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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 $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes ($PR_3 = P(p\text{-}ClC_6H_4)_3$, PPh_3, $P(p\text{-}MeOC_6H_4)_3$, $PMePh_2$, PMe_2Ph, PMe_3) with CF_3SO_3H at 25.0 °C in 1,2-dichloroethane solvent. The ΔH_{HM} values of the $CpIr(CO)(PR_3)$ compounds range from −29.2 ($PR_3 = P(p\text{-}ClC_6H_4)_3$) to −33.2 kcal mol^{-1} ($PR_3 = PMe_3$), and those of the $Fe(CO)_3(PR_3)_2$ compounds range from −14.1 ($PR_3 = PPh_3$) to −23.3 kcal mol^{-1} ($PR_3 = PMe_3$). Linear correlations of metal basicity (ΔH_{HM}) with phosphine basicity (ΔH_{HP} or pK_a) show that increasing the phosphine basicity by 1.0 kcal mol^{-1} increases the $CpIr(CO)(PR_3)$ basicity by 0.298 kcal mol^{-1} and the $Fe(CO)_3(PR_3)_2$ basicity by 0.458 kcal mol^{-1} per PR_3 ligand. For both the Ir and Fe complexes, the ΔH_{HM} values correlate linearly with the respective ν(CO) values. The effect of the indenyl, CS, and CO ligands on the basicities (ΔH_{HM}) of (indenyl)Ir(CO)(PPh_3), CpIr(CS)(PPh_3), and $Cp^*Ir(CO)_2$ are also discussed.

Introduction

There is considerable interest in the basicities of metals in transition-metal complexes[1-3] 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,l,9-11] are available concerning the relationship between phosphine basicity and metal basicity. Recently, we[7] reported heats of protonation (ΔH_{HP} in eq 1) of phosphines in 1,2-dichloroethane (DCE) solvent as a measure of phosphine basicity.

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

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 (CF_3SO_3H) in 1,2-dichloroethane (DCE) solution (eq 2), the same conditions that were used to determine the heats of protonation (ΔH_{HP}) of phosphines (eq 1).

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

Previously, it was established that the basicity (ΔH_{HM}) of the iridium in Cp′Ir(1,5-COD) complexes (Cp′ = η^5-$C_5Me_xH_{5-x}$, 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)(PPh_3) (**11**), CpIr(CS)(PPh_3) (**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 CH_2Cl_2 were refluxed over CaH_2 and then distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Benzene was distilled from $LiAlH_4$ and toluene from sodium metal. Deuteriochloroform (Aldrich) was stored over molecular sieves in air or distilled from P_2O_5 under nitrogen. Anhydrous ethanol was obtained by distillation of absolute ethanol from $Mg(OEt)_2$ under nitrogen. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygen-

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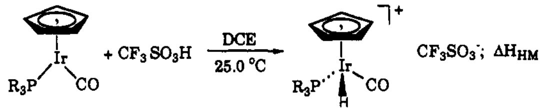
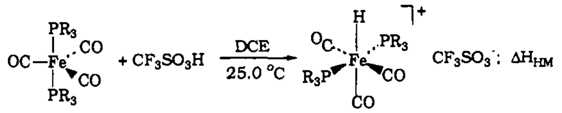


(3)

1 - 5 **1H**$^+$CF$_3$SO$_3^-$ - **5H**$^+$CF$_3$SO$_3^-$

PR$_3$: P(*p*-ClC$_6$H$_4$)$_3$ (**1**, **1H**$^+$), PPh$_3$ (**2**, **2H**$^+$), PMePh$_2$ (**3**, **3H**$^+$), PMe$_2$Ph (**4**, **4H**$^+$), PMe$_3$ (**5**, **5H**$^+$)



(4)

6 - 10 **6H**$^+$CF$_3$SO$_3^-$ - **10H**$^+$CF$_3$SO$_3^-$

PR$_3$: PPh$_3$(**6**, **6H**$^+$), P(*p*-MeOC$_6$H$_4$)$_3$ (**7**, **7H**$^+$), PMePh$_2$ (**8**, **8H**$^+$), PMe$_2$Ph (**9**, **9H**$^+$), PMe$_3$ (**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 ^{1}H NMR spectra were recorded in CDCl$_3$ on a Nicolet-NT 300 MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. A Varian VXR-300 MHz instrument was used to obtain the ^{13}C{H} NMR spectra in CDCl$_3$ solvent (internal reference, CDCl$_3$, δ = 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*-ClC$_6$H$_4$)$_3$ and P(*p*-MeOC$_6$H$_4$)$_3$ were purchased from Strem while PPh$_3$, PMePh$_2$, PMe$_2$Ph, and PMe$_3$ (1.0 M in toluene) were purchased from Aldrich. Vaska's complex, IrCl(CO)(PPh$_3$)$_2$, 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**,[19f,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$_6$H$_4$)$_3$] (1). The starting material, CpIr(I)$_2$[P(*p*-ClC$_6$H$_4$)$_3$]·CH$_2$Cl$_2$, was prepared using the same procedure described for the synthesis of CpIr(I)$_2$(PMe$_3$).[17] It coprecipitated with 1 equiv of CH$_2$Cl$_2$ as a deep red powder in 92% yield [^{1}H 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$_6$H$_4$)$_3$]·CH$_2$Cl$_2$ (908 mg, 0.944 mmol), Na$_2$CO$_3$ (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 ^{1}H NMR spectroscopy we observed a yellow intermediate [δ 5.35 (d, J_{PH} = 1.3 Hz, 5 H, Cp), 7.3–7.5 (m, 12 H, Ph)] which transformed to the desired yellow product **1**. The EtOH solvent was removed under vacuum, and the residue was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The extract solution was reduced to ~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 Et$_2$O/hexanes (1:5) gave a yellow band containing **1**. After evaporation of the solvents, the resulting solid was recrystallized from CH$_2$Cl$_2$/hexanes at -40 °C to give 390 mg of **1** as a yellow-orange powder in 63% yield [^{1}H NMR δ 5.13 (s, 5 H, Cp), 7.36 (m, 6 H, Ph), 7.48 (m, 6 H, Ph); IR (CH$_2$Cl$_2$) ν(CO) 1929 cm^{-1}]. The similarity of its spectra to those of the other CpIr(CO)(PR$_3$) complexes established its identity as **1**.

CpIr(CO)(PPh$_3$) (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] ^{1}H NMR δ 5.14 (d, J_{PH} = 1.0 Hz, 5 H, Cp), 7.34–7.61 (m, 15 H, Ph); IR (CH$_2$Cl$_2$) 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 PMePh$_2$ (0.27 mL, 1.45 mmol). The mixture was refluxed for 5 h when the starting material (**2**) was observed by ^{1}H 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 Et$_2$O/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): ^{1}H 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$_2$Cl$_2$) ν(CO) 1922 cm^{-1}.

CpIr(CO)(PMe$_2$Ph) (4). To a solution of **2** (403 mg, 0.735 mmol) in benzene (20 mL) was added PMe$_2$Ph (0.53 mL, 3.7 mmol). The mixture was refluxed for 2 h as the solution developed a yellow-red hue. The ^{1}H 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 × 1.5 cm) with a mixture of Et$_2$O/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 Et$_2$O/hexanes and filtered through a 2 × 3 cm column of alumina. Recrystallization from Et$_2$O/hexanes at -20 °C gave yellow crystals of **4** (178 mg, 56% yield): ^{1}H 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$_2$Cl$_2$) ν(CO) 1917 cm^{-1}. Anal. Calcd for C$_{14}$H$_{16}$IrOP: C, 39.71; H, 3.81. Found: C, 39.61; H, 3.88.

CpIr(CO)(PMe$_3$) (5). A mixture of CpIr(I)$_2$(PMe$_3$)[17] (435 mg, 0.741 mmol) and Na$_2$CO$_3$ (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 Et$_2$O/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%: ^{1}H NMR δ 1.77 (d, J_{PH} = 10.5 Hz, 9 H, Me), 5.30 (s, 5 H, Cp); IR (CH$_2$Cl$_2$) ν(CO) 1914 cm^{-1}; IR (hexanes) ν(CO) 1937 cm^{-1}. Anal. Calcd for C$_9$H$_{14}$IrOP: C, 29.91; H, 3.90. Found: C, 30.19; H, 3.95.

(Indenyl)Ir(CO)(PPh$_3$) (11). This compound was prepared in 63% yield from K(indenide)[3] (0.16 g, 4.1 mmol) and IrCl(CO)(PPh$_3$)$_2$ (0.83 g, 1.1 mmol) according to the procedure reported for the synthesis of **2**.[14] ^{1}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 (CH$_2$Cl$_2$) ν(CO) 1934 cm^{-1}. Anal. Calcd for C$_{28}$H$_{22}$IrOP: C, 56.27; H, 3.71. Found: C, 55.92; H, 3.69.

CpIr(CS)(PPh$_3$) (12). This complex was prepared from KCp[3] and IrCl(CS)(PPh$_3$)$_2$[24] 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:[16a] yield 64%; ^1H NMR δ 2.19 (s, 15 H, Cp*); IR (CH_2Cl_2) ν(CO) 2010 (s), 1938 (s) cm^{-1}.

$(1,2,3\text{-}C_5Me_3H_2)Ir(CO)(PPh_3)$ (14). Compound **14** was prepared using $K(1,2,3\text{-}C_5Me_3H_2)$[3] (0.39 g, 2.7 mmol) and $IrCl(CO)(PPh_3)_2$ (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-Me_2Cp), 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 (CH_2Cl_2) ν(CO) 1914 cm^{-1}. Anal. Calcd for $C_{27}H_{26}IrOP$: C, 54.99; H, 4.44. Found: C, 54.60; H, 4.61.

Preparation of Iron Complexes, $Fe(CO)_3(PR_3)_2$. Method A. To a solution of $Fe(CO)_3(bda)$[18a] (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 × 3 mL). Recrystallization by dissolution of the golden yellow solid in a minimum of CH_2Cl_2, layering this solution with Et_2O (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 CH_2Cl_2 gave a very pale yellow band. Evaporation of the eluent to dryness and recrystallization from CH_2Cl_2/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 (CH_2Cl_2) ν(CO) 1965 (w), 1881 (s) cm^{-1}.

$Fe(CO)_3[P(p\text{-}MeOC_6H_4)_3]_2$ (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 (CH_2Cl_2) ν(CO) 1964 (w), 1875 (s) cm^{-1}.

$Fe(CO)_3(PMePh_2)_2$ (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 (CH_2Cl_2) ν(CO) 1965 (w), 1876 (s) cm^{-1}.

$Fe(CO)_3(PMe_2Ph)_2$ (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 (CH_2Cl_2) ν(CO) 1965 (w), 1870 (s) cm^{-1}.

$Fe(CO)_3(PMe_3)_2$ (10). Method B: reaction time 96 h; yield 74%; ^1H NMR δ 1.59 (d, J_{PH} = 8.3 Hz, Me); IR (CH_2Cl_2) 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 ~30 mg of each compound in 3 mL of CH_2Cl_2 under N_2. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe. Immediately, the color of the solution was bleached. The IR spectra showed new ν(CO) bands at higher frequency (~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 = BPh_4^-, BF_4^-),[14a,17] **12H$^+$**Cl^-,[15] and **13H$^+$**BF_4^-,[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 CF_3SO_3H 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$^+$**$CF_3SO_3^-$ and **14H$^+$**$CF_3SO_3^-$ 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 CF_3SO_3H (1 equiv) in Et_2O (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.[14a,15,17,26]

Spectroscopic data for **1H$^+$**$CF_3SO_3^-$–**5H$^+$**$CF_3SO_3^-$ and **11H$^+$**$CF_3SO_3^-$–**14H$^+$**$CF_3SO_3^-$ are presented below.

$\{CpIr(H)(CO)[P(p\text{-}ClC_6H_4)_3]\}CF_3SO_3$ (1H$^+$$CF_3SO_3^-$): ^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 (CH_2Cl_2) ν(CO) 2063 cm^{-1}.

$[CpIr(H)(CO)(PPh_3)]CF_3SO_3$ (2H$^+$$CF_3SO_3^-$): ^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 (CH_2Cl_2) ν(CO) 2063 cm^{-1}.

$[CpIr(H)(CO)(PMePh_2)]CF_3SO_3$ (3H$^+$$CF_3SO_3^-$): ^1H NMR δ 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 (CH_2Cl_2) ν(CO) 2061 cm^{-1}.

$[CpIr(H)(CO)(PMe_2Ph)]CF_3SO_3$ (4H$^+$$CF_3SO_3^-$): ^1H NMR δ 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 (CH_2Cl_2) ν(CO) 2057 cm^{-1}.

$[CpIr(H)(CO)(PMe_3)]CF_3SO_3^-$ (5H$^+$$CF_3SO_3^-$): ^1H NMR δ 6.01 (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 (CH_2Cl_2) ν(CO) 2052 cm^{-1}.

$[(Indenyl)Ir(H)(CO)(PPh_3)]CF_3SO_3$ (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 (CH_2Cl_2) ν(CO) 2058 cm^{-1}.

$[CpIr(H)(CS)(PPh_3)]CF_3SO_3$ (12H$^+$$CF_3SO_3^-$): ^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 (CH_2Cl_2) ν(CS) 1372 cm^{-1}.

$[(C_5Me_5)Ir(H)(CO)_2]CF_3SO_3$ (13H$^+$$CF_3SO_3^-$): ^1H NMR δ 2.43 (s, 15 H, Me), −13.80 (br s, 1 H, Ir-H); IR (CH_2Cl_2) ν(CO) 2119 (s), 2080 (s) cm^{-1}.

$[(1,2,3\text{-}C_5Me_3H_2)Ir(H)(CO)(PPh_3)]CF_3SO_3$ (14H$^+$$CF_3SO_3^-$): ^1H NMR δ 1.93 (s, 3 H, 2-Me), 2.13 (s, 3 H, 1,3-Me_2), 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 (CH_2Cl_2) 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 $CDCl_3$ through a short column of Celite (2 × 0.5 cm), under N_2, resulted in better quality ^1H NMR spectra of the protonated products **6H$^+$**$CF_3SO_3^-$–**10H$^+$**$CF_3SO_3^-$. Yields of the protonated products as determined by IR and ^1H NMR spectroscopy are quantitative. Only the protonation of **6** in H_2SO_4 solution was reported previously.[27] Attempts to isolate the protonated complexes as solids were unsuccessful; however, solutions are stable if kept under N_2 or Ar. The spectroscopic data for **6H$^+$**$CF_3SO_3^-$–**10H$^+$**$CF_3SO_3^-$ are given below.

$[Fe(H)(CO)_3(PPh_3)_2]CF_3SO_3$ (6H$^+$$CF_3SO_3^-$): ^1H NMR δ 7.45–7.61 (m, 30 H, Ph), −7.90 (t, J_{PH} = 30.7 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) 2088 (w), 2039 (m, sh), 2026 (s) cm^{-1}.

$\{Fe(H)(CO)_3[P(p\text{-}MeOC_6H_4)_3]_2\}CF_3SO_3$ (7H$^+$$CF_3SO_3^-$): ^1H 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 (CH_2Cl_2) 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 δ 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) ν(CO) 2092 (w), 2027 (s) cm^{-1}.

$[Fe(H)(CO)_3(PMe_2Ph)_2]CF_3SO_3$ (9H$^+$$CF_3SO_3^-$): ^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 (CH_2Cl_2) ν(CO) 2090 (w), 2023 (s) cm^{-1}.

$[Fe(H)(CO)_3(PMe_3)_2]CF_3SO_3$ (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) ν(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 CF_3SO_3H 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 ~2.6 mM solution of the metal complex (~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 $Fe(CO)_3(PR_3)_2$ Complexes

metal complex	$-\Delta H_{HP}$,[a,b] kcal mol^{-1}	$-\Delta H_{HM}$,[a,c] kcal mol^{-1}
CpIr(CO)[P(p-$ClC_6H_4)_3$], **1**	17.9 (±0.2)	29.2 (±0.2)
CpIr(CO)(PPh_3), **2**	21.2 (±0.1)	30.1 (±0.2)
CpIr(CO)($PMePh_2$), **3**	24.7 (±0.0)	31.5 (±0.1)
CpIr(CO)(PMe_2Ph), **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-$MeOC_6H_4)_3]_2$, **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 CF_3SO_3H in DCE solvent at 25.0 °C. [b] Reference 7. [c] Numbers in parentheses are average deviations. [d] Reference 3.

where M = Co, Rh,[4a,9b] only the preparations of Ir complexes **2**[14] and **4**[28] 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 ^{1}H 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)$(PPh_3)_2$ or IrCl(CS)$(PPh_3)_2$, 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).

$$\text{KCp}' + \text{IrCl(CO)(PPh}_3)_2 \xrightarrow[\text{reflux}]{\text{benzene}} \text{Cp}'\text{Ir(CO)(PPh}_3) \qquad (5)$$

$$\text{Cp}' = \text{indenyl, } \mathbf{11}\text{, } 40\%$$
$$\text{Cp}' = 1,2,3\text{-C}_5\text{Me}_3\text{H}_2\text{, } \mathbf{14}\text{, } 45\%$$

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 PPh_3 ligand was completely replaced with $PMePh_2$ or PMe_2Ph (eq 6) under reflux.

$$\underset{\mathbf{2}}{\text{CpIr(CO)(PPh}_3)} \xrightarrow[\text{or xs PMe}_2\text{Ph, benzene reflux}]{\text{xs PMePh}_2\text{, toluene reflux}} \text{CpIr(CO)PR}_3 \qquad (6)$$

$$\text{PR}_3 = \text{PMePh}_2\text{, } \mathbf{3}\text{, } 60\%$$
$$\text{PR}_3 = \text{PMe}_2\text{Ph, } \mathbf{4}\text{, } 82\%$$

Unfortunately, the reaction conditions used to prepare **3** and **4** (eq 6) were not successful for the synthesis of the PMe_3 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 solution[32] under an atmosphere of carbon monoxide gave **5** (eq 7) in variable yields (27–54%)

$$\text{CpIr(I)}_2\text{(PR}_3) + \text{CO (1 atm)} \xrightarrow[\text{Na}_2\text{CO}_3]{\text{EtOH, reflux}} \text{CpIr(CO)(PR}_3) \qquad (7)$$

$$\text{PR}_3 = \text{P}(p\text{-ClC}_6\text{H}_4)_3\text{, } \mathbf{1}\text{, } 60\%$$
$$\text{PR}_3 = \text{PMe}_3\text{, } \mathbf{5}\text{, } 27\text{–}54\%$$

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 ^{1}H NMR spectroscopy. An intermediate, which is observed in each reaction (see Experimental Section), is tentatively assumed to be CpIr(H)(OEt)(PR_3).[33] Carbon monoxide-induced reductive elimination of EtOH then produces the CpIr(CO)(PR_3) product.

Protonation Reactions of the Iridium Complexes. The protonated complexes $\mathbf{2H^+X^-}$ (X = BPh_4^-, BF_4^-),[14a,17] $\mathbf{12H^+Cl^-}$,[15] and $\mathbf{13H^+BF_4^-}$[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 CF_3SO_3H to solutions of the neutral metal complexes (**1–5** and **11–14**) in CH_2Cl_2 results in quantitative formation of $\mathbf{1H^+}CF_3SO_3^-$–$\mathbf{5H^+}CF_3SO_3^-$ and $\mathbf{11H^+}CF_3SO_3^-$–$\mathbf{14H^+}CF_3SO_3^-$ as indicated by IR spectroscopy. The ν(CO) band moves by ~140 cm^{-1} (or 81 cm^{-1} for the ν(CS) band of **12**) to higher frequency (see Experimental Section). Quantitative formation of $\mathbf{1H^+}$–$\mathbf{5H^+}$ and $\mathbf{11H^+}$–$\mathbf{14H^+}$ in $CDCl_2$ solution is also observed by ^{1}H NMR spectroscopy. Hydride resonances for $\mathbf{1H^+}$–$\mathbf{5H^+}$ occur as doublets between −14.45 ($\mathbf{1H^+}$) and −15.32 ppm ($\mathbf{5H^+}$) with $^2J_{PH}$ = 24–25 Hz due to coupling with the phosphine phosphorus. The Ir–H resonances for $\mathbf{11H^+}$–$\mathbf{14H^+}$ are found in a wider range, −13.72 for $\mathbf{12H^+}$ to −17.14 ppm for $\mathbf{11H^+}$. Complexes $\mathbf{11H^+}CF_3SO_3^-$ and $\mathbf{14H^+}CF_3SO_3^-$ were isolated as white solids in yields of 70% and 75%, respectively, from reactions of **11** and **14** with CF_3SO_3H in Et_2O solution.

In $\mathbf{4H^+}CF_3SO_3^-$ the Me groups in the PMe_2Ph ligand are diastereotopic;[17] thus, they are observed as two sets of doublets centered at 2.32 ($^2J_{PH}$ = 11.6 Hz) and 2.39 ppm ($^2J_{PH}$ = 11.4 Hz) in the ^{1}H NMR spectrum. Also, the 1,3-Me groups in the 1,2,3-C_5Me_3H ligand of $\mathbf{14H^+}CF_3SO_3^-$ 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 ^{1}H NMR resonances.

The protonated complexes are stable in solution as long as they are kept under an atmosphere of N_2 or Ar. However, solutions of $\mathbf{5H^+}CF_3SO_3^-$ decompose readily upon exposure to air. The isolated complexes $\mathbf{11H^+}CF_3SO_3^-$ and $\mathbf{14H^+}CF_3SO_3^-$ are stable in air long enough to be weighed out. Also, $\mathbf{11H^+}CF_3SO_3^-$ did not isomerize (vide infra) or decompose after 24 h in refluxing DCE (bp 83 °C) under N_2. 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 $Fe(CO)_3(PPh_3)_2$ (**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 N_2) 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 ^{1}H NMR and IR spectra with those re-

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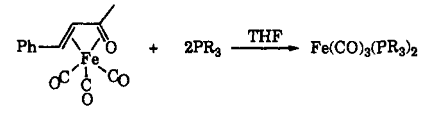


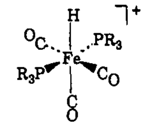
(8)

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)$_3$(PR$_3$)$_2$ 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 N_2 at 0 °C. Complex **10** is only moderately air-stable. However, solutions of **6–10** were handled under nitrogen or argon using Schlenk techniques.

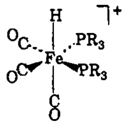
Protonation of Fe(CO)$_3$(PR$_3$)$_2$ Complexes. It has been shown previously by ^{1}H NMR and IR spectroscopy that **6** protonates at the metal center in concentrated H_2SO_4 solution.[27] With 1 equiv of CF_3SO_3H we observe quantitative protonation of **6** to give **6H$^+$**$CF_3SO_3^-$ (eq 4). Three ν(CO) infrared bands (2088 (w), 2039 (m, sh), 2026 (s) cm^{-1}) in CH_2Cl_2 solution are observed for **6H$^+$**$CF_3SO_3^-$ 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$^+$**$CF_3SO_3^-$ by adventitious water or even Cl$^-$ in the NaCl IR cells since titration calorimetry, vide infra, establishes that protonation of **6** with CF_3SO_3H is quantitative. The ^{1}H NMR spectrum of **6H$^+$**$CF_3SO_3^-$ in $CDCl_3$ 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 ^{1}H NMR spectroscopy with 1 equiv of CF_3SO_3H. The two ν(CO) bands of weak and strong intensity in **7H$^+$**$CF_3SO_3^-$–**10H$^+$**$CF_3SO_3^-$ are more than 100 cm^{-1} higher than those of their neutral precursors. The ^{1}H 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 PR$_3$ ligands are shifted downfield from those in the unprotonated complexes. The protonated complexes **6H$^+$**$CF_3SO_3^-$–**10H$^+$**$CF_3SO_3^-$ are stable in solution as long as they are kept under nitrogen or argon. Also, the solution (CH_2Cl_2) IR spectra of **6H$^+$**$CF_3SO_3^-$, **8H$^+$**$CF_3SO_3^-$, and **10H$^+$**$CF_3SO_3^-$ show no absorptions characteristic of coordinated $CF_3SO_3^-$.[36]

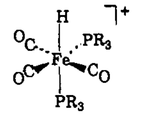
There are three possible isomers for **6H$^+$**–**10H$^+$** with structures **A**, **B**, and **C**.[37] The triplet Fe–H resonances and the equivalence of the PR$_3$ ligands in the ^{1}H NMR spectra of **6H$^+$**–**10H$^+$** eliminate structure **C** and rule out the possibility of having a mixture of isomers as it is unlikely that **A** and **B** would give the same ^{1}H NMR spectrum.



A



B

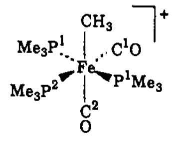


C

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_{2v} symmetry are expected to give three IR bands of weak, strong, and strong relative intensities corresponding to two A_1 and one B_1 vibrational modes, respectively.[38] For **6H$^+$**–**10H$^+$**, the weak band at high frequency corresponds to one A_1 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(CH$_3$)(CO)$_3$(PMe$_3$)$_2$]$^+$,[39] [Os(H)(CO)$_3$(PPh$_3$)$_2$]PF$_6$,[40a] Mn(H)(CO)$_3$(PPh$_3$)$_2$,[41] Mn(H)(CO)$_3$(PMePh$_2$)$_2$,[42] Re(H)(CO)$_3$(PPh$_3$)$_2$,[37] and Re(H)(CO)$_3$(PEt$_3$)$_2$.[37] The mer structures of Mn(H)(CO)$_3$(PPh$_3$)$_2$[41] and Mn(H)(CO)$_3$(PMePh$_2$)$_2$,[42] which are isoelectronic with **6H$^+$** and **8H$^+$**, respectively, and [Ru(H)(CO)$_3$(PPh$_3$)$_2$][CH(SO$_2$CF$_3$)$_2$][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]

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 ^{1}H 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)$_2$Me]$_2$[44] and *mer*-Mn(H)(CO)$_3$(PMePh$_2$)$_2$ also occur as doublets in spite of their having *trans*-PR$_3$ groups. Thus, in these cases the ^{1}H NMR spectra do not distinguish between the mer (**A**) and fac (**B**) structures.

The ^{13}C NMR for the CO ligands, however, are more conclusive in supporting the mer structure (**A**) for **6H$^+$**–**10H$^+$**. For **8H$^+$**, two 1:2:1 triplets[45] are observed at 204.71 ($^2J_{PC}$ = 23.65 Hz) and 203.56 ppm ($^2J_{PC}$ = 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 $^2J_{PC}$ values in **8H$^+$** with those in [Fe(CH$_3$)(CO)$_2$(PMe$_3$)$_3$]$^+$, **D**,[46] also supports structure **A** for these complexes. In **D**, the $^2J_{PC}$ values ($^2J_{P1C1}$ = 27.3 Hz, $^2J_{P2C2}$ = $^2J_{P1C2}$ = 18.4 Hz) for the cis CO and PMe$_3$ ligands are much smaller than those for trans CO and PMe$_3$ ligands ($^2J_{P2C1}$ = 41.3 Hz). The J_{PC} values in **8H$^+$** (23.65 and 13.35 Hz) indicate that there are only cis CO and PR$_3$ 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 PR$_3$ ligands as in structure **B**. Supporting the mer structure **A** for these cations is the ^{13}C NMR spectrum of **6H$^+$**$CF_3SO_3^-$ 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 ^{13}C NMR data strongly support structure **A** for the products of the protonation reactions (eq 4).



D

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)$_3$(PR$_3$)$_2$ **6–10** (eq 4) with 0.1 M CF_3SO_3H 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 $Fe(CO)_3(PMePh_2)_2$, **8**, for which the plots were slightly curved; the curvature was probably due to a small amount of decomposition of the reactant. However, the ΔH_{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 $Fe(CO)_3(PPh_3)_2$ (**6**) (−14.1 kcal mol^{-1}) and the more basic $Fe(CO)_3(PMe_2Ph)_2$ (**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$^+$**$CF_3SO_3^-$ appeared to be stable under the conditions of the titrations.

Discussion

In this section, we examine trends in the basicities of the $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes as a function of the PR_3 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)(PR$_3$) 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 $P(p\text{-}ClC_6H_4)_3$ (ΔH_{HP} = −17.9 kcal mol^{-1}, pK_a = 1.03) to the very basic PMe_3 (ΔH_{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 $CpIr(CO)[P(p\text{-}ClC_6H_4)_3]$ (**1**) to −33.2 kcal mol^{-1} for $CpIr(CO)(PMe_3)$ (**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

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

$$-\Delta H_{HM} = 0.540\text{p}K_a + 28.7, \text{ in kcal mol}^{-1} \quad (9b)$$

overall basicity of a complex is made up of a phosphine contribution (−0.298 ΔH_{HP}) and a metal fragment (CpIr(CO)) contribution (23.9).[48] The 0.298 coefficient for ΔH_{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 uncrowded reactants and products.

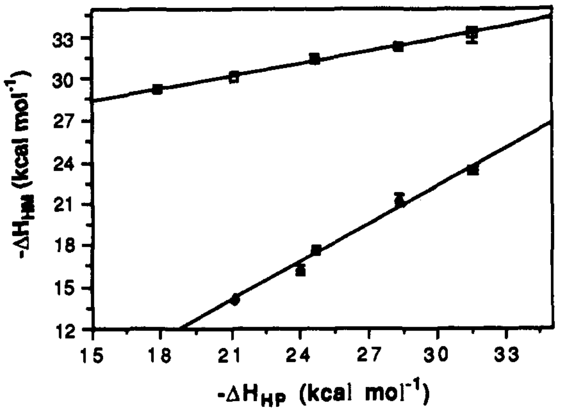

Figure 1. Correlations of metal basicity (ΔH_{HM}) with phosphine basicity (ΔH_{HP}) as determined by calorimetric titration with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. Upper line is for the $CpIr(CO)(PR_3)$ complexes. Lower line is for the $Fe(CO)_3(PR_3)_2$ complexes.

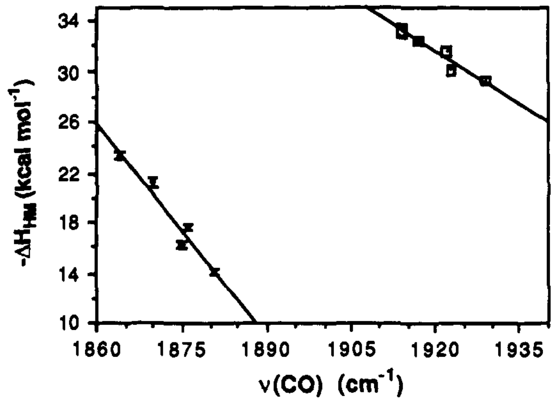

Figure 2. Correlation of metal basicity (ΔH_{HM}) with ν(CO) values (in CH_2Cl_2 solvent) of $CpIr(CO)(PR_3)$ complexes (upper line) and $Fe(CO)_3(PR_3)_2$ complexes (lower line).

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

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

(Figure 2) of the $CpIr(CO)(PR_3)$ 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 dπ → pπ^* 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 CH_2Cl_2 (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 $-\Delta H_{HM}$ 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.

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

Basicities of the Fe(CO)$_3$(PR$_3$)$_2$ 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 $CpIr(CO)(PR_3)$ 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 PR_3

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

$$-\Delta H_{HM} = 1.63\text{p}K_a + 9.68, \text{ in kcal mol}^{-1} \quad (12b)$$

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(47) Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Experiments in Thermometric and Titration Calorimetry*; Brigham Young University: Provo, UT, 1974.

(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 PR$_3$ is varied by 1.0 kcal mol^{-1}.

As for the CpIr(CO)(PR$_3$) system, the linear correlation between ΔH_{HM} and ΔH_{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 studies[50] 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).

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

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

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

Comparisons of the Basicities of the CpIr(CO)(PR$_3$) 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 PPh$_3$ complexes for comparison, CpIr(CO)(PPh$_3$) (**2**) ($\Delta H_{HM} = -30.1$ kcal mol^{-1}) is 16.0 kcal mol^{-1} more basic than Fe(CO)$_3$(PPh$_3$)$_2$ (**6**) ($\Delta H_{HM} = -14.1$ kcal mol^{-1}). Assuming $\Delta S° = 0$ eu, the estimated equilibrium constant ($\Delta G° = \Delta H_{HM} = -RT \ln K$) for the reaction (eq 15), is 5.4×10^{11}, which illustrates this very large difference in basicities. The free

$$\text{CpIr(CO)(PPh}_3) + \text{HFe(CO)}_3(\text{PPh}_3)_2^+ \xrightleftharpoons{K} \text{CpIr(H)(CO)(PPh}_3)^+ + \text{Fe(CO)}_3(\text{PPh}_3)_2 \quad (15)$$

phosphines, e.g., PPh$_3$ ($\Delta H_{HP} = -21.2$ 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)(PPh$_3$)$_2$]$^+$ cannot be deprotonated even with *n*-BuLi.[51]

In the correlations of ΔH_{HM} with ΔH_{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 ΔH_{HM} is indicated by the coefficients of the ΔH_{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 ΔH_{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 PR$_3$ 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)(PR$_3$) system is better able to dissipate additional PR$_3$ 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)$_3$(PR$_3$)$_2$ 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 ν(CO) values may be used to estimate ΔH_{HM} values of closely related compounds. However, it is also clear that ν(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 Kresge[10] measured equilibrium constants (K_{H^+}) for the oxidative addition (eq 16) of CF$_3$SO$_3$H to IrCl(CO)(PR$_3$)$_2$ in MeOH solvent at 25.0 °C. (Coordination of CF$_3$SO$_3^-$ or MeOH in the product was not

$$\text{IrCl(CO)(PR}_3)_2 + \text{CF}_3\text{SO}_3\text{H} \xrightleftharpoons{K_{H^+}} trans\text{-IrCl(CO)(PR}_3)_2(\text{H})(\text{O}_3\text{SCF}_3) \quad (16)$$

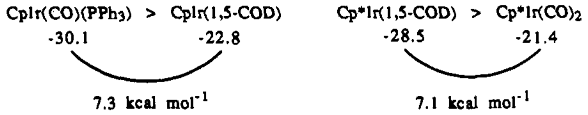
unequivocally established.) K_{H^+} values (in parentheses) increase with increasing basicity of the phosphine: PPh$_3$ (114 M^{-1}) < PMePh$_2$ (302 M^{-1}) < PMe$_2$Ph (631 M^{-1}). While the trend is the same as that for the ΔH_{HM} values in the CpIr(CO)(PR$_3$) and Fe(CO)$_3$(PR$_3$)$_2$ complexes, 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 coordination energy of the CF$_3$SO$_3^-$ (or MeOH) ligand.

Norton and co-workers[2b] measured the pK_a's of two Mn(H)(CO)$_4$(PR$_3$) complexes (pK_a = 20.4 for PR$_3$ = PPh$_3$ and pK_a = 21.6 for PR$_3$ = PEtPh$_2$) in acetonitrile solution at 25.0 °C. Converting these pK_a values to $\Delta G°$ ($\Delta G° = -RT \ln K_a$) for Mn(H)(CO)$_4$(PPh$_3$) (-27.8 kcal mol^{-1}) and Mn(H)(CO)$_4$(PEtPh$_2$) (-29.5 kcal mol^{-1}) and using ΔH_{HP} values of -21.2 kcal mol^{-1} for PPh$_3$[7] and -24.9 kcal mol^{-1} for PEtPh$_2$,[52] one obtains eq 17 which is analogous to 9a and 12a for the CpIr(CO)(PR$_3$)

$$-\Delta G° = -0.459\Delta H_{HP} + 18.06, \text{ in kcal mol}^{-1} \quad (17)$$

and Fe(CO)$_3$(PR$_3$)$_2$ systems. Although this equation is based on only two points, the ΔH_{HP} coefficient (0.459) indicates that a change in phosphine basicity in Mn(H)(CO)$_4$(PR$_3$) 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 PR$_3$. In order to establish the range and meaning of the ΔH_{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** ($\Delta H_{HM} = -30.1 \pm 0.2$ kcal mol^{-1}) and CpIr(1,5-COD) ($\Delta H_{HM} = -22.8 \pm 0.3$ kcal mol^{-1})[3] indicates the (CO)(PPh$_3$) 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)(PPh$_3$) ligand combination



(18)

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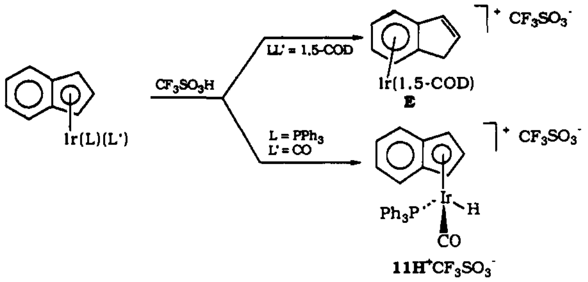
[50] (a) Inoue, H.; Kuroiwa, T.; Shirai, T.; Fluck, E. *Z. Naturforsch., B. Chem. Sci.* **1989**, *44*, 641–646. (b) Carroll, W. E.; Deeney, F. A.; Delaney, J. A.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1973**, 718–722.

[51] Habib, A.; Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 1225–1231.

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

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 PPh_3 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 CH_3CN by Norton and co-workers:[2b,d] $HCo(CO)_4$ (8.3) vs $HCo(CO)_3(PPh_3)$ (15.4), $HMn(CO)_5$ (15.1) vs $HMn(CO)_4(PPh_3)$ (20.4), and $CpW(CO)_3H$ (16.1) vs $CpW(CO)_2(PMe_3)(H)$ (26.6). It is evident, however, from these data that substitution of CO by PR_3 does not cause the same magnitude of increase in metal basicity in all metal complexes.

A variety of studies[53] indicate that CS is a more electron-withdrawing ligand than CO, as a result of its greater π-accepting ability. This is also evident in the ΔH_{HM} values of $CpIr(CS)(PPh_3)$ (**12**) (−26.51 kcal mol^{-1}) and $CpIr(CO)(PPh_3)$ (**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 CF_3SO_3H 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 $(CO)(PPh_3)$ 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 $\mathbf{11H^+}CF_3SO_3^-$ 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 ligand[54] and perhaps even as donating as Cp*.[55] However, this is not observed in the ΔH_{HM} value for $(indenyl)Ir(CO)(PPh_3)$ (**11**) (−29.8 ± 0.3 kcal mol^{-1}) which is the same within experimental error as that for the Cp analogue $CpIr(CO)(PPh_3)$ (**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 $[(indenyl)Ir(H)(PPh_3)_2]^+$ 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 ΔH_{HM} and phosphine basicity (ΔH_{HP} or pK_a) for the $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ series of complexes, respectively. For each 1.0 kcal mol^{-1} change in phosphine basicity (ΔH_{HP}), there is a greater change in $Fe(CO)_3(PR_3)_2$ basicity (0.916 kcal mol^{-1}) than in $CpIr(CO)(PR_3)$ basicity (0.298 kcal mol^{-1}). In general, the $CpIr(CO)(PR_3)$ complexes are much more basic than those in the $Fe(CO)_3(PR_3)_2$ series. The ΔH_{HM} values also correlate linearly with the respective $\nu(CO)$ frequencies of the $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes. These correlations permit the estimation of basicities (ΔH_{HM}) of other complexes in these series which contain different phosphines whose ΔH_{HP} (or pK_a) values or $\nu(CO)$ stretching frequencies are known.

Comparisons of ΔH_{HM} values for several CpIr(L)(L′) complexes demonstrate that the $(CO)(PPh_3)$ 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 $CpIr(CX)(PPh_3)$ 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 $CpIr(CO)(PPh_3)$ and $(indenyl)Ir(CO)(PPh_3)$ 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.

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