CF₃SO₃⁻, 8H⁺CF₃SO₃⁻, and 10H⁺CF₃SO₃⁻ show no absorptions characteristic of coordinated CF₃SO₃^{-.36}

There are three possible isomers for $6H^+-10H^+$ with structures A, B, and C.³⁷ The triplet Fe-H resonances and the equivalence of the PR₃ ligands in the ¹H NMR spectra of $6H^+-10H^+$ eliminate structure C and rule out the possibility of having a mixture of isomers as it is unlikely that A and B would give the same ¹H NMR spectrum.



The number and relative intensities of the ν (CO) bands in the IR spectra of **6H⁺-10H⁺** are consistent with the mer geometry **A**. Such complexes with $C_{2\nu}$ symmetry are expected to give three IR bands of weak, strong, and strong relative intensities corresponding to two A₁ and one B₁ vibrational modes, respectively.³⁸ For **6H⁺-10H⁺**, the weak band at high frequency corresponds to one A₁ mode, and the strong band at lower frequency corresponds

to the remaining A_1 and B_1 modes which are only partially resolved for **6H**⁺ and **7H**⁺ and unresolved for the remaining compounds.^{38b} The following related complexes have also been assigned the mer geometry **A** based on their IR spectra in the ν (CO) region: [Fe(CH₃)(CO)₃(PMe₃)₂]^{+,39} [Os(H)(CO)₃(PPh₃)₂]PF₆,^{40a} Mn-(H)(CO)₃(PPh₃)₂,⁴¹ Mn(H)(CO)₃(PMePh₂)₂,⁴² Re(H)(CO)₃-(PPh₃)₂,³⁷ and Re(H)(CO)₃(PEt₃)₂.³⁷ The mer structures of Mn(H)(CO)₃(PPh₃)₂⁴¹ and Mn(H)(CO)₃(PMePh₂)₂,⁴² which are isoelectronic with **6H**⁺ and **8H**⁺, respectively, and [Ru(H)-(CO)₃(PPh₃)₂][CH(SO₂CF₃)₂]^{40b} have been established by X-ray crystallography. The fac geometry **B** for **6H**⁺-**10H**⁺ is unlikely since this structure having C_s symmetry is predicted to give three ν (CO) bands of equal intensity (2A' + A'').³⁸

 ν (CO) bands of equal intensity (2A' + A'').³⁸ In principle, "virtual coupling"⁴³ of the trans phosphines in structure A should cause the Me resonances in **8H⁺-10H⁺** to appear as triplets in the ¹H NMR spectrum. However, they occur as broad singlets in **8H⁺** and **9H⁺** and as a doublet $(J_{PH} = 8.5$ Hz) in **10H⁺**. The Me resonances for *mer*-Mn(H)(CO)₃[P-(OPh)₂Me]₂⁴⁴ and *mer*-Mn(H)(CO)₃(PMePh₂)₂ also occur as doublets in spite of their having *trans*-PR₃ groups. Thus, in these cases the ¹H NMR spectra do not distinguish between the mer (A) and fac (B) structures.

The ¹³C NMR for the CO ligands, however, are more conclusive in supporting the mer structure (A) for **6H⁺-10H⁺**. For **8H⁺**, two 1:2:1 triplets⁴⁵ are observed at 204.71 (${}^{2}J_{PC} = 23.65$ Hz) and 203.56 ppm (${}^{2}J_{PC} = 13.35$ Hz). As the triplet at 204.71 ppm is about twice the intensity of that at 203.56 ppm, the 204.71 ppm triplet is assigned to the mutually trans CO groups leaving the remaining triplet to the CO trans to the hydride in A. A comparison of the ${}^{2}J_{PC}$ values in **8H⁺** with those in [Fe(CH₃)-(CO)₂(PMe₃)₃]⁺, **D**,⁴⁶ also supports structure A for these complexes. In **D**, the ${}^{2}J_{PC}$ values (${}^{2}J_{P1C1} = 27.3$ Hz, ${}^{2}J_{P2C2} = {}^{2}J_{P1C2}$



= 18.4 Hz) for the cis CO and PMe₃ ligands are much smaller than those for trans CO and PMe₃ ligands (${}^{2}J_{P2C1}$ = 41.3 Hz). The J_{PC} values in 8H⁺ (23.65 and 13.35 Hz) indicate that there are only cis CO and PR₃ groups as required by structure A; there are no coupling constants in the range of 41 Hz which should be observed if there were trans CO and PR₃ ligands as in structure **B**. Supporting the mer structure **A** for these cations is the ¹³C NMR spectrum of 6H⁺CF₃SO₃⁻ which also gives small ²J_{PC} values of 23.3 (204.88 ppm, t, 2CO) and 15.3 Hz (204.0 ppm, t, CO). Thus, the IR and ¹³C NMR data strongly support structure **A** for the products of the protonation reactions (eq 4).

Calorimetric Studies. Heats of protonation (ΔH_{HM}) determined by calorimetric titration of the complexes Cp'Ir(L)(L') 1-5, 11-13 (eq 3), and Fe(CO)₃(PR₃)₂ 6-10 (eq 4) with 0.1 M CF₃SO₃H are presented in Table I. As expected for titrations which occur stoichiometrically, rapidly, and without significant decomposition of the reactant or product, plots of temperature vs amount of acid added are linear.⁴⁷ The only exception to this behavior was that

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of Fe(CO)₃(PMePh₂)₂, **8**, for which the plots were slightly curved; the curvature was probably due to a small amount of decomposition of the reactant. However, the $\Delta H_{\rm HM}$ value (-17.6 kcal mol⁻¹) obtained from these plots, which has a larger error (±0.4 kcal mol⁻¹) than the other Fe complexes, is reasonable because it is between those of the less basic Fe(CO)₃(PPh₃)₂ (**6**) (-14.1 kcal mol⁻¹) and the more basic Fe(CO)₃(PMe₂Ph)₂ (**9**) (-21.2 kcal mol⁻¹).

Infrared spectra were taken of the titrated solutions. Those of the iridium complexes 1-5, 11, and 13 gave ν (CO) bands corresponding to the protonated products $1H^+-5H^+$, $11H^+$, and $13H^+$. The protonated iron complexes, $6H^+-10H^+$, which are much more acidic than those of iridium, were usually partially deprotonated by adventitious water or the NaCl windows in the IR cell.

Titrations of iridium complex 5 and iron complexes 8, 9, and 10 exhibited a slight amount of decomposition as evidenced by increased slopes during the pre- and post-titration baseline segments. However, the correction for this effect is small compared to the overall ΔH_{HM} value. For reasons which are not understood, we were unable to obtain a reproducible ΔH_{HM} value for 14 even though this complex and its protonated product 14H⁺CF₃SO₃⁻ appeared to be stable under the conditions of the titrations.

Discussion

In this section, we examine trends in the basicities of the CpIr(CO)(PR₃) and Fe(CO)₃(PR₃)₂ complexes as a function of the PR₃ ligand. Phosphine basicity is measured by ΔH_{HP} (eq 1);⁷ however, since ΔH_{HP} is linearly related to the pK_a of the phosphine, correlations involving ΔH_{HP} may also be expressed as correlations with pK_a.

Basicities of the CpIr(CO)(PR₃) Complexes 1–5. The basicity of the metal (ΔH_{HM}) in these complexes increases as the free phosphine basicity (ΔH_{HP}) increases (Table I). The basicities of the phosphines extend over a wide range from the weakly basic P(p-ClC₆H₄)₃ ($\Delta H_{HP} = -17.9$ kcal mol⁻¹, pK_a = 1.03) to the very basic PMe₃ ($\Delta H_{HP} = -31.6$ kcal mol⁻¹, pK_a = 8.65).⁷ However, the ΔH_{HM} values only range from -29.2 kcal mol⁻¹ for CpIr-(CO)[P(p-ClC₆H₄)₃] (1) to -33.2 kcal mol⁻¹ for CpIr(CO)(PMe₃) (5). A linear correlation (eq 9a) with a correlation coefficient (r) of 0.996 is obtained when ΔH_{HM} is plotted vs phosphine ΔH_{HP} (Figure 1). The correlation between the ΔH_{HM} and pK_a values (eq 9b) is also linear (r = 0.992). Equation 9a suggests that the

$$-\Delta H_{\rm HM} = -0.298 \Delta H_{\rm HP} + 23.9$$
, in kcal mol⁻¹ (9a)

$$-\Delta H_{\rm HM} = 0.540 \, {\rm pK_a} + 28.7$$
, in kcal mol⁻¹ (9b)

overall basicity of a complex is made up of a phosphine contribution (-0.298 $\Delta H_{\rm HP}$) and a metal fragment (CpIr(CO)) contribution (23.9).⁴⁸ The 0.298 coefficient for $\Delta H_{\rm HP}$ (eq 9a) indicates that a change in phosphine basicity of 1.0 kcal mol⁻¹ increases the basicity of the iridium complex by only 0.298 kcal mol⁻¹. Thus, only a fraction (0.298) of the phosphine basicity change is evident in the basicity change of the iridium.

As ΔH_{HP} is a measure of the σ -donor ability of the phosphine,⁷ the linear correlation with ΔH_{HM} (Figure 1) suggests, but does not prove, that the phosphine ligands in 1–5 behave as primarily σ -donor ligands thus supporting previous assignments of these phosphines as σ -donor ligands.^{5b} However, it is not possible to distinguish phosphine π -bonding if its contribution correlates linearly with σ -donor ability. Though cone angles (θ)⁵ of the phosphine ligands in 3 (136°), 4 (122°), and 5 (118°) change, they are the same (145°) for 1 and 2. Thus, the linear correlation (Figure 1) between metal basicity and phosphine basicity suggests that the steric bulk (θ) of the phosphine does not significantly affect the ΔH_{HM} values, as might be expected for these relatively un-



Figure 1. Correlations of metal basicity (ΔH_{HM}) with phosphine basicity (ΔH_{HP}) as determined by calorimetric titration with 0.1 M CF₃SO₃H in DCE solvent at 25.0 °C. Upper line is for the CpIr(CO)(PR₃) complexes. Lower line is for the Fe(CO)₃(PR₃)₂ complexes.



Figure 2. Correlation of metal basicity (ΔH_{HM}) with $\nu(CO)$ values (in CH₂Cl₂ solvent) of CpIr(CO)(PR₃) complexes (upper line) and Fe-(CO)₃(PR₃)₂ complexes (lower line).

crowded reactants and products.

The $-\Delta H_{\rm HM}$ values increase (eq 10, r = -0.969) as ν (CO) values

$$\Delta H_{\rm HM} = 0.274 [2034.3 - \nu(\rm CO)], \text{ in kcal mol}^{-1}$$
 (10)

(Figure 2) of the CpIr(CO)(PR₃) compounds 1–5, decrease, indicating that increasing phosphine basicity causes the electron density on the iridium center to increase. This results in an increase in iridium-to-CO $d\pi \rightarrow p\pi^*$ backbonding that decreases the CO stretching frequency.^{38b,c} It is apparent, however, that relatively small changes in ν (CO) (15 cm⁻¹) from 1 to 5 indicate substantial changes in metal basicity (4.0 kcal mol⁻¹ from 1 to 5). Therefore it is important that all of the ν (CO) values be measured in one solvent since changing solvents from CH₂Cl₂ (for 2, ν (CO) = 1923 cm⁻¹) to hexanes (for 2, ν (CO) = 1946 cm⁻¹) affects the ν (CO) value by ~20 cm^{-1.49}

A correlation (r = -0.986) (eq 11) of $-\Delta H_{\rm HM}$ with the Ir-H chemical shift (δ) in complexes $2H^+-5H^+$ and $12H^+$ is also obtained. However, it is of limited use since data for $1H^+$, $11H^+$, and $13H^+$ deviate significantly from it.

$$-\Delta H_{\rm HM} = -4.31(\delta) - 31.2$$
, in kcal mol⁻¹ (11)

Basicities of the Fe(CO)₃(PR₃)₂ Complexes 6–10. The ΔH_{HM} values for these complexes range from -14.1 kcal mol⁻¹ for 6 to -23.3 kcal mol⁻¹ for 10. As for the CpIr(CO)(PR₃) series, there is a linear correlation (eq 12a, r = 0.993) of ΔH_{HM} with ΔH_{HP} (Figure 1). The corresponding pK_a correlation (r = 0.981) is given in eq 12b. Equation 12a shows that as the basicity of the PR₃

$$-\Delta H_{\rm HM} = -0.916 \Delta H_{\rm HP} - 5.36$$
, in kcal mol⁻¹ (12a)

$$-\Delta H_{\rm HM} = 1.63 \, {\rm pK_a} + 9.68$$
, in kcal mol⁻¹ (12b)

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⁽⁴⁸⁾ If there is a constant contribution by all phosphines, it would be included in the metal fragment term. Our treatment does not distinguish between these two potential types of contribution.

⁽⁴⁹⁾ For a discussion of solvent effects on ν (CO) stretching frequencies see: Braterman, P. S. Struct. Bond. 1976, 26, 2-42, and references 38b and c.

ligand increases by 1.0 kcal mol^{-1} , the basicity of the iron complex increases by 0.916 kcal mol^{-1} . Thus, each phosphine ligand contributes 0.458 kcal mol⁻¹ toward the metal basicity as PR₃ is varied by 1.0 kcal mol⁻¹.

As for the $CpIr(CO)(PR_3)$ system, the linear correlation between $\Delta H_{\rm HM}$ and $\Delta H_{\rm HP}$ suggests the metal basicity is determined by the σ -donor ability of the phosphine. However, as noted in the iridium discussion, it is not possible to exclude unequivocally some contribution of phosphorus π -bonding; Mossbauer studies⁵⁰ of $Fe(CO)_3(PR_3)_2$ complexes have been interpreted to support such π -bonding.

There is also a linear correlation (eq 13, r = -0.972) of ΔH_{HM} with the broad low-frequency band corresponding to the E mode CO stretching vibration in the ν (CO) region of the infrared spectra of 6-10 (Figure 2).

$$-\Delta H_{\rm HM} = 0.562[1906.8 - \nu(\rm CO)], \text{ in kcal mol}^{-1}$$
 (13)

As for the protonated iridium complexes, we observe a limited linear correlation (r = -0.983) of $\Delta H_{\rm HM}$ with the Fe–H chemical shift (δ) in 6H⁺ and 8H⁺-10H⁺ (eq 14). However, 7H⁺ deviates significantly from this correlation.

$$-\Delta H_{\rm HM} = -5.66(\delta) - 29.9$$
, in kcal mol⁻¹ (14)

Comparisons of the Basicities of the CpIr(CO)(PR₃) and Fe- $(CO)_3(PR_3)_2$ Complexes. The iridium complexes 1-5 are much more basic than the corresponding $Fe(CO)_3(PR_3)_2$ complexes 6-10 (Figure 1). Using the PPh₃ complexes for comparison, CpIr- $(CO)(PPh_3)$ (2) $(\Delta H_{HM} = -30.1 \text{ kcal mol}^{-1})$ is 16.0 kcal mol⁻¹ more basic than $Fe(CO)_3(PPh_3)_2$ (6) ($\Delta H_{HM} = -14.1 \text{ kcal mol}^{-1}$). Assuming $\Delta S^{\circ} = 0$ eu, the estimated equilibrium constant (ΔG° = ΔH_{HM} = -RT ln K) for the reaction (eq 15), is 5.4 × 10¹¹, which illustrates this very large difference in basicities. The free

$$CpIr(CO)(PPh_{3}) + HFe(CO)_{3}(PPh_{3})_{2}^{+} \stackrel{\kappa}{\longleftarrow} \\CpIr(H)(CO)(PPh_{3})^{+} + Fe(CO)_{3}(PPh_{3})_{2}$$
(15)

phosphines, e.g., PPh₃ ($\Delta H_{\rm HP} = -21.2 \text{ kcal mol}^{-1}$), have basicities which are intermediate between those of their $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes. The very basic nature of the iridium in these types of complexes is emphasized by the observation that the related [CpIr(H)(PPh₃)₂]⁺ cannot be deprotonated even with *n*-BuLi.⁵¹

In the correlations of $\Delta H_{\rm HM}$ with $\Delta H_{\rm HP}$ (Figure 1), the contributions of the metal fragments are -23.9 kcal mol⁻¹ for CpIr(CO) (eq 9a) and +5.36 kcal mol⁻¹ for Fe(CO)₃ (eq 12a).⁴⁸ Thus, the major factor which makes the $CpIr(CO)(PR_3)$ complexes more basic than the $Fe(CO)_3(PR_3)_2$ complexes is the greater contribution of the CpIr(CO) fragment, which is reasonable since the CO ligands are less electron-donating than Cp⁻;^{2b} also the proton is likely to form stronger bonds with Ir than with Fe as third row transition metals are generally more basic^{1a,2d,f} and form stronger bonds to hydrogen than first row metals.^{1a,2m}

As noted above, the contribution of phosphine ligand basicity to $\Delta H_{\rm HM}$ is indicated by the coefficients of the $\Delta H_{\rm HP}$ terms in eq 9a (0.298) for $CpIr(CO)(PR_3)$ and in eq 12a (0.916) for $Fe(CO)_3(PR_3)_2$. If a change in phosphine basicity were to produce the same change in metal basicity in both series of complexes, one would expect the $\Delta H_{\rm HP}$ coefficient to be twice as large for the iron complexes than for the iridium because two phosphines are being substituted in the iron series. However, in the Fe- $(CO)_3(PR_3)_2$ series each PR₃ contributes 0.458 kcal mol⁻¹ (0.916/2) for 1.0 kcal mol⁻¹ change in ΔH_{HP} , while in the $CpIr(CO)(PR_3)$ complexes each PR_3 contributes only 0.298 kcal mol^{-1} . Thus, it appears that the CpIr(CO)(PR₃) system is better able to dissipate additional PR₃ electron density than the Fe- $(CO)_3(PR_3)_2$ complexes. One might have expected that the strongly π -accepting CO ligands in Fe(CO)₃(PR₃)₂ would have

been more effective at removing electron density from the metal than the Cp and CO ligands in $CpIr(CO)(PR_3)$. Thus, it is not clear why changes in phosphine basicity affect these series of complexes differently. However, the structures and bonding in the reactants and products (eqs 3 and 4) are very different, and it would not be surprising if their ΔH_{HM} values behaved differently. In fact, it might be considered surprising that the phosphine contributions (0.298 and 0.458) are so similar given their structural differences and the much higher overall basicity of the iridium series as compared with that of the iron.

From the linear plots (Figure 2) of ΔH_{HM} vs ν (CO), it is evident that $\nu(CO)$ values may be used to estimate ΔH_{HM} values of closely related compounds. However, it is also clear that $\nu(CO)$ values are not of general use in predicting ΔH_{HM} since the correlations (Figure 2) for the Ir and Fe complexes lie on distinctly different lines.

It is instructive to compare our results to related quantitative data reported in the literature. Pearson and Kresge¹⁰ measured equilibrium constants (K_{H^+}) for the oxidative addition (eq 16) of CF_3SO_3H to $IrCl(CO)(PR_3)_2$ in MeOH solvent at 25.0 °C. (Coordination of CF₃SO₃⁻ or MeOH in the product was not

$$IrCl(CO)(PR_3)_2 + CF_3SO_3H \xrightarrow{K_{H^+}} trans-IrCl(CO)(PR_3)_2(H)(O_3SCF_3) (16)$$

unequivocally established.) K_{H^+} values (in parentheses) increase with increasing basicity of the phosphine: PPh_3 (114 M^{-1}) < $PMePh_2$ (302 M^{-1}) < PMe_2Ph (631 M^{-1}). While the trend is the same as that for the ΔH_{HM} values in the CpIr(CO)(PR₃) and $Fe(CO)_3(PR_3)_2$ complexes, the K_{H^+} values change relatively little with different phosphines. This is most likely due to the fact that the equilibrium constant K_{H^+} for reaction (eq 16) not only involves the free energy of protonation of the iridium but also the coor-

dination energy of the CF₃SO₃⁻ (or MeOH) ligand. Norton and co-workers^{2b} measured the pK_a 's of two Mn-(H)(CO)₄(PR₃) complexes ($pK_a = 20.4$ for PR₃ = PPh₃ and pK_a = 21.6 for $PR_3 = PEtPh_2$) in acetonitrile solution at 25.0 °C. Converting these pK_a values to ΔG° ($\Delta G^\circ = -RT \ln K_a$) for $Mn(H)(CO)_4(PPh_3)$ (-27.8 kcal mol⁻¹) and $Mn(H)(CO)_4$ -(PEtPh₂) (-29.5 kcal mol⁻¹) and using $\Delta H_{\rm HP}$ values of -21.2 kcal mol⁻¹ for PPh₃⁷ and -24.9 kcal mol⁻¹ for PEtPh₂,⁵² one obtains eq 17 which is analogous to 9a and 12a for the $CpIr(CO)(PR_3)$

$$-\Delta G^{\circ} = -0.459 \Delta H_{\rm HP} + 18.06$$
, in kcal mol⁻¹ (17)

and $Fe(CO)_3(PR_3)_2$ systems. Although this equation is based on only two points, the $\Delta H_{\rm HP}$ coefficient (0.459) indicates that a change in phosphine basicity in Mn(H)(CO)₄(PR₃) affects the metal basicity to the same extent that it did in $Fe(CO)_3(PR_3)_2$, with 0.458 kcal mol⁻¹ for each PR_3 . The similar effects of phosphines in the Mn and Fe complexes may be related to the close similarities of the unprotonated, $[Mn(CO)_4(PR_3)]^-$ and $Fe(CO)_3(PR_3)_2$, and the protonated, $Mn(H)(CO)_4(PR_3)$ and $[Fe(H)(CO)_3(PR_3)_2]^+$, species involved in these reactions; they are isoelectronic except for the substitution of a CO ligand by PR₃. In order to establish the range and meaning of the $\Delta H_{\rm HP}$ coefficient, other studies of the effects of phosphine basicity on metal basicity are required.

Basicities of Iridium Complexes 11-13. Comparison of the basicities of 2 ($\Delta H_{\rm HM} = -30.1 \pm 0.2 \text{ kcal mol}^{-1}$) and CpIr(1,5-COD) ($\Delta H_{HM} = -22.8 \pm 0.3 \text{ kcal mol}^{-1}$)³ indicates the (CO)-(PPh₃) ligand combination makes the metal 7.3 kcal mol⁻¹ more basic than does the 1,5-COD ligand (eq 18). However, the 1,5-COD ligand in Cp*Ir(COD) makes the iridium 7.1 kcal mol⁻¹ more basic than two CO ligands in $Cp^*Ir(CO)_2$ (13) (eq 18). Thus, we can estimate that the (CO)(PPh₃) ligand combination



(52) Calculated from the pK_a value of 4.9 (ref 5b) using eq 8 in ref 7.

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metallics 1989, 8, 1225-1231.

Scheme I



makes the iridium 14.4 kcal mol⁻¹ more basic than $(CO)_2$, if one assumes that the Cp and Cp^{*} contributions remain the same in the two pairs of compounds in eq 18. Thus, the replacement of a CO ligand on Ir by a PPh₃ produces a very large increase in the basicity of the metal. This effect is also observed in the pK_a values for the following pairs of compounds determined in CH₃CN by Norton and co-workers:^{2b,d} HCo(CO)₄ (8.3) vs HCo(CO)₃-(PPh₃) (15.4), HMn(CO)₅ (15.1) vs HMn(CO)₄(PPh₃) (20.4), and CpW(CO)₃H (16.1) vs CpW(CO)₂(PMe₃)(H) (26.6). It is evident, however, from these data that substitution of CO by PR₃ does not cause the same magnitude of increase in metal basicity in all metal complexes.

A variety of studies⁵³ indicate that CS is a more electronwithdrawing ligand than CO, as a result of its greater π -accepting ability. This is also evident in the ΔH_{HM} values of CpIr(CS)(PPh₃) (12) (-26.51 kcal mol⁻¹) and CpIr(CO)(PPh₃) (2) (-30.1 kcal mol⁻¹), which show that the metal in the CS compound 12 is 3.6 kcal mol⁻¹ less basic than that in 2.

Recently,³ we showed that (indenyl)Ir(1,5-COD) is initially protonated with CF₃SO₃H at the iridium, but the proton migrates within 15 min to the indenyl ligand to form $[(\eta^6\text{-indene})Ir(1,5\text{-}COD)]CF_3SO_3$ (E) (Scheme I). However, knowing that the (CO)(PPh₃) ligand combination in 2 increases the iridium basicity by 7.3 kcal mol⁻¹ relative to the 1,5-COD ligand in the analogous CpIr(1,5-COD) complex (vide supra) we predicted that the iridium in 11 would be sufficiently basic that proton transfer from it to the indenyl ligand would probably not occur (Scheme I). Indeed, the protonated complex $11H^+CF_3SO_3^-$ is stable as we detect no proton migration to the indenyl ligand upon reflux in DCE (bp 83 °C) for 24 h.

Recent electrochemical and PES studies of transition-metal indenyl complexes^{54,55} indicate that the indenyl ligand is at least as electron-donating as the MeCp ligand⁵⁴ and perhaps even as donating as Cp^{*,55} However, this is not observed in the $\Delta H_{\rm HM}$ value for (indenyl)Ir(CO)(PPh₃) (11) (-29.8 ± 0.3 kcal mol⁻¹) which is the same within experimental error as that for the Cp analogue CpIr(CO)(PPh₃) (2) (-30.1 ± 0.2 kcal mol⁻¹), suggesting that the indenyl and Cp ligands have the same donor properties. Since the crystal structure of [(indenyl)Ir(H)(PPh₃)₂]⁺ shows the indenyl ligand to be substantially slipped toward η^3 -coordination,^{23,56} the indenyl donor ability may be variable and depend on the electronic structure of each complex.

Conclusion

These studies demonstrate several important properties of basic metal complexes that have not been previously reported. We observe linear correlations between metal basicity as determined by $\Delta H_{\rm HM}$ and phosphine basicity ($\Delta H_{\rm HP}$ or pK_a) for the CpIr-(CO)(PR₃) and Fe(CO)₃(PR₃)₂ series of complexes, respectively. For each 1.0 kcal mol⁻¹ change in phosphine basicity ($\Delta H_{\rm HP}$), there is a greater change in Fe(CO)₃(PR₃)₂ basicity (0.916 kcal mol⁻¹) than in CpIr(CO)(PR₃) basicity (0.298 kcal mol⁻¹). In general, the CpIr(CO)(PR₃) complexes are much more basic than those in the Fe(CO)₃(PR₃)₂ series. The $\Delta H_{\rm HM}$ values also correlate linearly with the respective ν (CO) frequencies of the CpIr-(CO)(PR₃) and Fe(CO)₃(PR₃)₂ complexes. These correlations permit the estimation of basicities ($\Delta H_{\rm HM}$) of other complexes in these series which contain different phosphines whose $\Delta H_{\rm HP}$ (or pK_a) values or ν (CO) stretching frequencies are known.

Comparisons of ΔH_{HM} values for several CpIr(L)(L') complexes demonstrate that the (CO)(PPh₃) ligand combination makes the Ir 7.3 kcal mol⁻¹ more basic than the bidentate 1,5-COD ligand does; however, the 1,5-COD makes the metal more basic than (CO)₂ by 7.1 kcal mol⁻¹. For the CpIr(CX)(PPh₃) complexes (X = O, S), the CS ligand reduces the basicity of the iridium by 3.6 kcal mol⁻¹ as compared with the CO-containing complex. The donor properties of the Cp and indenyl ligands are very similar since the ΔH_{HM} values of the complexes CpIr(CO)(PPh₃) and (indenyl)Ir(CO)(PPh₃) are the same. These studies provide a quantitative basis for understanding how systematic changes in ligands affect the proton basicity of the metal in complexes.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8719744) for support of this research and Johnson Matthey Inc. for a loan of iridium.

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