Effects of Cyclopentadienyl and Phosphine Ligands on the Basicities and Nucleophilicities of Cp′Ir(CO)(PR_3) Complexes†

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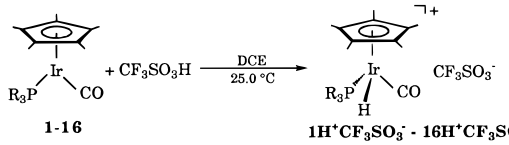
Basicities of the series of complexes CpIr(CO)(PR_3) [PR_3 = P(*p*-$C_6H_4CF_3$)$_3$, P(*p*-C_6H_4F)$_3$, P(*p*-C_6H_4Cl)$_3$, PPh_3, P(*p*-$C_6H_4CH_3$)$_3$, P(*p*-$C_6H_4OCH_3$)$_3$, PPh_2Me, $PPhMe_2$, PMe_3, PEt_3, PCy_3] have been measured by the heat evolved (ΔH_{HM}) when the complex is protonated by CF_3SO_3H in 1,2-dichloroethane (DCE) at 25.0 °C. The $-\Delta H_{HM}$ values range from 28.0 kcal/mol for CpIr(CO)[P(*p*-$C_6H_4CF_3$)$_3$] to 33.2 kcal/mol for CpIr(CO)(PMe_3) and are directly related to the basicities of the PR_3 ligands in the complexes. For the more basic pentamethylcyclopentadienyl analogs, the $-\Delta H_{HM}$ values range from 33.8 kcal/mol for the weakest base Cp*Ir(CO)[P(*p*-$C_6H_4CF_3$)$_3$] to 38.0 kcal/mol for the strongest Cp*Ir(CO)(PMe_3). The nucleophilicities of the Cp′Ir(CO)(PR_3) complexes were established from second-order rate constants (k) for their reactions with CH_3I to give [Cp′Ir(CO)(PR_3)(CH_3)]$^+I^-$ in CD_2Cl_2 at 25.0 °C. There is an excellent linear correlation between the basicities (ΔH_{HM}) and nucleophilicities (log k) of the CpIr(CO)(PR_3) complexes. Only the complex CpIr(CO)(PCy_3) with the bulky tricyclohexylphosphine ligand deviates dramatically from the trend. In general, the pentamethylcyclopentadienyl complexes react 40 times faster than the cyclopentadienyl analogs. However, they do not react as fast as predicted from electronic properties of the complexes, which suggests that the steric size of the Cp* ligand reduces the nucleophilicities of the Cp*Ir(CO)(PR_3) complexes. In addition, heats of protonation (ΔH_{HP}) of tris(2-methoxyphenyl)phosphine, tris(2,6-dimethoxyphenyl)phosphine, and tris(2,4,6-trimethylphenyl)phosphine were measured and used to estimate pK_a values for these highly basic phosphines.

Introduction

Basicities of transition-metal complexes[1−3] are of much interest because they are assumed to be indicators of other types of reactivity that depend upon electron richness at the metal center. As pK_a values of organic acids and bases are useful predictors of their reactivities, so too might one expect the basicities of metal complexes to be a guide to predicting their nucleophilicities[4] and tendencies to undergo oxidative addition as well as simple oxidation and reduction reactions. However, few quantitative data[1f] are available that correlate metal complex basicities with other reactivities of metal complexes.

In this paper, we report values for the basicities and nucleophilicities of a series of Cp′Ir(CO)(PR_3) complexes, where Cp′ = η^5-C_5H_5 or η^5-C_5Me_5, and seek correlations between these parameters. The basicities are defined as the enthalpies of protonation (ΔH_{HM}) of the metal complexes with triflic acid (CF_3SO_3H) in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1); these values are determined by (eq 1) calorimetry. The

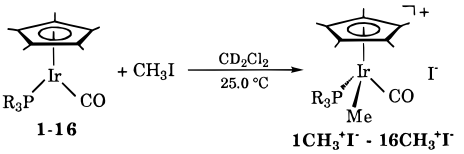


(1)

For Cp' = η^5-C_5H_5: PR_3 = P(*p*-$C_6H_4CF_3$)$_3$ (**1**), P(*p*-C_6H_4Cl)$_3$ (**2**), P(*p*-C_6H_4F)$_3$ (**3**), PPh_3 (**4**), P(*p*-C_6H_4Me)$_3$ (**5**), P(*p*-C_6H_4OMe)$_3$ (**6**), PPh_2Me (**7**), $PPhMe_2$ (**8**), PMe_3 (**9**), PEt_3 (**10**), PCy_3 (**11**)

For Cp' = η^5-C_5Me_5: PR_3 = P(*p*-$C_6H_4CF_3$)$_3$ (**12**), P(*p*-C_6H_4Cl)$_3$ (**13**), PPh_3 (**14**), PPh_2Me (**15**), PMe_3 (**16**)

nucleophilicities are defined by rate constants (k) for their reactions with CH_3I to form [Cp′(CO)(PR_3)Ir(CH_3)]$^+I^-$ in CD_2Cl_2 at 25.0 °C (eq 2). These studies provide a quantitative basis



(2)

for understanding how systematic changes in metal basicity affect rate constants for reactions in which the metal in the complex acts as the nucleophile. Moreover, the results allow a

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comparison of the electronic and steric effects of the η^5-C_5H_5 and η^5-C_5Me_5 ligands, which were so widely discussed recently.[5]

In this paper, we also examine the basicities (ΔH_{HP}) of tris(2-methoxyphenyl)phosphine [P(2-$C_6H_4OMe)_3$] (**17**), tris(2,6-dimethoxyphenyl)phosphine {P[2,6-$C_6H_3(OMe)_2]_3$} (**18**), tris-(2,4,6-trimethoxyphenyl)phosphine {P[2,4,6-$C_6H_2(OMe)_3]_3$} (**19**), and tris(2,4,6-trimethylphenyl)phosphine [P(2,4,6-$C_6H_2Me_3)_3$] (**20**) by measuring their heats of protonation (ΔH_{HP}) in DCE solvent (eq 3). The methoxy and methyl groups make these the most basic triarylphosphines known.[3]

$$PR_3 + CF_3SO_3H \xrightarrow[25\ ^\circ C]{DCE} HPR_3^+CF_3SO_3^-; \quad \Delta H_{HP} \qquad (3)$$

Experimental Section

General Procedures. All preparative reactions, chromatography, and manipulations were carried out under an atmosphere of nitrogen or argon with use of vacuum line, Schlenk, syringe, or drybox techniques similar to those described in the literature.[6] The solvents were purified under nitrogen as described below using standard methods.[7] Toluene, decane, hexanes, and methylene chloride were refluxed over CaH_2 and then distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. 1,2-Dichloroethane (DCE) was purified by washing with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and water again; the solvent was then predried over anhydrous $MgSO_4$, stored in amber bottles over molecular sieves (4 Å), and then distilled from P_4O_{10} under argon immediately before use. Triflic acid (CF_3SO_3H) was purchased from 3M Co. and purified by fractional distillation under argon before use. Methyl iodide was distilled over P_4O_{10} and stored away from sunlight in a brown bottle containing a small amount of powdered copper.[7] Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under vacuum (10^{-5} mmHg) for 12 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2.

The phosphines P(*p*-$C_6H_4Cl)_3$, P(*p*-$C_6H_4F)_3$, P(*p*-$C_6H_4CF_3)_3$, P(*p*-$C_6H_4Me)_3$, P(*p*-$C_6H_4OMe)_3$, and PCy_3 were purchased from Strem, while PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3, tris(2-methoxyphenyl)-phosphine, tris(2,6-dimethoxyphenyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, and tris(2,4,6-trimethylphenyl)phosphine were purchased from Aldrich. The ^{1}H NMR spectra were obtained on samples dissolved in $CDCl_3$ or CD_2Cl_2 on a Nicolet NT 300-MHz spectrometer using TMS ($\delta = 0.00$ ppm) as the internal reference. The $^{31}P\{^1H\}$ NMR spectra of samples in $CDCl_3$ in 10-mm tubes were recorded on a Varian VXR 300-MHz NMR spectrometer using 85% phosphoric acid ($\delta = 0.00$ ppm) as the external reference. Solution infrared spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1-mm spacers. Elemental microanalyses were performed by National Chemical Consulting, Inc., Tenafly, NJ.

Syntheses of CpIr(CO)(PR_3) Complexes. The starting material, *cis*-Ir$(CO)_2$(Cl)(*p*-$NH_2C_6H_4CH_3$), was prepared as a purple powder from $IrCl_3 \cdot xH_2O$ in 86% yield according to a known procedure.[8] Although complexes **7**− **9** were prepared previously by other methods,[9] complexes **1**−**10** were synthesized from reactions of *cis*-Ir$(CO)_2$(Cl)(*p*-$NH_2C_6H_4CH_3$) with the appropriate phosphine (eq 4), followed by reaction with potassium cyclopentadienide (KCp) *in situ* (eq 5). The

$$cis\text{-}IrCl(CO)_2(p\text{-}NH_2C_6H_4CH_3) + 2PR_3 \xrightarrow[\text{reflux}]{\text{toluene}} trans\text{-}IrCl(CO)(PR_3)_2 \qquad (4)$$

$$trans\text{-}IrCl(CO)(PR_3)_2 + KCp \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\mathbf{1-10}}{CpIr(CO)(PR_3)} \qquad (5)$$

purity and identity of each compound were estabished by comparison of their infrared and ^{1}H NMR spectra with those of other CpIr(CO)-(PR_3) complexes reported in the literature.[9]

CpIr(CO)(PPh_3) (4). This compound was prepared in 67% yield from the reaction of KCp[10] with $IrCl(CO)(PPh_3)_2$[11] according to the previously reported procedure;[12] it was also prepared in 62% yield by the method given in the next paragraph. ^{31}P NMR ($CDCl_3$): δ 16.66 ppm. ^{1}H NMR (CD_2Cl_2): δ 7.34−7.55 (m, 15 H, Ph), 5.11 (d, J_{PH} = 0.9 Hz, 5 H, Cp). IR (CH_2Cl_2): υ(CO) 1923 cm^{-1}.

CpIr(CO)[P(*p*-$C_6H_4Cl)_3$] (2). A solution of *cis*-Ir$(CO)_2$(Cl)(*p*-$NH_2C_6H_4CH_3$) (200 mg, 0.51 mmol) in toluene (25 mL) was treated with a slight excess of 2 equiv of tris(*p*-chlorophenyl)phosphine (400 mg, 1.1 mmol). The mixture was refluxed for about 1 h until the IR spectrum showed only the new band (υ(CO), toluene: 1965 cm^{-1}) for *trans*-IrCl(CO)[P(*p*-$C_6H_4Cl)_3]_2$ and no bands corresponding to the starting material (υ(CO), toluene: 2074 s, 1991 s cm^{-1}). The color of the reaction solution changed from the initial dark purple to yellow. After cooling to room temperature, it was filtered through a cannula into a flask containing white crystalline KCp;[10] the KCp was prepared by allowing 25 mg (0.60 mmol) of K to react with freshly cracked CpH (0.06 mL, 0.7 mmol) in THF (25 mL) under reflux for 2 h and removing the solvent under vacuum. The mixture containing *trans*-IrCl(CO)[P(*p*-$C_6H_4Cl)_3]_2$ and KCp in toluene was refluxed for about 3 h until the IR spectrum showed only the new band (υ(CO), toluene: 1938 cm^{-1}) for **2** and the complete disappearance of the 1965 cm^{-1} band for *trans*-IrCl(CO)[P(*p*-$C_6H_4Cl)_3]_2$. After cooling to room temperature, the solution was filtered and reduced to ∼5 mL under vacuum. The residue was passed through a short column (8 × 1.5 cm) of Florisil; eluting with toluene yielded the orange product band, which was collected. After the solvent was removed 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 containing the product was eluted with Et_2O/hexanes (1:10). During slow evaporation of the solvents under vacuum, a yellow precipitate began to form. Cooling to −20 °C yielded 210 mg of **2** (63% based on *cis*-Ir$(CO)_2$(Cl)(*p*-$NH_2C_6H_4CH_3$) as yellow crystals. ^{1}H NMR (CD_2Cl_2): δ 7.34−7.50 (m, 12 H, C_6H_4), 5.14 (d, J_{PH} = 0.9 Hz, 5 H, Cp). IR (CH_2Cl_2): υ(CO) 1930 cm^{-1}.

CpIr(CO)(PR_3) Compounds 1, 3, and 5−10. These compounds were synthesized in the two steps given in eqs 4 and 5 according to the procedure outlined for the preparation of **2** above. The amounts of reactants (mmol) and solvents were the same as for **2**. Below are given, in order, the times for reaction 4, υ(CO) values for the *trans*-IrCl(CO)(PR_3)$_2$ intermediates in toluene, times for reaction 5, yields, and spectral data for the isolated CpIr(CO)(PR_3) products.

CpIr(CO)[P(*p*-$C_6H_4CF_3)_3$] (1): 30 min, 1974 cm^{-1}, 3 h, 73%. ^{1}H NMR (CD_2Cl_2): δ 7.5−7.7 (m, 12 H, C_6H_4), 5.18 (d, J_{PH} = 0.9 Hz, 5 H, Cp). $^{31}P\{^1H\}$ ($CDCl_3$): δ 18.58 (s). IR (CH_2Cl_2): υ(CO) 1936 cm^{-1}.

CpIr(CO)[P(*p*-$C_6H_4F)_3$] (3): 3 h, 1967 cm^{-1}, 2 h, 52%. ^{1}H NMR (CD_2Cl_2): δ 7.2−7.5 (m, 12 H, C_6H_4), 5.14 (d, J_{PH} = 0.9 Hz, 5 H, Cp). $^{31}P\{^1H\}$ ($CDCl_3$): δ 14.01 (s). IR (CH_2Cl_2): υ(CO) 1928 cm^{-1}.

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CpIr(CO)[P(*p*-C$_6$H$_4$Me)$_3$] (5): 50 min, 1963 cm^{-1}, 1 h, 50%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.34−7.50 (m, 12 H, C$_6$H$_4$), 5.11 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.39 (s, 9 H, CH$_3$). ^{31}P{^{1}H} (CDCl$_3$): δ 13.67 (s). IR (CH$_2$Cl$_2$): υ(CO) 1921 cm^{-1}.

CpIr(CO)[P(*p*-C$_6$H$_4$OMe)$_3$] (6): 20 min, 1961 cm^{-1}, 1 h, 64%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.3−7.5 (m, 12 H, C$_6$H$_4$), 5.12 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 3.90 (s, 9 H, CH$_3$O). IR (CH$_2$Cl$_2$): υ(CO) 1919 cm^{-1}.

CpIr(CO)(PPh$_2$Me) (7): 20 min, 1958 cm^{-1}, 30 min, 46%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.4−7.7 (m, 10 H, C$_6$H$_5$), 5.13 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.30 (d, J_{PH} = 9.9 Hz, 3 H, Me). IR (CH$_2$Cl$_2$): υ(CO) 1922 cm^{-1}.

CpIr(CO)(PMe$_2$Ph) (8): 20 min, 1950 cm^{-1}, 30 min, 42%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.4−7.7 (m, 5 H, C$_6$H$_5$), 5.24 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.02 (d, J_{PH} = 10.2 Hz, 6 H, Me). IR (CH$_2$Cl$_2$): υ(CO) 1918 cm^{-1}.

CpIr(CO)(PMe$_3$) (9): 10 min, 1945 cm^{-1}, 30 min, 42%. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.30 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.77 (d, J_{PH} = 10.2 Hz, 9 H, Me). IR (CH$_2$Cl$_2$): υ(CO) 1916 cm^{-1}.

CpIr(CO)(PEt$_3$) (10): 30 min, 1940 cm^{-1}, 40 min, 40%. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.26 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.77 (m, 6 H, CH$_2$), 1.02 (m, 9 H, CH$_3$). ^{31}P{^{1}H} (CDCl$_3$): δ 6.63 (s). IR (CH$_2$Cl$_2$): υ(CO) 1912 cm^{-1}.

CpIr(CO)(PCy$_3$) (11). To a flask containing KCp (5 mmol) was added a dark purple solution of *cis*-Ir(CO)$_2$(Cl)(*p*-NH$_2$C$_6$H$_4$CH$_3$) (400 mg, 1.0 mmol) in toluene (25 mL). The mixture was refluxed 14 h until the IR spectrum showed two new bands (υ(CO), toluene: 2035 s, 1966 s cm^{-1}) for CpIr(CO)$_2$[13] and no bands corresponding to the starting material (υ(CO), toluene: 2074 s, 1991 s cm^{-1}). The color of the reaction solution changed from the initial dark purple to yellow. After cooling to room temperature, the yellow solution was filtered and reduced to 5 mL under vacuum. This concentrated solution was passed through a short column (8 × 1.5 cm) of neutral alumina packed in hexanes; eluting with hexanes yielded a yellow band, which was collected. After the solution volume was concentrated to 5 mL under vacuum, 15 mL of decane was added. To the yellow solution was added 850 mg of tricyclohexylphosphine (PCy$_3$) (1.5 mmol). The mixture was refluxed overnight until the IR spectrum showed a new band (υ(CO), decane: 1928 cm^{-1}) for **11** and the complete disappearance of CpIr(CO)$_2$. After cooling to room temperature, the solution was added to a neutral alumina column (15 × 1.5 cm). Eluting with hexanes (150 mL) removed decane and unreacted PCy$_3$. The yellow product band was eluted with Et$_2$O/hexanes (1:5). During slow evaporation of the solvents under vacuum, a yellow precipitate began to form. Cooling to −20 °C yielded 220 mg of **11** (40% based on *cis*-Ir(CO)$_2$(Cl)(*p*-NH$_2$C$_6$H$_4$CH$_3$) as yellow crystals. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.23 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.3−2.1 (m, 33 H, Cy). IR (CH$_2$Cl$_2$): υ(CO) 1909 cm^{-1}.

Synthesis of Cp*Ir(CO)(PR$_3$) Compounds 12−16. The starting material, [Cp*IrCl$_2$]$_2$ was prepared as an orange powder in 85% yield from the reaction of IrCl$_3$·*x*H$_2$O with Cp*H (Aldrich) in MeOH under reflux for 48 h according to a known procedure.[14,15] Cp*Ir(CO)$_2$ was synthesized as yellow crystals from Fe$_3$(CO)$_{12}$ (Aldrich) and [Cp*IrCl$_2$]$_2$ by refluxing in benzene for 24 h as previously reported.[9,15] Yield: 80%. ^{1}H NMR (CDCl$_3$): δ 2.18 (s, Cp*). IR (CH$_2$Cl$_2$): ν(CO) 2009 (s), 1938 (s) cm^{-1}. All of the Cp*Ir(CO)(PR$_3$) complexes were synthesized in reactions of Cp*Ir(CO)$_2$ with the appropriate phosphine in decane. The purity and identity of each compound were established by comparing its infrared and ^{1}H NMR spectra with the previously reported literature values for Cp*Ir(CO)(PEt$_3$)[16] and by selected elemental analyses. Below is given the general procedure for these preparations.

To a yellow solution of Cp*Ir(CO)$_2$ (200 mg, 0.50 mmol) in decane (10 mL) was added 1.5 equiv of PR$_3$ (0.75 mmol). The mixture was refluxed for 2−24 h until the IR spectrum showed only the new band for Cp*Ir(CO)(PR$_3$) and the complete disappearance of Cp*Ir(CO)$_2$ (υ-(CO), decane: 2058 s, 1918 s cm^{-1}). After the mixture cooled to room temperature, yellow to orange crystals began to precipitate. The crystals were filtered off and washed with hexanes (3 × 2 mL). The combined filtrates were chromatographed on a neutral alumina column (15 × 1.5 cm). Eluting with hexanes (150 mL) removed decane and free PR$_3$; a yellow band containing additional Cp*Ir(CO)(PR$_3$) was eluted with Et$_2$O/hexanes (1:5). During slow evaporation of the solvents under vacuum, a yellow precipitate began to form. Cooling to −20 °C yielded more crystals. The combined yellow product was obtained in 75−90% yield. Crystals of **13** and **14** were obtained by dissolving the compound in a minimum amount of CH$_2$Cl$_2$, layering the solution with a 5-fold volume of hexanes, and then cooling to −20 °C for 24 h.

Below are given reaction times, υ(CO) values of the products in decane, yields, and spectral data for all Cp*Ir(CO)(PR$_3$) complexes prepared by the above method.

Cp*Ir(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$] (12): 24 h, 1944 cm^{-1}, 75%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.6 (m, 12 H, C$_6$H$_4$), 1.82 (d, J_{PH} = 1.5 Hz, 15 H, Cp*). ^{31}P{^{1}H} (CDCl$_3$): δ 21.69 (s). IR (CH$_2$Cl$_2$): υ(CO) 1920 cm^{-1}.

Cp*Ir(CO)[P(*p*-C$_6$H$_4$Cl)$_3$] (13): 24 h, 1939 cm^{-1}, 83%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.4 (m, 12 H, C$_6$H$_4$), 1.82 (d, J_{PH} = 1.5 Hz, 15 H, Cp*). ^{31}P{^{1}H} (CDCl$_3$): δ 20.76 (s). IR (CH$_2$Cl$_2$): υ(CO) 1917 cm^{-1}. Anal. Calcd for C$_{29}$H$_{27}$IrOPCl$_3$: C, 48.30; H, 3.77. Found: C, 48.43; H, 3.84.

Cp*Ir(CO)(PPh$_3$) (14): 4 h, 1935 cm^{-1}, 90%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.4 (m, 15 H, C$_6$H$_5$), 1.81 (d, J_{PH} = 1.5 Hz, 15 H, Cp*). ^{31}P{^{1}H} (CDCl$_3$): δ 20.47 (s). IR (CH$_2$Cl$_2$): υ(CO) 1912 cm^{-1}. Anal. Calcd for C$_{29}$H$_{30}$IrOP: C, 56.38; H, 4.90. Found: C, 56.46; H, 4.90.

Cp*Ir(CO)(PPh$_2$Me) (15): 2 h, 1928 cm^{-1}, 78%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.6 (m, 10 H, C$_6$H$_5$), 1.82 (d, J_{PH} = 1.5 Hz, 15 H, Cp*). ^{31}P{^{1}H} (CDCl$_3$): δ 25.18 (s). IR (CH$_2$Cl$_2$): υ(CO) 1910 cm^{-1}.

Cp*Ir(CO)(PMe$_3$) (16): 2 h, 1928 cm^{-1}, 75%. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.08 (d, J_{PH} = 1.5 Hz, 15 H, Cp*), 1.58 (d, J_{PH} = 9.9 Hz, 9 H, Me). IR (CH$_2$Cl$_2$): υ(CO) 1909 cm^{-1}.

Protonation Reactions. Compounds **1**−**16** were protonated for NMR characterization of the [Cp′Ir(CO)(PR$_3$)(H)]CF$_3$SO$_3$ products by dissolving approximately 5 mg of the complex in 0.50 mL of CD$_2$Cl$_2$ in an NMR tube under nitrogen. To the solution was added 1 equiv of CF$_3$SO$_3$H with a gastight microliter syringe through a rubber septum. The color of the solution changed from yellow to colorless immediately upon mixing. Yields of the protonated products as determined by IR and ^{1}H NMR spectroscopy were quantitative. The [CpIr(CO)(PR$_3$)(H)]CF$_3$SO$_3$ compounds were characterized by their spectra as compared with those of **2H**$^+$, **4H**$^+$, and **7**−**9H**$^+$, which were previously reported.[9] **4H**$^+$ and **5H**$^+$ were isolated as white solids by evaporating their solutions and recrystallizing the residues from CH$_2$Cl$_2$/Et$_2$O at 25 °C.

Spectroscopic data for the [Cp*Ir(CO)(PR$_3$)(H)]CF$_3$SO$_3$ compounds are similar to those for [CpIr(CO)(PR$_3$)(H)]CF$_3$SO$_3$ except the ν(CO) values are lower than those in the Cp complexes, which is consistent with the stronger electron donating ability of Cp* compared with Cp.[5]

Compound **14H**$^+$**CF$_3$SO$_3$**$^-$ was isolated as a white solid precipitate when **14** (50 mg) was protonated with CF$_3$SO$_3$H (1 equiv) in Et$_2$O (5 mL) solution. Crystals of **14H**$^+$**CF$_3$SO$_3$**$^-$ were obtained by dissolving the white solid in a minimum amount of CH$_2$Cl$_2$, layering the solution with a 3-fold volume of diethyl ether, and then cooling to −20 °C for 24 h.

Spectroscopic data at room temperature for compounds **1H**$^+$−**16H**$^+$ are listed below.

{CpIr(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$](H)}CF$_3$SO$_3$ (1H$^+$CF$_3$SO$_3$$^-$). ^{1}H NMR (CD$_2Cl_2$): δ 7.3−7.6 (m, 12 H, C$_6H_4$), 5.94 (d, J_{PH} = 0.9 Hz, 5 H, Cp), −14.26 (d, J_{PH} = 25.2 Hz, 1 H, Ir−H). ^{31}P{^{1}H} (CDCl$_3$): δ 5.11 (s). IR (CH$_2$Cl$_2$): υ(CO) 2067 cm^{-1}.

{CpIr(CO)[P(*p*-C$_6$H$_4$Cl)$_3$](H)}CF$_3$SO$_3$ (2H$^+$CF$_3$SO$_3$$^-$). ^{1}H NMR (CD$_2Cl_2$): δ 7.3−7.6 (m, 12 H, C$_6H_4$), 5.94 (d, J_{PH} = 0.9 Hz, 5 H, Cp), −14.45 (d, J_{PH} = 24.4 Hz, 1 H, Ir−H). IR (CH$_2$Cl$_2$): υ(CO) 2063 cm^{-1}.

{CpIr(CO)[P(*p*-C$_6$H$_4$F)$_3$](H)}CF$_3$SO$_3$ (3H$^+$CF$_3$SO$_3$$^-$). ^{1}H NMR (CD$_2Cl_2$): δ 7.3−7.6 (m, 12 H, C$_6H_4$), 5.86 (d, J_{PH} = 0.9 Hz, 5 H, Cp), −14.41 (d, J_{PH} = 24.6 Hz, 1 H, Ir−H). ^{31}P{^{1}H} (CDCl$_3$): δ 0.99 (s). IR (CH$_2$Cl$_2$): υ(CO) 2068 cm^{-1}.

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[CpIr(CO)(PPh$_3$)(H)]CF$_3$SO$_3$ (4H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.5−7.8 (m, 15 H, C_6H_5), 5.88 (d, J_{PH} = 0.9 Hz, 5 H, Cp), −14.44 (d, J_{PH} = 24.1 Hz, 1 H, Ir−H); ^{31}P{^{1}H} ($CDCl_3$): δ 3.65 (s). IR (CH_2Cl_2): ν(CO) 2063 cm^{-1}.

{**CpIr(CO)[P(*p*-C$_6$H$_4$Me)$_3$](H)}CF$_3$SO$_3$ (5H$^+$CF$_3$SO$_3^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.3−7.6 (m, 12 H, C_6H_4), 5.79 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.45 (s, 3 H, Me), −14.46 (d, J_{PH} = 23.7 Hz, 1 H, Ir−H). ^{31}P{^{1}H} ($CDCl_3$): δ 1.29 (s). IR (CH_2Cl_2): ν(CO) 2060 cm^{-1}.

{**CpIr(CO)[P(*p*-C$_6$H$_4$OMe)$_3$](H)}CF$_3$SO$_3$ (6H$^+$CF$_3$SO$_3^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.3−7.6 (m, 12 H, C_6H_4), 5.78 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 3.91 (s, 9 H, MeO), −14.52 (d, J_{PH} = 24.0 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2058 cm^{-1}.

[CpIr(CO)(PPh$_2$Me)(H)]CF$_3$SO$_3$ (7H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3−7.6 (m, 10 H, C_6H_5), 5.90 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.70 (d, J_{PH} = 12.0 Hz, 3 H, Me), -14.66 (d, J_{PH} = 23.2 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2061 cm^{-1}.

[CpIr(CO)(PPhMe$_2$)(H)]CF$_3$SO$_3$ (8H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3−7.6 (m, 5 H, C_6H_5), 5.89 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.36 (d, J_{PH} = 11.4 Hz, 3 H, Me), 2.39 (d, J_{PH} = 11.4 Hz, 3 H, Me), −15.03 (d, J_{PH} = 25.1 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2057 cm^{-1}.

[CpIr(CO)(PMe$_3$)(H)]CF$_3$SO$_3$ (9H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 5.90 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.12 (d, J_{PH} = 12.0 Hz, 9 H, Me), −15.32 (d, J_{PH} = 25.3 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2052 cm^{-1}.

[CpIr(CO)(PEt$_3$)(H)]CF$_3$SO$_3$ (10H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 5.89 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.77 (m, 6 H, CH_2), 1.01 (m, 9 H, Me), −14.66 (d, J_{PH} = 23.2 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2061 cm^{-1}.

[CpIr(CO)(PCy$_3$)(H)]CF$_3$SO$_3$ (11H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 5.91 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.3−2.1 (m, 33 H, Cy), −14.64 (d, J_{PH} = 23.2 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2059 cm^{-1}.

{**Cp*Ir(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$](H)}CF$_3$SO$_3$ (12H$^+$CF$_3$SO$_3^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.6−7.8 (m, 12 H, C_6H_4), 1.99 (s, 15 H, Cp*), −14.05 (d, J_{PH} = 27.6 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2051 cm^{-1}.

{**Cp*Ir(CO)[P(*p*-C$_6$H$_4$Cl)$_3$](H)}CF$_3$SO$_3$ (13H$^+$CF$_3$SO$_3^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.4−7.6 (m, 12 H, C_6H_4), 1.96 (s, 15 H, Cp*), −14.28 (d, J_{PH} = 27.6 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2045 cm^{-1}.

{**Cp*Ir(CO)[P(C$_6$H$_5$)$_3$](H)}CF$_3$SO$_3$ (14H$^+$CF$_3$SO$_3^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.3−7.5 (m, 15 H, C_6H_5), 1.93 (s, 15 H, Cp*), −14.28 (d, J_{PH} = 26.1 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2042 cm^{-1}. Anal. Calcd for $C_{30}H_{31}IrF_3O_4PS$: C, 46.93; H, 4.07. Found: C, 46.91; H, 4.09.

[Cp*Ir(CO)(PPh$_2$Me)(H)]CF$_3$SO$_3$ (15H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3−7.6 (m, 10 H, C_6H_5), 2.00 (s, 15 H, Cp*), 2.50 (d, J_{PH} = 12.0 Hz, 3 H, Me), −14.66 (d, J_{PH} = 27.2 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2040 cm^{-1}.

[Cp*Ir(CO)(PMe$_3$)(H)]CF$_3$SO$_3$ (16H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 2.09 (s, 15 H, Cp*), 1.91 (d, J_{PH} = 12.0 Hz, 9 H, Me), −15.30 (d, J_{PH} = 29.1 Hz, 1 H, Ir−H). IR (CH_2Cl_2): ν(CO) 2038 cm^{-1}.

Reactions of 1−16 with CH$_3$I. Compounds **1**−**16** were reacted (eq 2) with CH_3I for ^{1}H NMR characterization of the [Cp′Ir(CO)(PR_3)(CH_3)]I products by dissolving approximately 5 mg of the complex in 0.50 mL of CD_2Cl_2 in an NMR tube under nitrogen. To the solution was added 10 equiv of CH_3I with a gastight microliter syringe through a rubber septum. The color of the solution changed from yellow to colorless during the time of the study (2 s−4 h). Both NMR and IR spectra showed quantitatively the disappearance of the starting material and the appearance of new bands for [Cp′Ir(CO)(PR_3)(CH_3)]I. **4CH$_3^+$I$^-$** and **9CH$_3^+$I$^-$** were isolated as white solids by evaporating their solutions and recrystallizing them from CH_2Cl_2/Et_2O at 25 °C. Compound **14CH$_3^+$I$^-$** was isolated as a white solid by the reaction of **14** (50 mg) with CH_3I (10 equiv) in Et_2O (5 mL) solution. Crystals of **14CH$_3^+$I$^-$** were formed by dissolving the white solid in a minimum amount of CH_2Cl_2, layering the solution with a 3-fold volume of diethyl ether, and then cooling to −20 °C for 24 h.

Spectroscopic data for **1CH$_3^+$I$^-$**−**11CH$_3^+$I$^-$** are very similar to those previously reported[12] for **4CH$_3^+$I$^-$**. ^{1}H NMR and IR data for the [Cp*Ir(CO)(PR_3)(CH_3)]I complexes are similar to those for [CpIr(CO)(PR_3)(CH_3)]I except the ν(CO) values are lower for the Cp* compounds, which indicates that Cp* is a stronger donor than Cp. Below are listed spectral data for all of the [Cp′Ir(CO)(PR_3)(CH_3)]I complexes.

{**CpIr(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$](CH$_3$)}I (1CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.6−7.8 (m, 12 H, C_6H_4), 6.09 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.18 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2054 cm^{-1}.

{**CpIr(CO)[P(*p*-C$_6$H$_4$Cl)$_3$](CH$_3$)}I (2CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.4−7.7 (m, 12 H, C_6H_4), 5.97 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.13 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2051 cm^{-1}.

{**CpIr(CO)[P(*p*-C$_6$H$_4$F)$_3$](CH$_3$)}I (3CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.4−7.7 (m, 12 H, C_6H_4), 5.99 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.15 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2046 cm^{-1}.

[CpIr(CO)(PPh$_3$)(CH$_3$)]I (4CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 7.4−7.7 (m, 15 H, C_6H_5), 5.87 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.15 (d, J_{PH} = 5.1 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2049 cm^{-1}.

{**CpIr(CO)[P(*p*-C$_6$H$_4$Me)$_3$](CH$_3$)}I (5CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.4−7.7 (m, 12 H, C_6H_4), 5.87 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.46 (s, 9 H, Me), 1.13 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2046 cm^{-1}.

{**CpIr(CO)[P(*p*-C$_6$H$_4$OMe)$_3$](CH$_3$)}I (6CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.3−7.6 (m, 12 H, C_6H_4), 5.87 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 3.90 (s, 9 H, MeO), 1.14 (d, J_{PH} = 5.1 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2045 cm^{-1}.

[CpIr(CO)(PPh$_2$Me)(CH$_3$)]I (7CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 7.4−7.7 (m, 10 H, C_6H_5), 5.92 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.57 (d, J_{PH} = 10.5 Hz, 3 H, Me), 1.07 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2047 cm^{-1}.

[CpIr(CO)(PPhMe$_2$)(CH$_3$)]I (8CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 7.4−7.7 (m, 5 H, C_6H_5), 5.95 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.42 (d, J_{PH} = 11.4 Hz, 3 H, Me), 2.32 (d, J_{PH} = 11.4 Hz, 3 H, Me), 1.06 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2045 cm^{-1}.

[CpIr(CO)(PMe$_3$)(CH$_3$)]I (9CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 6.06 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.07 (d, J_{PH} = 11.7 Hz, 9 H, Me), 1.05 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2041 cm^{-1}.

[CpIr(CO)(PEt$_3$)(CH$_3$)]I (10CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 6.06 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.77 (m, 6 H, CH_2), 1.05 (m, 9 H, Me), 1.14 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2041 cm^{-1}.

[CpIr(CO)(PCy$_3$)(CH$_3$)]I (11CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 6.06 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.3−2.1 (m, 33 H, Cy), 1.14 (d, J_{PH} = 3.0 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2037 cm^{-1}.

{**Cp*Ir(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$](CH$_3$)}I (12CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.6−7.8 (m, 12 H, C_6H_4), 1.84 (d, J_{PH} = 2.4 Hz, 15 H, Cp*), 0.75 (d, J_{PH} = 5.7 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2032 cm^{-1}.

{**Cp*Ir(CO)[P(*p*-C$_6$H$_4$Cl)$_3$](CH$_3$)}I (13CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.4−7.7 (m, 12 H, C_6H_4), 1.81 (d, J_{PH} = 2.4 Hz, 15 H, Cp*), 0.70 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2032 cm^{-1}.

{**Cp*Ir(CO)[P(C$_6$H$_5$)$_3$](CH$_3$)}I (14CH$_3^+$I$^-$).** ^{1}H NMR (CD_2Cl_2): δ 7.3−7.5 (m, 15 H, C_6H_5), 1.77 (d, J_{PH} = 2.4 Hz, 15 H, Cp*), 0.73 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2030 cm^{-1}. Anal. Calcd for $C_{30}H_{33}IrOPI$: C, 47.43; H, 4.38. Found: C, 47.37; H, 4.44.

[Cp*Ir(CO)(PPh$_2$Me)(CH$_3$)]I (15CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3−7.5 (m, 10 H, C_6H_5), 2.37 (d, J_{PH} = 10.5 Hz, 3 H, Me), 1.85 (d, J_{PH} = 2.1 Hz, 15 H, Cp*), 0.68 (d, J_{PH} = 5.4 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2030 cm^{-1}.

[Cp*Ir(CO)(PMe$_3$)(CH$_3$)]I (16CH$_3^+$I$^-$). ^{1}H NMR (CD_2Cl_2): δ 2.05 (d, J_{PH} = 2.1 Hz, 15 H, Cp*), 1.82 (d, J_{PH} = 10.8 Hz, 9 H, Me), 0.61 (d, J_{PH} = 6.0 Hz, 3 H, Ir−CH_3). IR (CH_2Cl_2): ν(CO) 2030 cm^{-1}.

Protonation of Phosphines. Phosphines **17**−**20** were protonated for NMR characterization by dissolving approximately 5 mg of the phosphine in 0.50 mL of $CDCl_3$ in an NMR tube under nitrogen. To the solution was added 1 equiv of CF_3SO_3H with a gastight microliter syringe through a rubber septum. Both ^{1}H and ^{31}P NMR spectra showed the disappearance of the starting material and the appearance of new bands for the [HPR_3]CF_3SO_3. The ^{1}H NMR data for **19** are the same as those reported previously.[17] Yields of the protonated products as determined by ^{1}H NMR spectroscopy are quantitative. Spectroscopic data at room temperature for **17**−**19** and **17H$^+$**−**19H$^+$** are listed below.

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P(2-$C_6H_4OMe)_3$ (17). ^{1}H NMR ($CDCl_3$): δ 7.32 (m, 3 H), 6.85 (m, 6 H), 6.65 (m, 3 H), 3.74 (s, 9 H).

P[2,6-$C_6H_3(OMe)_2]_3$ (18). ^{1}H NMR ($CDCl_3$): δ 7.12 (td, 8.1 Hz, 0.6 Hz, 3 H), 6.45 (dd, 8.4 Hz, 3.0 Hz, 6 H), 3.47 (s, 18 H). ^{31}P NMR ($CDCl_3$): δ 10.17 (s).

P[2,4,6-$C_6H_2(OMe)_3]_3$ (19). ^{1}H NMR ($CDCl_3$): δ 6.03 (d, 2.4 Hz, 6 H), 3.78 (s, 9 H), 3.49 (s, 18 H). ^{31}P NMR ($CDCl_3$): δ 8.99 (s).

[HP(2-$C_6H_4OMe)_3$]CF_3SO_3 (17H$^+$$CF_3SO_3^-$). ^{1}H NMR ($CDCl_3$): δ 8.65 (d, J_{PH} = 530 Hz, 1 H), 7.64 (m, 3 H), 7.05 (m, 9 H), 3.82 (s, 9 H).

{**HP[2,6-$C_6H_3(OMe)_2]_3$**}**CF_3SO_3 (18H$^+$$CF_3SO_3^-$).** ^{1}H NMR ($CDCl_3$): δ 8.50 (d, J_{PH} = 533 Hz, 1 H), 7.59 (t, 8.4 Hz, 3 H), 6.64 (dd, 8.4 Hz, 5.7 Hz, 6 H), 3.68 (s, 18 H). ^{31}P NMR ($CDCl_3$): δ −50.17 (s).

{**HP[2,4,6-$C_6H_2(OMe)_3]_3$**}**CF_3SO_3 (19H$^+$$CF_3SO_3^-$).** ^{1}H NMR ($CDCl_3$): δ 8.35 (d, J_{PH} = 541 Hz, 1 H), 6.17 (b s, 6 H), 3.88 (s, 9 H), 3.69 (s, 18 H). ^{31}P NMR ($CDCl_3$): δ −52.23 (s).

It has been reported[17] that **19** (pK_a = 11.2, cone angle = 184°) reacts with CH_2Cl_2 to form $ClCH_2PR_3^+Cl^-$ in $t_{1/2}$ < 15 min, with (*i*-Pr)Br in 1 h, and with (*i*-Pr)Cl in 15 h. We found that **19** reacts with DCE solvent within 50 min at room temperature; reaction of **18** with DCE cannot be detected for 20 h; **17** and **20** are stable in DCE. The NMR results are given below.

Product of the Reaction of 18 with DCE. ^{1}H NMR ($CDCl_3$): δ 7.59 (t, 8.4 Hz, 3 H), 6.67 (dd, 8.4 Hz, 5.4 Hz, 6 H), 3.74 (b s, 4 H), 3.65 (s, 18 H). ^{31}P NMR ($CDCl_3$): δ 2.32 (s).

Product of the Reaction of 19 with DCE. ^{1}H NMR ($CDCl_3$): δ 6.16 (d, J_{PH} = 4.8 Hz, 6 H), 3.92 (s, 9 H), 3.74 (b s, 4 H), 3.66 (s, 18 H). ^{31}P NMR ($CDCl_3$): δ 8.98 (s).

Calorimetric Studies of Reaction 1. Determinations of the heats of protonation (ΔH_{HM}) of the Cp′Ir(CO)(PR_3) complexes with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C were performed using a Tronac Model 458 isoperibol calorimeter as originally described[18] and then modified.[10] A 5-mL aliquot of a freshly prepared solution of the complex (weighed in a N_2-filled glovebox for the air-sensitive Cp*Ir(CO)(PR_3) complexes) in DCE (approximately 0.020 M) was injected into the reaction Dewar vessel via syringe, followed by 45 mL of DCE. Typically a calorimetric run consisted of three sections:[19] initial heat capacity calibration, titration, and final heat capacity calibration. Each section was preceded by a baseline acquisition period. A 3- or 2-min titration period was used for the compounds in this study. During the titration period, approximately 1.2 or 0.8 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE solvent was added at a constant rate (0.3962 mL/min) to 50.0 mL of a 2.6 or 1.7 mM solution of the complex (5−10% excess) in DCE at 25.0 °C. Infrared spectra of the titrated solutions showed ν(CO) bands for the Cp′Ir(CO)(PR_3)H$^+$ products and weak bands for the excess Cp′Ir(CO)(PR_3) reactants.

The ΔH_{HM} values for each complex were measured using two different standardized acid solutions and are reported as the average of at least four titrations and as many as six. The heat of dilution (ΔH_{dil}) of the acid in DCE (−0.2 kcal/mol)[10] was used to correct the reaction enthalpies. The error in ΔH_{HM} is reported as the average deviation from the mean of all the determinations. The accuracy of the calorimeter was monitored before each set of ΔH_{HM} determinations by titrating 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (−37.0 ± 0.3 kcal/mol; lit.[18] −37.2 ± 0.4 kcal/mol).

Determinations of the heats of protonation (ΔH_{HP}) of the phosphines **17**, **18**, and **20** with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C were performed in the same manner as described above. A 3-min titration period was used for these studies. The phosphine solutions were prepared by adding the solid compound to the argon-filled Dewar flask. The flask was then attached to the calorimeter's insert assembly and flushed with argon; then 50 mL of DCE was added by syringe.

Kinetic Studies of CpIr(CO)(PR_3) in Reaction 2. In a typical experiment, 2−10 mg of CpIr(CO)(PR_3) and 10 mg (0.0410 mmol) of the internal standard Ph_3CH (recrystallized from ethanol[7]) were introduced into a 5-mm NMR tube. To the tube was added a 0.50 mL solution of CH_3I in CD_2Cl_2 with a gastight syringe. The ^{1}H NMR spectra of samples thermostated at 298 K were taken on the VXR 300 NMR spectrometer using the methine proton of Ph_3CH (5.56 ppm) as the internal reference. A 15-s pulse delay ensured complete relaxation of all the protons. Integrals of peaks at δ ∼6.0 (Cp, product), 5.56 (Ph_3CH), ∼5.2 (Cp, reactant), 2.15 (free CH_3I), and ∼1.14 (Ir−CH_3, product) were obtained from each of the 15−21 spectra per sample recorded over a period of 3 half-lives. The sum of the integrals of all reactants and products was constant throughout each kinetic run. The initial concentrations $[Ir]_0$ were calculated using eq 6, and the initial concentrations $[CH_3I]_0$ were calculated using eq 7, where $I_{Cp}{}^p$ = integral

$$[Ir]_0 = \frac{(I_{Cp}{}^p + I_{Cp}{}^r)[Ph_3CH]}{5I_S} \quad (6)$$

$$[MeI]_0 = \frac{(I_{MeI} + I_{Ir-Me})[Ph_3CH]}{3I_S} \quad (7)$$

of product Cp signal, $I_{Cp}{}^r$ = integral of reactant Cp signal, $[Ph_3CH]$ = concentration of internal standard Ph_3CH, M, I_S = integral of the methine proton of Ph_3CH , I_{MeI} = integral of reactant MeI signal, and I_{Ir-Me} = integral of product Ir−CH_3 signal. The $[Ir]_0$ and $[CH_3I]_0$ concentrations in Table 1 are averages of the concentrations obtained from 15−21 spectra taken during the kinetic runs.

The expressions (eqs 8 and 9) used for calculating the pseudo-first-order rate constant k_{obs} and the second-order rate constant k were derived as described in the Supporting Information. When the ratio $[CH_3I]_0/[Ir]_0 = a$ was greater than 10, eq 8 was used to evaluate k_{obs}:

$$\ln\left(1 + \frac{I_{Cp}{}^p}{I_{Cp}{}^r}\right) = k_{obs}t \quad (8)$$

The slope of a plot of $\ln(1 + I_{Cp}{}^p/I_{Cp}{}^r)$ vs time is k_{obs}; and $k = k_{obs}/[MeI]_0$. When a was less than 10, eq 9 was used to calculate k:

$$\ln\left[a + (a-1)\frac{I_{Cp}{}^p}{I_{Cp}{}^r}\right] = \ln a + (a-1)[Ir]_0kt \quad (9)$$

The second-order rate constant k is calculated from the slope of a plot of $\ln[a + (a-1)I_{Cp}{}^p/I_{Cp}{}^r]$ vs time, where the slope is $\{(a-1)[Ir]_0k\}$.

Kinetic Studies of Cp*Ir(CO)(PR_3) (PR_3 = P(*p*-$C_6H_4CF_3)_3$, P(*p*-$C_6H_4Cl)_3$) in Reaction 2. The same procedure and amounts of reactants were used as described above for the CpIr(CO)(PR_3) reactions. Integrals of peaks at δ ∼1.9 (Cp*, product), 5.56 (Ph_3CH), ∼1.8 (Cp*, reactant), 2.15 (free CH_3I), and ∼0.7 (Ir−CH_3, product) were obtained from each of the 15−18 spectra recorded over a period of 3 half-lives. The sum of the integrals of all reactants and products was constant throughout each kinetic run. The initial concentrations $[Ir]_0$ were calculated by eq 10, while the initial concentrations $[CH_3I]_0$ were calculated by eq 7

$$[Ir]_0 = \frac{(I_{Cp^*}{}^p + I_{Cp^*}{}^r)[Ph_3CH]}{15I_S} \quad (10)$$

using integrations of proton NMR resonances of each species, where $I_{Cp^*}{}^p$ = integral of product Cp* signal, $I_{Cp^*}{}^r$ = integral of reactant Cp* signal, and the other terms are the same as in eqs 6 and 7. The $[Ir]_0$ and $[CH_3I]_0$ concentrations in Table 2 are averages of the concentrations obtained from 15−18 spectra. Second-order rate constants k were calculated from eq 9, except that I_{Cp^*} values were used instead of I_{Cp}. The reproducibility of rate constants is ±10% or better.

Kinetic Studies of the Reactions (Eq 2) of Cp*Ir(CO)(PR_3) (PR_3 = PPh_3, PPh_2Me, PMe_3) with CH_3I. Since the rates of reaction of these three compounds were too fast to be measured by ^{1}H NMR spectroscopy, we used the following technique. All the kinetic experiments were carried out at 25.0 ± 0.2 °C in CH_2Cl_2 solvent under argon using a Shimadzu UV-3101PC spectrophotometer equipped with

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Table 1. Rates of $CpIr(CO)(PR_3)-CH_3I$ Reactions in CD_2Cl_2 at 25.0 °C (Eq 2)

PR_3	$10^3[Ir]_0$,[a] M	$10^3[CH_3I]_0$,[b] M	a[c]	10^4k_{obs},[d] s^{-1}	10^2k,[e] $M^{-1}\,s^{-1}$
$P(p\text{-}C_6H_4CF_3)_3$	67	350	5.2		0.15
	21	320	15	4.3	0.13
	6.9	110	16	1.6	0.15
	6.9	160	23	2.4	0.15
$P(p\text{-}C_6H_4Cl)_3$	2.4	58	25	3.7	0.62
	2.6	67	25	4.2	0.63
	2.8	120	40	7.6	0.61
	2.5	180	60	11	0.61
$P(p\text{-}C_6H_4F)_3$	4.2	74	18	8.0	1.10
	2.6	51	20	6.2	1.22
	1.6	65	40	8.1	1.24
	0.54	52	100	7.3	1.35
PPh_3	4.1	36	8.7		2.7
	3.1	37	12	12	3.3
	2.3	39	15	11	2.8
	2.7	53	20	15	2.9
	3.3	104	30	30	2.9
$P(p\text{-}C_6H_4Me)_3$	31	50	1.6		6.9
	5.2	54	10	36	6.7
	1.2	29	25	20	6.9
	2.0	54	27	38	6.9
	2.2	66	30	45	6.8
	2.4	91	38	62	6.8
$P(p\text{-}C_6H_4OMe)_3$	4.9	43	8.8		7.3
	6.3	56	8.9		6.7
	8.7	82	9.4		6.9
	4.4	72	16	50	7.0
PPh_2Me	8.4	7.0	0.8		11
	8.0	8.8	1.1		9.7
	4.2	22	5.1		10
	2.5	38	15	38	10
	2.5	41	17	29	9.4
	3.3	57	18	53	9.4
PMe_2Ph	5.8	4.7	0.8		24
	7.6	6.7	0.9		21
	9.6	8.6	0.9		18
	9.2	8.3	0.9		20
	11	9.7	0.9		18
	5.4	9.5	1.8		21
PMe_3	7.4	8.0	1.1		46
	6.9	7.9	1.2		43
	5.7	7.9	1.4		43
	3.6	12.8	3.5		42
PEt_3	8.3	41	4.9		15
	4.9	54	11	67	12
	3.5	39	11	78	20
	3.9	48	12	118	25
PCy_3	30	83	2.8		0.82
	7.4	25	3.4		0.86
	12	114	9.6	8.0	0.78
	9.8	150	15	12	0.78

[a] Average concentrations using eq 6. [b] Average concentrations using eq 7. [c] Ratio of $[MeI]_0/[Ir]_0$. [d] Calculated using eq 8. [e] Calculated from k_{obs} or using eq 9.

an internal timer and a thermostated cell holder. The rates of reaction were monitored directly by following the disappearance of the band at 312 nm for the $Cp^*Ir(CO)(PR_3)$ complexes. Since the ratio $[CH_3I]_0/[Ir]_0$ was greater than 10, the absorbance (A)−time data were fitted to the pseudo-first-order equation (11) by use of the program Spectracalc

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t) \qquad (11)$$

or GraFit in order to obtain k_{obs} values.[20] The k values were calculated from the expression $k = k_{obs}/[MeI]_0$.

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Table 2. Rates of $Cp^*Ir(CO)(PR_3)-CH_3I$ Reactions at 25.0 °C (Eq 2)

PR_3	$10^3[Ir]_0$,[a] M	$10^3[CH_3I]_0$,[b] M	a[c]	10^3k_{obs},[d] s^{-1}	k,[e] $M^{-1}\,s^{-1}$
$P(p\text{-}C_6H_4CF_3)_3$[f]	24.1	37.7	1.56		0.048
	17.5	28.9	1.65		0.051
	11.2	27.5	2.46		0.047
	7.2	35.0	4.88		0.046
$P(p\text{-}C_6H_4Cl)_3$[f]	33.5	23.4	0.70		0.120
	15.9	22.2	1.39		0.123
	14.7	23.0	1.57		0.112
	23.7	47.0	1.98		0.123
PPh_3[g]	0.10	1.07	11	1.62	1.51
	0.10	1.60	16	2.19	1.37
	0.10	2.14	21	3.39	1.58
	0.13	2.67	21	3.98	1.49
	0.13	3.73	29	5.70	1.53
	0.13	4.80	37	6.76	1.41
	0.13	5.87	45	8.63	1.47
PPh_2Me[g]	0.10	2.12	21	8.24	3.89
	0.10	3.20	32	10.6	3.33
	0.10	4.27	43	13.6	3.19
	0.10	5.33	53	17.6	3.30
	0.10	6.40	64	20.8	3.25
	0.10	7.47	75	24.6	3.29
PMe_3[g]	0.10	1.06	11	2.83	26.7
	0.10	1.60	16	4.30	26.8
	0.10	2.12	21	5.32	25.1
	0.10	2.67	27	6.60	24.7
	0.10	3.20	32	8.20	25.6
	0.10	3.73	37	9.00	24.1

[a] Average concentrations using eq 10. [b] Average concentrations using eq 7. [c] Ratio of $[MeI]_0/[Ir]_0$. [d] Calculated using eq 11. [e] Calculated from k_{obs} or using eq 9. [f] Reaction rate monitored by ^1H NMR in CD_2Cl_2. [g] Reaction rate monitored by UV−vis spectroscopy at 312 nm in CH_2Cl_2.

Results

Syntheses of Iridium Complexes 1−11. In spite of known syntheses for $CpM(CO)(PR_3)$ (M = Co, Rh) complexes[21] and $(C_5H_4R)Ir(CO)(PPh_3)$ (R = $COCH_3$, CH_3, $C(O)C_6H_5$, CHO),[22] only the preparations of complexes **2, 4,** and **7−9** have been reported previously using different synthetic routes often in relatively low yields.[9,12] We developed a general method (eqs 4 and 5) to synthesize all of the $CpIr(CO)(PR_3)$ complexes, except **11**, from KCp and *trans*-$IrCl(CO)(PR_3)_2$. The reported synthetic procedure for the preparation of "Vaska's complex"[23] *trans*-$IrCl(CO)(PPh_3)_2$ involves refluxing $IrCl_3$ and PPh_3 in *N*,*N*-dimethylformamide.[11] The preparation of other *trans*-$IrCl(CO)(PR_3)_2$ complexes where PR_3 is a phosphine other than PPh_3, however, cannot be accomplished by this method. Although other methods[24,25] have been reported in the literature, most of them require many steps and give low overall yields, as for *trans*-$IrCl(CO)(PEt_3)_2$.[24a] We developed a simple, reliable method (eq 4) for the preparation of the *trans*-$IrCl(CO)(PR_3)_2$ complexes which are used *in situ* to make the final products **1−10** (eq 5). While this work was in progress, Rahim and

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(25) The use of *cis*-$IrCl(CO)_2(p\text{-}NH_2C_6H_4CH_3)$ in synthesizing *trans*-$IrCl(CO)(PR_3)_2$ complexes, where R = C_6H_{11} and OPh, was reported by: Hieber, W.; Frey, V. *Chem. Ber.* **1966**, *99*, 2607.

Ahmed[26] reported the synthesis of some of the *trans*-$IrCl(CO)(PR_3)_2$ complexes by essentially the same method. The starting complex *cis*-$IrCl(CO)_2(p\text{-}NH_2C_6H_4CH_3)$[25] is available from $IrCl_3 \cdot xH_2O$ in high yield in a "one-pot" reaction,[8] and the *trans*-$IrCl(CO)(PR_3)_2$ complexes are produced in high yield. The subsequent reaction (eq 5) of *trans*-$IrCl(CO)(PR_3)_2$ with KCp gave the $CpIr(CO)(PR_3)$ complexes in overall isolated yields of 40−73%. When the phosphine is tricyclohexylphosphine, *trans*-$IrCl(CO)(PCy_3)_2$ does not react with KCp in refluxing toluene to give **11**, presumably because of the bulky PCy_3 ligands. However, complex **11** was synthesized (eqs 12 and 13) in 40% yield by reacting PCy_3 with $CpIr(CO)_2$, which was prepared *in situ* from the reaction of *cis*-$IrCl(CO)_2(p\text{-}NH_2C_6H_4CH_3)$ with KCp.

$$cis\text{-}IrCl(CO)_2(p\text{-}NH_2C_6H_4CH_3) + KCp \xrightarrow[\text{reflux}]{\text{toluene}} CpIr(CO)_2 \quad (12)$$

$$CpIr(CO)_2 + PCy_3 \xrightarrow[\text{reflux}]{\text{decane}} \underset{\mathbf{11}}{CpIr(CO)(PCy_3)} \quad (13)$$

Complexes **1**−**11** have the half-sandwich geometry shown in eq 1 as confirmed for **4** by an X-ray crystallographic determination.[27] Only compounds **9**−**11** are air-sensitive in the solid state. As a precaution, all compounds were stored under N_2, and solutions were prepared using dry deaerated solvents.

Syntheses of Iridium Complexes 12−16. The complexes $Cp^*Ir(CO)(PR_3)$ (PR_3 = PEt_3, $P(OMe)_3$, $P(O\text{-}i\text{-}Pr)_3$) were previously prepared by refluxing $Cp^*Ir(CO)_2$ with the phosphine or phosphite in toluene.[16] However, of the phosphines used in the present study, only PMe_3 gave the product (**16**) under these conditions. For all of the other phosphines, it was necessary to use the higher boiling solvent decane (bp 174 °C) (eq 14).

$$Cp^*Ir(CO)_2 + PR_3 \xrightarrow[\text{reflux}]{\text{decane}} Cp^*Ir(CO)(PR_3) \quad (14)$$

PR_3 in product: $P(p\text{-}C_6H_4CF_3)_3$, **12**, 75%; $P(p\text{-}C_6H_4Cl)_3$, **13**, 83%; PPh_3, **14**, 90%; PPh_2Me, **15**, 78%; PMe_3, **16**, 75%

Complexes **12**−**16** have the half-sandwich geometry shown in eq 1. This was confirmed for **13** by an X-ray crystallographic determination;[28] its structure is similar to that of $CpIr(CO)(PPh_3)$.[27] All of compounds **12**−**16** are air-sensitive in the solid state, so they were stored under N_2 and solutions were prepared using dry deaerated solvents.

Characterization of Products in Reactions 1 and 2. Quantitative formation of the three-legged piano-stool complexes $\mathbf{1H^+CF_3SO_3^-}$−$\mathbf{16H^+CF_3SO_3^-}$ occurs upon addition of 1 equiv of CF_3SO_3H to the neutral complexes **1**−**16** (eq 1), as evidenced by ^1H NMR and IR spectroscopy. The Ir−H resonances in the ^1H NMR spectra occur as doublets between −14.05 and −15.32 ppm with $^2J_{PH}$ = 24−29 Hz due to coupling with the phosphine phosphorus atom. Protonation causes the Cp proton resonances to shift ∼0.8 ppm downfield; the ν(CO) bands move ∼140 cm^{-1} to higher frequency. The IR and ^1H NMR spectra of these complexes are very similar to those of $\mathbf{2H^+}$, $\mathbf{4H^+}$, and $\mathbf{7}$−$\mathbf{9H^+}$, which have been previously reported.[9] The protonated complexes are air-sensitive in solution. Complexes $\mathbf{4H^+CF_3SO_3^-}$, $\mathbf{5H^+CF_3SO_3^-}$, and $\mathbf{14H^+CF_3SO_3^-}$ were isolated as white solids from reactions of **4**, **5**, and **14** with CF_3SO_3H in Et_2O.

As established previously[12] for the reaction of $CpIr(CO)(PPh_3)$, all of the $Cp'Ir(CO)(PR_3)$ complexes (**1**−**16**) in this study react (eq 2) with CH_3I in CD_2Cl_2 to give the methyl complexes $\mathbf{1CH_3^+}$−$\mathbf{16CH_3^+}$ quantitatively, as observed by ^1H NMR spectroscopy. The Ir−CH_3 ^1H NMR resonances for these compounds occur as doublets between 1.18 and 0.61 ppm with $^2J_{PH}$ = 3−6 Hz due to coupling with the phosphine phosphorus atom. The Cp proton signals are ∼0.8 ppm downfield of those in the starting complexes (**1**−**11**). The ν(CO) bands move ∼130 cm^{-1} to higher frequency upon methylation of the Ir, as expected for the formation of a cationic complex. The somewhat higher (∼10 cm^{-1}) ν(CO) values for $Cp'Ir(CO)(PR_3)(H)^+$ than $Cp'Ir(CO)(PR_3)(CH_3)^+$ indicate that the H^+ ligand is more electron-withdrawing than CH_3^+. The IR and ^1H NMR spectra of these complexes are similar to those of $\mathbf{4CH_3^+}$, which was characterized previously.[12] Complexes $\mathbf{4CH_3^+}$, $\mathbf{9CH_3^+}$, $\mathbf{13CH_3^+}$, and $\mathbf{14CH_3^+}$ were isolated as white solids.

Calorimetric Studies. The heats of protonation (ΔH_{HM}) determined by calorimetric titration of the $Cp'Ir(CO)(PR_3)$ complexes with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) at 25.0 °C according to eq 1 are presented in Tables 3 and 4. Table 3 includes data for compounds **2**, **4**, and **7**−**9**, which were reported earlier.[9] Plots of temperature vs amount of acid added were linear, indicating that the protonations occur rapidly and stoichiometrically.[19] Except for compounds **15** and **16**, there was no decomposition of either the neutral or protonated species during the titration as evidenced by the normal pre- and

Table 3. Heats of Protonation and Rate Constants for $CpIr(CO)(PR_3)$ Complexes

PR_3	cone angle θ,[a] deg	$-\Delta H_{HM}$,[c,d] kcal/mol	$-\Delta H_{HP}$,[b] kcal/mol	10^2k,[e] $M^{-1}\ s^{-1}$
$P(p\text{-}C_6H_4CF_3)_3$ (**1**)	145	28.0(2)	13.6(2)	0.15(1)
$P(p\text{-}C_6H_4Cl)_3$ (**2**)	145	29.2(2)[f]	17.9(2)	0.62(1)
$P(p\text{-}C_6H_4F)_3$ (**3**)	145	29.8(2)	19.6(2)	1.23(7)
PPh_3 (**4**)	145	30.0(1)[h]	21.2(1)	2.9(2)
$P(p\text{-}C_6H_4CH_3)_3$ (**5**)	145	31.1(3)	23.2(3)	6.8(1)
$P(p\text{-}C_6H_4OCH_3)_3$ (**6**)	145	31.2(2)	24.1(2)	7.0(2)
PPh_2Me (**7**)	136	31.5(1)[f]	24.7(2)	10.0(4)
$PPhMe_2$ (**8**)	122	32.5(2)[f]	28.4(2)	20(2)
PMe_3 (**9**)	118	33.2(3)[f]	31.6(2)	44(2)
PEt_3 (**10**)	132[g]	32.9(2)	33.7(3)	18(4)
PCy_3 (**11**)	170	32.7(2)	33.2(4)	0.81(3)

[a] Reference 30a. [b] Reference 3, eq 3. [c] For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C, eq 1. [d] Numbers in parentheses are average deviations from the mean of at least four titrations. [e] Average of values in Table 1; numbers in parentheses are average deviations from the mean. [f] From ref 9. [g] Other values in the literature are 137[30b] and 166.[30g,h] [h] 30.1 ± 0.2 kcal/mol in ref 9.

Table 4. Heats of Protonation of $Cp^*Ir(CO)(PR_3)$ Complexes (ΔH_{HM}) and Phosphines (ΔH_{HP})

compound	$-\Delta H_{HM}$,[a,b] kcal/mol	$-\Delta H_{HP}$,[a,b] kcal/mol
$Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$, **12**	33.8(2)	13.6(2)[c]
$Cp^*Ir(CO)[P(p\text{-}C_6H_4Cl)_3]$, **13**	36.9(2)	17.9(2)[c]
$Cp^*Ir(CO)(PPh_3)$, **14**	37.1(2)	21.2(1)[c]
$Cp^*Ir(CO)(PPh_2Me)$, **15**	37.1(3)	24.7(0)[c]
$Cp^*Ir(CO)(PMe_3)$, **16**	38.0(2)	31.6(2)[c]
$P(2\text{-}C_6H_4OMe)_3$, **17**		25.5(2)
$P[2,6\text{-}C_6H_3(OMe)_2]_3$, **18**		33.8(2)
$P(2,4,6\text{-}C_6H_2Me_3)_3$, **20**		29.4(2)

[a] For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b] Numbers in parentheses are average deviations. [c] ΔH_{HP} for eq 3 of free PR_3; see ref 18.

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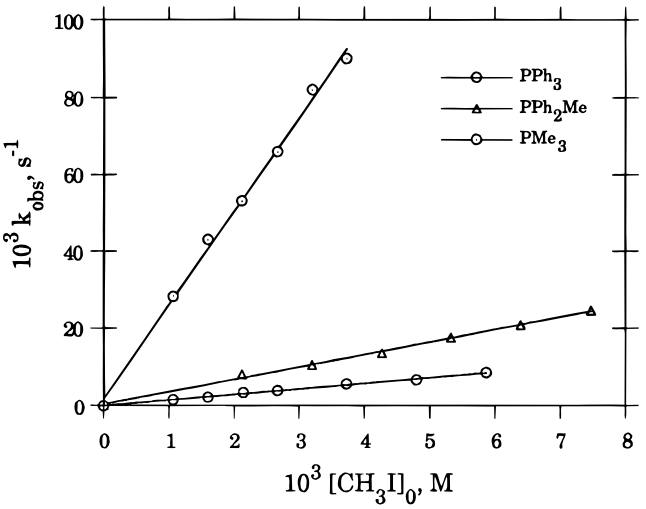

Figure 1. Plots of k_{obs} vs $[CH_3I]_0$ for reactions of $Cp^*Ir(CO)(PR_3)$ with CH_3I at 25 °C in CD_2Cl_2 (eq 2).

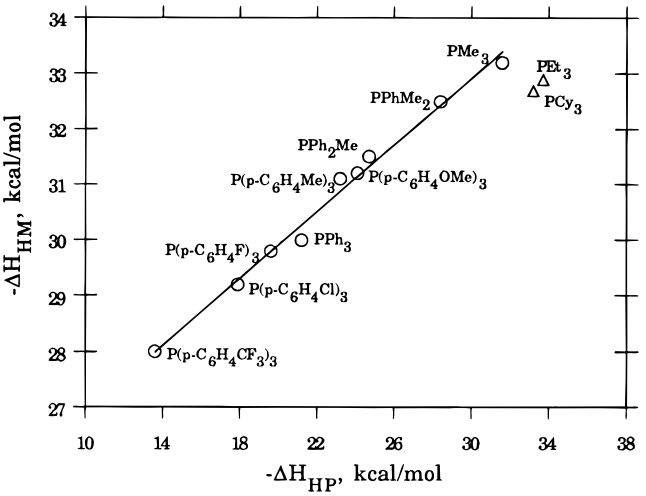

Figure 2. Correlation (eq 15) of metal basicity ($-\Delta H_{HM}$, eq 1) for $CpIr(CO)(PR_3)$ with phosphine basicity ($-\Delta H_{HP}$, eq 3).

post-titration curves. For **15** and **16**, the increase in baseline slope was only ~5% of the titration slope, indicating that the heat contributed by decomposition is small and the effect on the ΔH_{HM} values is probably within the experimental error. Infrared spectra of the titrated solutions showed ν(CO) bands characteristic of the protonated products $\mathbf{1H^+}-\mathbf{16H^+}$. The ΔH_{HM} value for **4** (30.0 ± 0.1 kcal/mol) agrees well with the literature value of (30.1 ± 0.2).[9]

The heats of protonation (ΔH_{HP}) of the phosphines **17**, **18**, and **20** according to eq 3 are also presented in Table 4. The titration of phosphine **19** was unsuccessful due to its reaction with the DCE solvent, as was evident from the release of heat before the acid titration began. The product of this reaction was probably $\{(ClCH_2CH_2)P[2,4,6\text{-}C_6H_2(OMe)_3]_3\}^+Cl^-$.

Kinetic Studies. Rate studies showed that the reactions (eq 2) of complexes **1**−**16** with CH_3I obeyed the following rate law: rate = $k[Cp'Ir(CO)(PR_3)][CH_3I]$. For reactions in which a 10-fold excess of CH_3I was used, plots (Figure 1) of pseudo-first-order rate constants k_{obs} vs $[CH_3I]_0$ gave straight lines with near-zero intercepts. The observed rate constants (k_{obs}) and the second-order rate constants ($k = k_{obs}/[MeI]_0$) are listed in Tables 1 and 2; average k values are collected in Tables 3 and 5. For reactions which are not run under pseudo-first order conditions, only the k values are obtained (eq 9) and listed in Tables 1 and 2. The values of k (Tables 1 and 2) in the four to six runs for each complex are within 10% of the average value listed in Tables 3 and 5. The rates of the reactions were not noticeably affected by wrapping the flasks in aluminum foil. The k for **4** ((2.9 ± 0.2) × 10^{-2} M^{-1} s^{-1}) agrees well with the literature value ((2.5 ± 0.2) × 10^{-2} M^{-1} s^{-1}), which was determined in CH_2Cl_2 at 25 °C by monitoring the disappearance of the ν(CO) band of the starting material.[12]

Discussion

Basicities of $CpIr(CO)(PR_3)$ Complexes 1−11. As has been noted in previous studies of basicities (ΔH_{HM} or pK_a)[1,3] of transition metal complexes, increasing the basicities of the ligands bound to a metal increases the basicity of the metal. In the $CpIr(CO)(PR_3)$ series of complexes, we use ΔH_{HP} for the protonation of the free phosphine (eq 3) as the measure of the phosphine basicity. Earlier[9] we reported a correlation ($-\Delta H_{HM} = 23.9 - 0.298\Delta H_{HP}$) between the basicities of the phosphine ligands and the basicities of five $CpIr(CO)(PR_3)$ complexes (**2**, **4**, **7**−**9**). In this study, we add four additional compounds to the correlation (Figure 2). For all nine compounds (**1**−**9**), the correlation (eq 15) is the same within experimental error as that obtained previously.

$$-\Delta H_{HM} = (23.9 \pm 0.2) + (0.30 \pm 0.01)(-\Delta H_{HP}), \quad r = 0.996 \quad (15)$$

The basicities of the phosphines extend over a wide range from the weakly basic $P(p\text{-}C_6H_4CF_3)_3$ ($-\Delta H_{HP}$ = 13.6 kcal/mol) to the very basic PEt_3 ($-\Delta H_{HP}$ = 33.7 kcal/mol).[3] However, the $-\Delta H_{HM}$ values only range from 28.0 kcal/mol for $CpIr(CO)[P(p\text{-}C_6H_4CF_3)_3]$ (**1**) to 33.2 kcal/mol for $CpIr(CO)(PMe_3)$ (**9**). The relatively small change in metal basicity with a much larger change in phosphine basicity is reflected in the 0.30 coefficient for the $-\Delta H_{HP}$ term in eq 15; this coefficient shows that a 1.0 kcal/mol change in phosphine basicity results in only a 0.30 kcal/mol change in metal basicity. Possible reasons for this insensitivity of metal basicity to phosphine ligand basicity were discussed earlier.[29]

Two compounds, $CpIr(CO)(PEt_3)$ (**10**) and $CpIr(CO)(PCy_3)$ (**11**), were not included in the correlation (eq 15) because they appear to deviate significantly from it (Figure 2). Both of these complexes are less basic by about 1.1−1.2 kcal/mol than expected on the basis of their PR_3 basicity. The bulky PCy_3 ligand (cone angle 170°)[30] might especially be expected to reduce the basicity of $CpIr(CO)(PCy_3)$ due to steric crowding in the more highly coordinated $CpIr(CO)(PCy_3)(H)^+$ product (eq 1), which would make protonation less favorable. The PEt_3 ligand in **10** is not as large as PCy_3 in **11**, yet the cone angle for PEt_3 is variously reported to be 132,[30a] 137,[30b] and 166°.[30g,h] The smaller-than-expected $-\Delta H_{HM}$ value for **10** suggests that PEt_3 does induce a steric effect which is consistent with the largest cone angle (166°).[30g,h]

Basicities of $Cp^*Ir(CO)(PR_3)$ Complexes 12−16. In the $Cp^*Ir(CO)(PR_3)$ series of complexes, the basicities ($-\Delta H_{HM}$, eq 1) of the complexes generally increase with the basicities of the phosphine ligands (Table 4): $P(p\text{-}C_6H_4CF_3)_3$ (33.8 kcal/mol) < $P(p\text{-}C_6H_4Cl)_3$ (36.9) < PPh_3, PPh_2Me (37.1) < PMe_3 (38.0). However, unlike the case of the $CpIr(CO)(PR_3)$

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Table 5. Comparison of ΔH_{HM}[a] and k[b] Values for Cp*Ir(CO)(PR_3) and CpIr(CO)(PR_3) Complexes

	Cp*[c]		Cp[d]		ΔH(Cp*) − ΔH(Cp):[c,d]
PR_3	$-\Delta H_{HM}$	k	$-\Delta H_{HM}$	10^2k	$\Delta\Delta H_{HM}$
P(*p*-$C_6H_4CF_3$)$_3$	33.8	0.048	28.0	0.15	5.8
P(*p*-C_6H_4Cl)$_3$	36.9	0.120	29.2	0.62	7.7
PPh_3	37.1	1.44	30.0	2.9	7.1
PPh_2Me	37.1	3.11	31.5	10	5.6
PMe_3	38.0	23.4	33.2	44	4.8

[a] $-\Delta H_{HM}$ in kcal/mol. [b] k in M^{-1} s^{-1}. [c] For Cp*Ir(CO)(PR_3). [d] For CpIr(CO)(PR_3).

complexes, there is a poor correlation between ΔH_{HM} and ΔH_{HP} resulting from the very similar ΔH_{HM} values for the complexes (**13**−**15**) with the P(*p*-C_6H_4Cl)$_3$ (36.9 kcal/mol), PPh_3 (37.1 kcal/mol), and PPh_2Me (37.1 kcal/mol) ligands, respectively. The ΔH_{HM} values for these compounds have been measured many times with up to four different acid concentrations, each standardized independently. In all cases, the ΔH_{HM} values are reproducible within our normal error limits (±0.2 or 0.3). We do not understand why the ΔH_{HM} values do not correlate with ΔH_{HP}, especially because excellent correlations are observed for CpIr(CO)(PR_3) and for other series of phosphine complexes $Fe(CO)_3(PR_3)_2$,[9] $W(CO)_3(PR_3)_3$,[31] and $CpOs(PR_3)_2Br$.[29]

The availability of $-\Delta H_{HM}$ for Cp*Ir(CO)(PPh_3) (37.1 kcal/mol) allows one to determine the effect on Ir basicity of replacing a CO ligand in $Cp^*Ir(CO)_2$ (21.4 kcal/mol)[9] by PPh_3. The large increase in $-\Delta H_{HM}$ by 15.7 kcal/mol indicates that the equilibrium constant for protonation of Cp*Ir(CO)(PPh_3) is 3.5×10^{11} larger than that for $Cp^*Ir(CO)_2$; this estimate [$\Delta\Delta H_{HM} = \Delta\Delta G = -RT \ln(K_2/K_1)$] assumes that ΔS is the same for the protonation of both complexes.[3] The $\Delta\Delta H_{HM}$ difference (15.7 kcal/mol) confirms an earlier indirect estimate (14.4 kcal/mol) for the difference in basicities between Cp′Ir(CO)(PPh_3) and Cp′Ir(CO)$_2$ complexes.[9] The effect of replacing a CO ligand by a phosphine on metal basicity has also been observed in pK_a values for the following pairs of compounds determined in MeCN: $HCo(CO)_4$ (8.4) vs $HCo(CO)_3(PPh_3)$ (15.4),[32b] $HMn(CO)_5$ (14.2) vs $HMn(CO)_4(PPh_3)$ (20.4),[32a] $CpW(CO)_3H$ (16.1)[32c] vs $CpW(CO)_2(PMe_3)H$ (26.6),[32b] $CpCr(CO)_3H$ (13.3)[32c] vs $CpCr(CO)_2(PPh_3)H$ (21.8),[2d] and $CpW(CO)_3H^{\bullet+}$ (−3.3) vs $CpW(CO)_2(PMe_3)H^{\bullet+}$ (5.1).[34] 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.

Effects of Cp* and Cp on Metal Basicity (ΔH_{HM}) in Cp′Ir(CO)(PR_3). In order to understand the effects of Cp* and Cp on the basicities of the CpIr(CO)(PR_3) complexes, we examined differences ($\Delta\Delta H_{HM}$ in Table 5) between ΔH_{HM} values for Cp*Ir(CO)(PR_3) and the CpIr(CO)(PR_3) analogs. The values of $\Delta\Delta H_{HM}$ range from 4.8 to 7.7 kcal/mol following no obvious trend. The average value (6.2 kcal/mol) is similar to that (5.7 kcal/mol) for the Cp′Ir(COD) compounds,[10] where Cp′ is Cp* or Cp. Other $\Delta\Delta H_{HM}$ values for Cp* vs Cp complexes are $Cp'Ru(PMe_3)_2Cl$ (9.0 kcal/mol)[29] and $Cp'Ru(PPh_3)_2H$ (5.5 kcal/mol).[29] This effect of the Cp′ ligand on metal basicity has also been found in pK_a values for the following pairs of compounds determined in MeCN: $Cp^*Mo(CO)_3H$ (17.1)[32b] vs $CpMo(CO)_3H$ (13.9),[32c] $Cp^*Fe(CO)_2H$ (26.3) vs $CpFe(CO)_2H$ (19.4),[32b] $Cp^*Cr(CO)_3H$ (16.1)[2e] vs $CpCr(CO)_3H$ (13.3),[32c] and $Cp^*Mo(CO)_3H^{\bullet+}$ (−2.5) vs $CpMo(CO)_3H^{\bullet+}$ (−6.0).[34] Thus, the basicity enhancement caused by the replacement of Cp by Cp* depends on the metal and the ligands in the complex.

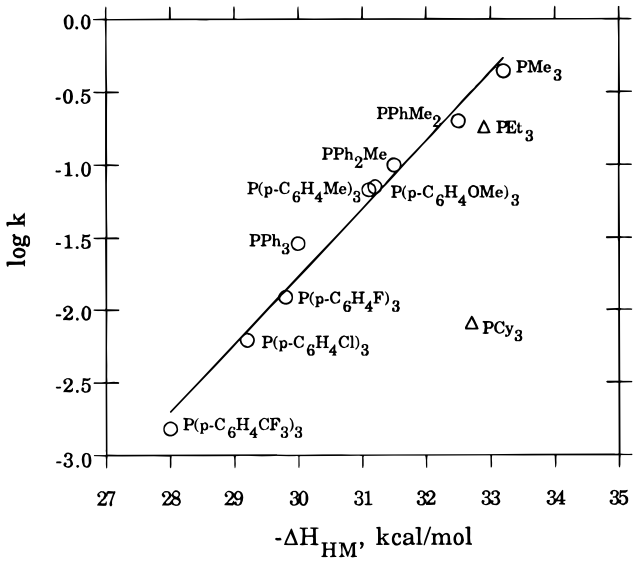

Figure 3. Correlation (eq 16) of rate constants (log k for eq 2) with metal basicity ($-\Delta H_{HM}$ for eq 1) for CpIr(CO)(PR_3) at 25.0 °C.

Rates of Reaction of CpIr(CO)(PR_3) with MeI (Eq 2). All of the compounds **1**−**16** react (eq 2) with CH_3I by a second-order rate law: rate = k[Cp′Ir(CO)(PR_3)][CH_3I]. The same rate law was observed[12] in a more limited study of the reaction of CpIr(CO)(PPh_3) with CH_3I. This rate law suggests that the mechanism of reaction is one that involves nucleophilic attack of the iridium in the complex on the carbon of CH_3I, which results in displacement of I^- and formation of the [Cp′Ir(CO)(PR_3)(CH_3)]$^+I^-$ product. Since the nucleophilicity of the Ir is expected to depend on the electron richness of the metal and the basicity (ΔH_{HM}, eq 1) of the metal also reflects electron richness at the metal center, one might expect a correlation between the rate constant (k) for the reaction in eq 2 and the basicity (ΔH_{HM}, eq 1). Indeed, for CpIr(CO)(PR_3) complexes **1**−**9**, there is an excellent correlation between log k and $-\Delta H_{HM}$ (Figure 3 and eq 16). Changing the basicity ($-\Delta H_{HM}$) of CpIr(CO)(PR_3) from 28.0 kcal/mol for **1** (PR_3 = P(*p*-$C_6H_4CF_3$)$_3$) to 33.2 kcal/mol for **9** ($PR_3 = PMe_3$) increases the rate of reaction 2 by approximately 300-fold.

$$\log k = (-15.8 \pm 0.8) + (0.47 \pm 0.03)(-\Delta H_{HM}), \quad r = 0.993 \quad (16)$$

Again the PEt_3 and PCy_3 complexes (**10** and **11**) are not included in the correlation (eq 16). The PEt_3 complex (**10**) appears to deviate only slightly from the line (Figure 3). However, the rate for the PCy_3 complex (**11**) is approximately 46 times slower than is predicted from eq 16. This large reduction in iridium nucleophilicity is almost certainly due to the bulkiness of the PCy_3 ligand. The effects of PCy_3 and other bulky phosphines on rates of CO substitution in $CpRh(CO)_2$ complexes by PR_3 nucleophiles were reported earlier by Basolo and co-workers.[35] The rates of these reactions were also dramatically slower for the bulky phosphines.

Graham and co-workers[12] previously reported a related kinetic study of the reaction of $CpCo(CO)(PR_3)$ with CH_3I to give

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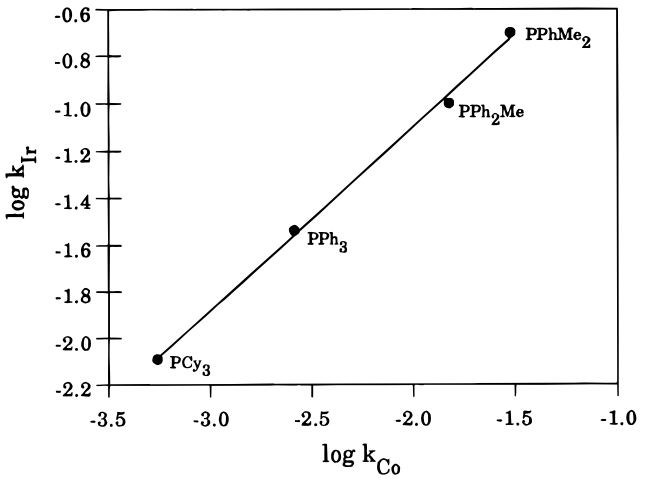

Figure 4. Correlation between log k_{Ir} for $CpIr(CO)(PR_3)$ and log k_{Co} for $CpCo(CO)(PR_3)$ for their reactions with CH_3I in CH_2Cl_2 at 25.0 °C (eq 2).

$[CpCo(CO)(PR_3)(CH_3)]^+I^-$ in CH_2Cl_2 at 25.0 °C. The second-order rate constants decreased with the PR_3 ligand, $PPhMe_2$ (3.0×10^{-2} M^{-1} s^{-1}) > PPh_2Me (1.5×10^{-2} M^{-1} s^{-1}) > PPh_3 (0.26×10^{-2} M^{-1} s^{-1}) > PCy_3 (0.055×10^{-2} M^{-1} s^{-1}), in the same order as observed in our $CpIr(CO)(PR_3)$ series. These data also demonstrate the unusually poor nucleophilicity of the PCy_3 complex which reacts more slowly than any of the other $CpCo(CO)(PR_3)$ complexes. In fact, the steric effect of bulky ligands is greater for the Co complexes than for the Ir complexes; this may be seen in the ratio (k_{Ir}/k_{Co}) of rate constants k for the $CpM(CO)(PR_3)$ complexes which increase with the bulkiness of the ligand: $PPhMe_2$ (6.6) ~ PPh_2Me (6.6) < PPh_3 (11) < PCy_3 (15). With the least bulky phosphines, the Ir complex reacts 6.6 times faster than the Co. However, as the bulkiness of the phosphine increases, the rate decreases more for the Co complexes than for the Ir. In fact, there is linear correlation ($\log k_{Ir} = (0.47 \pm 0.06) + (0.78 \pm 0.03) \log k_{Co}$, $r = 0.999$, Figure 4) between log k_{Ir} for $CpIr(CO)(PR_3)$ and log k_{Co} for $CpCo(CO)(PR_3)$. The slope (0.78), which is less than 1.0, in this correlation reflects the greater effect of bulky PR_3 ligands on the nucleophilicity of the smaller Co as compared with Ir.

In contrast to the excellent correlation (eq 16) between log k and $-\Delta H_{HM}$ for the $CpIr(CO)(PR_3)$ complexes, there is only a poor correlation (Table 5) between these parameters for the $Cp^*Ir(CO)(PR_3)$ complexes. This is probably related to the unexpectedly similar ΔH_{HM} values for these complexes, as discussed above.

Effects of Cp* and Cp on Rate Constants for the Reaction (Eq 2) of Cp′Ir(CO)(PR_3) with CH_3I. In order to understand the effects of Cp* and Cp on the nucleophilicities of the Cp′Ir-(CO)(PR_3) complexes, we plot (Figure 5) log k values (Table 5) versus the basicities ($-\Delta H_{HP}$) of the PR_3 ligands in the complexes. These correlations (eqs 17 and 18) show that the

$$\log k = (-3.4 \pm 0.4) + (0.16 \pm 0.02)(-\Delta H_{HP}), \quad r = 0.99 \quad \text{for } Cp^*Ir(CO)(PR_3) \quad (17)$$

$$\log k = (-4.6 \pm 0.3) + (0.14 \pm 0.01)(-\Delta H_{HP}), \quad r = 0.99 \quad \text{for } CpIr(CO)(PR_3) \quad (18)$$

metal becomes more nucleophilic as its PR_3 ligand becomes more basic. Within experimental error, the slopes, i.e., the coefficients for the $-\Delta H_{HP}$ terms in eqs 17 and 18, are the same for both the Cp* and Cp complexes. Thus, for all Cp′Ir(CO)-

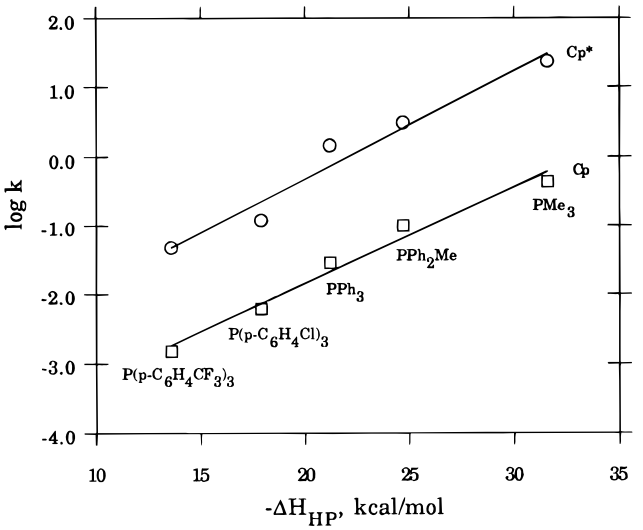

Figure 5. Plots of log k for eq 2 vs $-\Delta H_{HP}$ for PR_3 (eq 3), showing a comparison of the effects of Cp* and Cp ligands on the nucleophilicities of Cp′Ir(CO)(PR_3) complexes.

(PR_3) pairs of complexes, the rate constant for the reaction of the Cp* complex is approximately 40 times larger than that for the analogous Cp complex. This presumably reflects the greater electron-donating ability of the Cp* ligand, as was also noted in the ΔH_{HM} values above.

In order to determine if the Cp* ligand exerts a steric effect in addition to its electronic effect, we compare the nucleophilicities (log k) of the Cp* and Cp compounds in relation to their basicities ($-\Delta H_{HM}$). One might assume that the correlation in eq 16 (Figure 3) for the $CpIr(CO)(PR_3)$ compounds would predict the value of k for the $Cp^*Ir(CO)(PR_3)$ complexes if the Cp* ligand does not exhibit a steric effect. However, if one compares the actual values of k (Table 5) with those calculated from eq 16 using the measured ΔH_{HM} values (Table 4), one finds that the actual rate constants are always less than those predicted from eq 16. For the $Cp^*Ir(CO)(PR_3)$ compounds, predicted k values (eq 16) and measured k's are as follows: **12**, 1.22, 0.048; **13**, 34.9, 0.120; **14**, 43.4, 1.44; **15**, 43.4, 3.11; **16**, 115, 23.4. Thus, it appears that the rates of reaction (eq 2) of the $Cp^*Ir(CO)(PR_3)$ complexes are slower than is expected from their basicities ($-\Delta H_{HM}$) because of steric inhibition by the methyl groups on the Cp* ligand.

Basicities (ΔH_{HP}) of Phosphines. Basicities (Table 4) of the tris(methoxyphenyl)phosphines increase in the order P(4-$C_6H_4OMe)_3$ (24.1 kcal/mol)[18] < P(2-$C_6H_4OMe)_3$ (**17**; 25.5 kcal/mol) ≪ P[2,6-$C_6H_3(OMe)_2]_3$ (**18**; 33.8 kcal/mol) < P[2,4,6-$C_6H_2(OMe)_3]_3$ (**19**; 36.7 kcal/mol). The $-\Delta H_{HP}$ value of P[2,4,6-$C_6H_2(OMe)_3]_3$ (**19**) could not be determined experimentally because this compound reacts with DCE under the conditions of the calorimetric titrations. However, it can be estimated using eq 19, which correlates[18] ΔH_{HP} and pK_a values

$$-\Delta H_{HP} = 1.82 pK_a(H_2O) + 16.3 \quad \text{(kcal/mol)} \quad (19)$$

of 12 phosphines. With this equation, the reported pK_a (11.2)[36] of **19** can be used to estimate the $-\Delta H_{HP}$ value (36.7 kcal/mol). Thus, **19** is much more basic than pyridine (29.3 kcal/mol)[3] but is not as basic as Et_3N (39.3).[3] The strong donor ability of **19** is also evident in the low ν(CO) values for its $Ni(CO)_3(PR_3)$ complex.[37] The electron-donating ability of the methoxy groups also makes **18** (33.8 kcal/mol) as basic as PEt_3

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(33.7 kcal/mol),[18] although its cone angle is larger (close to that of **19**, 184°)[17] than that (132−166°) for PEt_3.[30] The pK_a (9.61) of **18** calculated with eq 19 is in reasonable agreement with that (9.33)[36] obtained by a titration method. The calculated pK_a (5.05) of **17** is also similar to that (4.47) determined by titration.[36]

The basicities ($-\Delta H_{HP}$) of the tris(methylphenyl)phosphines increase in the order: $P(2\text{-}C_6H_4Me)_3$ (22.6 kcal/mol)[18] < $P(4\text{-}C_6H_4Me)_3$ (23.2 kcal/mol)[18] ≪ $P(2,4,6\text{-}C_6H_2Me_3)_3$ (**20**; 29.4 kcal/mol). The pK_a for $P(2,4,6\text{-}C_6H_2Me_3)_3$ estimated with use of eq 19 is 7.20. The basicity ($-\Delta H_{HP}$) of **20** is intermediate between those of $PPhMe_2$ (28.4 kcal/mol) and PMe_3 (31.6 kcal/mol).[3]

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Supporting Information Available: Derivations of eqs 8 and 9 (1 page). Ordering information is given on any current masthead page.

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