Calorimetric studies of the basicities of organometallic compounds

John R. Sowa Jr.
Iowa State University

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Calorimetric studies of the basicities of organometallic compounds

Sowa, John R., Jr., Ph.D.

Iowa State University, 1991
Calorimetric studies of the basicities of organometallic compounds

by

John R. Sowa, Jr.

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1991
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</table>
to my father and the memory of my grandfather
This dissertation contains four sections describing the research I performed at Iowa State University, as it was submitted for journal publication. In each section, the literature citations, tables, and figures pertain only to those sections in which they appear. The first section is a literature survey of the solution acid-base strengths of organometallic compounds. After the final section is a general summary.

Valerio Zanotti and Giacomo Facchin contributed to the research in Sections III and V as they synthesized, characterized, and studied the protonation reactions of most of the Fe(CO)$_3$(PR$_3$)$_2$ and Fe(CO)$_3$(L$^\text{L}$) compounds. Also in Section III, Valerio worked out the preparation of CpIr(CO)(PMe$_2$Ph). Their expert collaboration is greatly appreciated.
SECTION I. SOLUTION ACID-BASE STRENGTHS OF ORGANOMETALLIC COMPLEXES: A REVIEW
INTRODUCTION

Quantitative data on the acid-base strengths of organic compounds have had a major impact on the understanding of the properties and reactivities of organic compounds. The acid-base strengths of organometallic complexes are also of interest. Numerous metal complexes behave as bases and undergo protonation at the metal center forming a M-H bond. There is evidence that this basicity influences many stoichiometric reactions such as oxidative addition and nucleophilic reactions, and catalytic reactions including hydrogenation, hydroformylation, and C-H activation. Thus, measures of transition-metal basicity will contribute to the understanding of these reactions. An interesting aspect of transition-metal hydrides is their ability to undergo intra- and intermolecular proton transfer. Hydrogenation and hydroformylation are two important catalytic processes involving M-H intermediates. Thermodynamic data on the acidity of organometallic hydrides may also distinguish between reactions of a transition-metal hydride or its conjugate base. Recently, Tilset and Parker have used metal-hydride pKa values to calculate M-H bond dissociation energies from a thermochemical cycle. Quantitative measures of transition-metal acid-base strengths can also serve as a guide to the design of organometallic complexes whose acid-base properties are selectively controlled. These data will provide
information about metal-ligand bonding and periodic trends in organometallic compounds.

Kinetic factors are also important when considering transition-metal acid-base behavior.\textsuperscript{8,10} Rates of metal protonation and deprotonation are usually slow compared to those of organo-nitrogen and organo-oxygen bases because metal complexes undergo substantial electronic rearrangement and changes in geometry.\textsuperscript{8a,b} In some cases the rates of kinetic acidities parallel trends in thermodynamic acidities.\textsuperscript{8a} Rates of protonation and deprotonation of polymetallic complexes are slower than monometallic compounds even when the thermodynamic acid-base strengths are comparable.\textsuperscript{10a} The many interesting studies of proton transfer rates are beyond the scope of this review but leading references are listed in the bibliography.\textsuperscript{2a,c,8,10,11}

Transition-metal Bronsted acid-base strengths are usually expressed as pK\textsubscript{a} values derived from eq 1. Thus, the simplest measure would be the determination of the pK\textsubscript{a} of [HML\textsubscript{x}]\textsuperscript{n}

\[
[HML_x]^n \xrightleftharpoons{K_a}{K_b} [ML_x]^{n-1} + H^+ \quad (1)
\]

in H\textsubscript{2}O.\textsuperscript{12} However, for reasons of stability, solubility, and that several metal hydrides are completely dissociated in H\textsubscript{2}O, very few values have been determined in this solvent. Also, K\textsubscript{b} values have been measured (eq 1); however, in this review, these are converted to K\textsubscript{a} values (K\textsubscript{a} = 1/K\textsubscript{b}). Most pK\textsubscript{a} determinations involve the
measurement of \( K_{eq} \) (eq 2a) of neutral or cationic transition-metal hydrides by deprotonation with organic bases of known strength \( (pK_a(BH^+)) \) in nonaqueous solvents.\(^2a\)

\[
[HML_x]^n + B \xrightleftharpoons{K_{eq}} [MLx]^{n-1} + BH^+ \quad (2a)
\]

\[
pK^s_a = pK_{eq} + pK_a(BH^+) \quad (2b)
\]

The \( M-H \) \( pK_a^s \) value is then calculated from eq 2b (the superscript \( s \) indicates the solvent in which the measurement was made). If the \( pK_a \) of the organic base is known in water, e.g., organophosphines (PR\(_3\)), then the \( pK_a^s(M-H) \) value (eq 2b) is an estimate of the aqueous \( pK_a(M-H) \) value; these are indicated as \( pK_a^a \). Usually spectroscopic probes (IR, NMR, UV-Visible)\(^2\) are used to determine the equilibrium constants (eq 1 or 2a) but \( pK_a^s \) values have also been calculated from kinetic\(^{10b,11}\) and electrochemical\(^{13}\) measurements. A few gas phase determinations\(^{14}\) and theoretical studies\(^{15}\) of acid-base strengths are reported; although important, these will not be discussed here. In this review, trends in ligand and periodic effects on the solution Brønsted acid-base strengths of monometallic and polymetallic complexes will be presented.
ABBREVIATIONS

Cp, $\eta^5$-C$_5$H$_5$ ligand
Cp*, $\eta^5$-C$_5$Me$_5$ ligand
Cp', substituted cyclopentadienyl ligand
M-H, metal hydride
M-H+, metal hydride cation radical
pK$_a$®, proton dissociation constant in solvent s
pK$_a$', proton dissociation constant extrapolated to H$_2$O
H$_2$, dihydride or $\eta^2$-dihydrogen ligand
(H)$_2$, dihydride ligands
($\eta^2$-H$_2$), $\eta^2$-dihydrogen ligand
dppm, Ph$_2$PCH$_2$PPh$_2$
dtfpe, (p-CF$_3$C$_6$H$_4$)$_2$P(CH$_2$)$_2$P(p-CF$_3$C$_6$H$_4$)$_2$
dppe, Ph$_2$P(CH$_2$)$_2$PPh$_2$
dape, (p-MeOC$_6$H$_4$)$_2$P(CH$_2$)$_2$P(p-MeOC$_6$H$_4$)$_2$
dmpe, Me$_2$P(CH$_2$)$_2$PMe$_2$
dppp, Ph$_2$P(CH$_2$)$_3$PPh$_2$
cis-dppv, cis-Ph$_2$P(CH=CH)PPh$_2$
dmgH, monoanion of dimethylglyoxime
Cy, cyclohexyl group
Phosphine, Arsine, Phosphite, CO Ligand Effects

Replacing CO with P(OPh)$_3$ or PPh$_3$ causes the acidities of metal carbonyl hydrides (M-H) to decrease (Table I) in the order: CO $>$ P(OPh)$_3$ $>$ PPh$_3$. Thus, Co(H)(CO)$_4$ is completely dissociated in H$_2$O but Co(H)(CO)$_3$[P(OPh)$_3$] ($pK_a^{H_2O} = 4.95$) is more acidic than Co(H)(CO)$_3$(PPh$_3$) ($pK_a^{H_2O} = 6.69$). In MeCN solvent, the $pK_a^{MeCN}$ value of Co(H)(CO)$_4$ (8.3) is comparable to that estimated for HCl (8.9). For Co(H)(CO)$_3$(PPh$_3$) ($pK_a^{MeCN} = 15.4$), the Co-H acidity is decreased by 7.1 units but only an estimate of the $pK_a^{MeCN}$ value of Co(H)(CO)$_3$[P(OPh)$_3$] (11.3) is obtained as the P(OPh)$_3$ ligand is partially dissociated in MeCN solvent (eq 3).$	extsuperscript{17a}$

\[
\text{MeCN} \quad \text{Co(H)(CO)$_3$[P(OPh)$_3$] } \rightleftharpoons \text{Co(H)(CO)$_3$(MeCN) + P(OPh)$_3$ (3)}
\]

Also, Mn(H)(CO)$_4$(PPh$_3$) ($pK_a^{MeCN} = 20.4$) is less acidic by 5.3 $pK_a^{MeCN}$ units than Mn(H)(CO)$_5$ ($pK_a^{MeCN} = 15.1$),$	extsuperscript{17b}$ and V(H)(CO)$_5$(PPh$_3$) ($pK_a^{H_2O} = 6.8$) is less acidic than V(H)(CO)$_6$ which is a strong acid in H$_2$O.$	extsuperscript{12b,18}$ The greater $\sigma$-donor and poorer $\pi$-acceptor ability of PPh$_3$ compared to P(OPh)$_3$ and CO in these complexes increases metal basicity and decreases M-H acidity.

Limited data show that increasing the basicity of the phosphine ligand also results in a further increase in the M-H $pK_a$ value. Thus, on going from PPh$_3$ ($pK_a' = 2.73$)$	extsuperscript{20}$ to PEtPh$_2$ ($pK_a' = 4.9$)$	extsuperscript{19a}$ in Mn(H)(CO)$_4$(L) ($L = $ PPh$_3$, PEtPh$_2$), the Mn-H $pK_a^{MeCN}$
Table I. \( pK_a \) values for organometallic complexes in various solvents

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<thead>
<tr>
<th>complex</th>
<th>( pK_a ) solvent =</th>
<th>( pK_a ) solvent =</th>
<th>( pK_a ) solvent =</th>
<th>( pK_a ) solvent =</th>
<th>( pK_a ) solvent =</th>
<th>( pK_a ) solvent =</th>
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</thead>
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<tr>
<td>( \text{V(HXCO)}_6 )</td>
<td>strong</td>
<td></td>
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<td></td>
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<tr>
<td>( \text{V(H)(CO)}_5(\text{PPh}_3) )</td>
<td>6.8</td>
<td></td>
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<tr>
<td>( \text{CpCr(HXCO)}_3 )</td>
<td>5.4(^a)</td>
<td>13.3</td>
<td></td>
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<tr>
<td>( \text{CpMo(H)(CO)}_3 )</td>
<td>6.2(^a)</td>
<td>13.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Cp*Mo(H)(CO)}_3 )</td>
<td></td>
<td>17.1</td>
<td></td>
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<tr>
<td>( \text{CpW(H)(CO)}_3 )</td>
<td>8.0(^a)</td>
<td>16.1</td>
<td></td>
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<tr>
<td>( \text{Mn(H)(CO)}_5 )</td>
<td>7.1</td>
<td>15.1</td>
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<tr>
<td>( \eta^6-\text{C}_6\text{H}_6\text{Mn(H)(CO)}_2 )</td>
<td>26.6</td>
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<tr>
<td>( \eta^4-\text{C}_6\text{H}_9\text{Mn(CO)}_3 )(^b)</td>
<td>22.2</td>
<td></td>
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<tr>
<td>( \text{Re(H)(CO)}_5 )</td>
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<td>21.1</td>
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<tr>
<td>( \text{CpReH}_2(\text{CO})_2 )</td>
<td>23.0(pK_a)</td>
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<tr>
<td>( [\text{Cp}_2\text{ReH}_2]^+ )</td>
<td></td>
<td></td>
<td>8.5(^c)</td>
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<tr>
<td>( [\text{CpReH}_2(\text{COXNO})]^+ )</td>
<td></td>
<td></td>
<td>( \sim 2)(^d)</td>
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<tr>
<td>( \text{FeH}_2(\text{CO})_4 )</td>
<td>4.00(pK_a)</td>
<td>5.88(pK_a)(^a)</td>
<td>11.4(pK_a)</td>
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<td></td>
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<td>12.68(pK_a)(^e)</td>
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\(^a\)In 70% aqueous MeOH extrapolated to H\(_2\)O.

\(^b\)This is an agostic C-H complex. See text.

\(^c\)In 60% aqueous dioxane. In this solvent the \( pK_a \) of \( \text{NH}_4^+ \) is 8.85.

\(^d\)In CH\(_2\)Cl\(_2\) with Et\(_2\)O base.

\(^e\)Too weak to be measured.
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<td>CpRu(H)(CO)(PPh₃)</td>
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<td>Co(H)(CO)₄</td>
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<td>strong</td>
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<td>Co(H)(CO)₃(PPh₃)</td>
<td>6.96</td>
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<td>Co(H)(CO)₃(PF₃)</td>
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<tr>
<td>[CpCo(H)(cis-dppv)]⁺</td>
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<td>[CpCo(H)(P(OMe)₃)]⁺</td>
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<td>6.5g</td>
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<td>Rh(H)(dmgH)₂(PPh₃)</td>
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<td>~9.5h</td>
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<td>35b,c</td>
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*50% aqueous MeOH/hexanes.*

§In CH₂Cl₂.

h50% aqueous MeOH.
<table>
<thead>
<tr>
<th>complex</th>
<th>H₂O</th>
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<th>MeCN</th>
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<tr>
<td>{Ni(H)[P(Ph(OEt)₂)]₄}⁺</td>
<td>2.0</td>
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<td>{Ni(H)[P(OEt)₃]₄}⁺</td>
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<td>{Ni(H)[P(OMc)₃]₄}⁺</td>
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<tr>
<td>{Ni(H)[P(OCH₂CH₂Cl)₃]₄}⁺</td>
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<td>{Ni(H)[P(OCH₂CCl₃)]₄}⁺</td>
<td>e</td>
<td></td>
<td></td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>{Pd(H)[P(OMe)₃]₄}⁺</td>
<td>0.7</td>
<td>8.0</td>
<td></td>
<td></td>
<td>16k,1</td>
</tr>
<tr>
<td>{Pt(H)[P(OMe)₃]₄}⁺</td>
<td>10.2</td>
<td>18.5</td>
<td></td>
<td></td>
<td>16k,1</td>
</tr>
</tbody>
</table>
values (Table I) increase by 1.2 units. Above, it was shown that replacement of CO by PPh₃ increases the Mn-H or Co-H pKₐ MeCN value by 5.3-7.1 units, respectively. However, replacing a CO by the more basic PMe₃ ligand (pKₐ' = 8.65) in CpW(H)(CO)₂(L) (L = CO, PMe₃) results in a larger 10.5 unit increase in the W-H pKₐ MeCN value (Table I).

Systematic substitution of phosphite ligands in NiL₄ complexes (L = PPh(OEt)₂, P(OEt)₃, P(OCH₂CH₂Cl)₃, P(OCH₂CCl₃)₃) showed a linear correlation (eq 4) between the Ni-H pKₐ MeOH values (Table I) and Tolman's ν(CO) values (for the A₁ band in Ni(CO)₃L). The latter is a measure of the electronic properties of the phosphite ligands. Use of eq 4b permits the estimate of pKₐ MeOH values of NiL₄ complexes if Tolman's ν(CO) value for L is known.

Equilibrium constants for the protonation of IrCl(CO)(PR₃)₂ complexes (eq 5) with CF₃SO₃H in MeOH solvent (given as pKₐ MeOH in Table II) increase, IrCl(CO)(PPh₃)₂ (2.06) < IrCl(CO)(PMePh₂)₂ (2.48) < IrCl(CO)(PMe₂Ph)₂ (2.80), with increasing phosphine basicity. However, this reaction is not a simple metal protonation because it was shown that either the CF₃SO₃⁻ anion or a solvent molecule of MeOH (X) also coordinates to the square planar Ir center. Increases in PR₃ basicity should shift the
Table II. $pK_a^{\text{MeOH}}$ values for the protonation$^a$ of $\text{MY(CO)(L)}_2$ complexes$^b$

<table>
<thead>
<tr>
<th>$\text{MY(CO)(L)}_2$</th>
<th>$pK_a^{\text{MeOH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{IrCl(CO)(PPh}_3)_2$</td>
<td>2.06</td>
</tr>
<tr>
<td>$\text{IrBr(CO)(PPh}_3)_2$</td>
<td>2.61</td>
</tr>
<tr>
<td>$\text{IrI(CO)(PPh}_3)_2$</td>
<td>2.85</td>
</tr>
<tr>
<td>$\text{IrCl(CO)(PMePh}_2)_2$</td>
<td>2.48</td>
</tr>
<tr>
<td>$\text{IrBr(CO)(PMePh}_2)_2$</td>
<td>2.93</td>
</tr>
<tr>
<td>$\text{IrI(CO)(PMePh}_2)_2$</td>
<td>3.21</td>
</tr>
<tr>
<td>$\text{IrCl(CO)(PMe}_2\text{Ph})_2$</td>
<td>2.80</td>
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<tr>
<td>$\text{IrBr(CO)(PMe}_2\text{Ph})_2$</td>
<td>3.27</td>
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<tr>
<td>$\text{IrI(CO)(PMe}_2\text{Ph})_2$</td>
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<td>$\text{IrCl(CO)(AsPh}_3)_2$</td>
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</tr>
<tr>
<td>$\text{IrCl(CO)(AsMePh}_2)_2$</td>
<td>2.71</td>
</tr>
<tr>
<td>$\text{IrCl(CO)(AsMe}_2\text{Ph})_2$</td>
<td>3.94</td>
</tr>
<tr>
<td>$\text{IrCl(CO)[P(t-Bu)Me}_2)_2$</td>
<td>2.78</td>
</tr>
<tr>
<td>$\text{IrCl(CO)[P(t-Bu)Et}_2)_2$</td>
<td>2.70</td>
</tr>
<tr>
<td>$\text{IrCl(CO)[P(t-Bu)_2Me}_2$</td>
<td>2.66</td>
</tr>
<tr>
<td>$\text{IrCl(CO)[P(t-Bu)_2Et}_2$</td>
<td>2.58</td>
</tr>
<tr>
<td>$\text{RhCl(CO)(PPh}_3)_2$</td>
<td>1.80</td>
</tr>
<tr>
<td>$\text{RhBr(CO)(PPh}_3)_2$</td>
<td>1.94</td>
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<td>$\text{RhI(CO)(PPh}_3)_2$</td>
<td>2.01</td>
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<tr>
<td>$\text{RhCl(CO)(AsPh}_3)_2$</td>
<td>1.78</td>
</tr>
<tr>
<td>$\text{RhBr(CO)(AsPh}_3)_2$</td>
<td>2.00</td>
</tr>
<tr>
<td>$\text{RhI(CO)(AsPh}_3)_2$</td>
<td>2.04</td>
</tr>
</tbody>
</table>

$^a$With $\text{CF}_3\text{SO}_3\text{H}$ in $\text{MeOH}$ solvent. There is evidence for coordination of $\text{CF}_3\text{SO}_3^-$ or $\text{MeOH}$. See text.

$^b$Ref 11.
equilibrium to the right for the addition of H⁺ (eq 5) and to the left for the addition of X. As a result of this the relative changes in the M-H pKₐ MeOH values with PR₃ basicity are small.

$$\text{Ir} + \text{CF₃SO₃H} \rightleftharpoons \text{MeOH} \rightleftharpoons \text{Ir} + \text{CF₃SO₃}^- + \text{MeOH}$$

(eq 5)

Steric effects in the PR₃ ligands are indicated by the decreasing pKₐ MeOH values (eq 6) of IrCl(CO)(PR₃)₂ as the bulkiness of the phosphine ligand is increased:

$$\text{IrCl(CO)[P(t-Bu)Me₂]₂} (2.78) > \text{IrCl(CO)[P(t-Bu)Et₂]₂} (2.70) > \text{IrCl(CO)[P(t-Bu)₂Me]₂} (2.66) > \text{IrCl(CO)[(t-Bu)₂Et]₂} (2.58)$$

(eq 6)

The pKₐ MeOH values (Table II) also indicates that IrCl(CO)(AsR₃)₂ complexes are slightly more basic than IrCl(CO)(PR₃)₂ complexes; e.g., the pKₐ MeOH value of IrCl(CO)(AsPh₃)₂ (2.31) is larger than that of IrCl(CO)(PR₃)₂ (2.06). This is surprising since PR₃ ligands are much stronger bases toward H⁺ and BH₃ than are AsR₃ ligands. However, since As is softer than P, the AsR₃ ligand may induce more electron density on the Ir(I) center thereby increasing iridium's proton affinity. Also, because of the larger As atom, the R substituents in metal complexes of AsR₃ are further from the metal than in PR₃ complexes; this reduces steric hindrance and may
increase metal basicity. Since these reactions are not simple metal protonations further evaluation of these trends and the magnitude of these ligand effects is warranted.

**Chelate Phosphine Ligand Effects**

Tolman demonstrated that Ni(dppe)$_2$ ($pK_a^{\text{MeOH}} = 2.6$) is more basic than Ni[P(OMe)$_3$]$_4$ ($pK_a^{\text{MeOH}} = 1.5$), however, this may be due to the better donor ability of the phosphine ligands as compared to the phosphite ligands as discussed above. In contrast, protonation constants (eq 7) of CpCo(cis-dppv) ($pK_a^{\text{CH}_2\text{Cl}_2} = 5.1$) and CpCo[P(OMe)$_3$]$_2$ ($pK_a^{\text{CH}_2\text{Cl}_2} = 6.5$) indicate greater basicity for the bis(phosphite) complex.

\[
\text{CpCo(L)}_2 + \text{H}^+ \rightleftharpoons \text{CpCo(H)(L)}_2^+ \quad (7a)
\]

\[
K_a = \frac{[\text{CpCo(L)}_2][\text{H}^+]}{[\text{CpCo(H)(L)}_2^+]} \quad (7b)
\]

The effects of chelate size and basicity on the coordination of dihydrogen and $pK_a'$ values of [Cp'RuH$_2$(L'\text{L})]BF$_4$ complexes have been recently investigated by Jia and Morris. Since the $pK_a'$ values (Table III) determined in CD$_2$Cl$_2$ or THF solvent were based on the $pK_a'$ value of PCy$_3$ (9.7, determined in MeNO$_2$ and extrapolated to H$_2$O) they are regarded as estimates of aqueous $pK_a$ values (i.e., $pK_a'$). Most values were obtained in THF solvent (Table III) with use of gated decoupled $^3$P NMR spectroscopy; these values are 0.2-0.5 $pK_a'$ units larger than those determined in CD$_2$Cl$_2$ by $^1$H NMR spectroscopy; however, the trends are the same. Table III and the discussion below list only the $pK_a'$ values in THF solvent.
<table>
<thead>
<tr>
<th>Ru complex</th>
<th>$(H)_2/(\eta^2-H_2)$</th>
<th>$pK_a'(H)_2$</th>
<th>$pK_a'(\eta^2-H_2)$</th>
<th>$E_{pa} (\Sigma E_L)$</th>
<th>$pK_a'(calc)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CpRuH}_2(\text{dtfpe})]^+$</td>
<td>1.6</td>
<td>4.9</td>
<td>4.6</td>
<td>0.77 (0.72)</td>
<td>5.3</td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{dppe})]^+$</td>
<td>2</td>
<td>7.5</td>
<td>7.2</td>
<td>0.51 (0.50)</td>
<td>7.6</td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{dppm})]^+$</td>
<td>&lt;10^{-3}</td>
<td>-</td>
<td>7.5</td>
<td>0.56 (0.64)</td>
<td>6.1</td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{PPh}_3)_2]^+$</td>
<td>&gt;10^{3}</td>
<td>8.0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{dppp})]^+$</td>
<td>&gt;10^{3}</td>
<td>8.6</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{dape})]^+$</td>
<td>2.6</td>
<td>9.0</td>
<td>8.6</td>
<td>0.38 (0.44)</td>
<td>9.2</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{RuH}_2(\text{dppm})]^+$</td>
<td>0.5</td>
<td>8.8</td>
<td>9.2</td>
<td>0.35 (0.39)</td>
<td>6.8</td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{dmpe})]^+$</td>
<td>0.17</td>
<td>-</td>
<td>9.8</td>
<td>(0.3)</td>
<td>10</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{RuH}_2(\text{PMePh}_2)_2]^+$</td>
<td>&gt;10^{-3}</td>
<td>12.1</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{RuH}_2(\text{CO})_2]^+$</td>
<td>&lt;0^f</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{RuH}_2(\text{dmpe})]^+$</td>
<td>unknown^f</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{CO})]^+$</td>
<td>unknown^f</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{CpRuH}_2(\text{CO})(\text{PMe}_3)]^+$</td>
<td>unknown^f</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>Oxidation Potential (V)</td>
<td>pKa Value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-------------------------</td>
<td>-----------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CpRuH₂(CO)(CNPh)]⁺</td>
<td>unknown&lt;sup&gt;f&lt;/sup&gt;</td>
<td>(1.2)</td>
<td>0</td>
<td></td>
<td></td>
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<tr>
<td>[Ru(H)H₂(dppc)₂]⁺</td>
<td>&gt;10&lt;sup&gt;f&lt;/sup&gt;</td>
<td>(0.8)</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(H)₂H₂(PPh₃)₃]⁺</td>
<td>~16&lt;sup&gt;f&lt;/sup&gt;</td>
<td>(0.3)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Measured in THF and extrapolated to H₂O. Ref 26.

<sup>b</sup> In CH₂Cl₂.

<sup>c</sup> Oxidation potential of Ru complexes vs NHE (V) in THF.

<sup>d</sup> Values in parentheses are calculated from Lever's electrochemical parameters (E_<sub>L</sub>), ref 28.

<sup>e</sup> Calculated from eq 9 independent of the form of the H₂ ligand.

<sup>f</sup> For these complexes the pKa values correspond to hydride or η<sup>2</sup>-dihydrogen co-ordination.
Most of the $\text{H}_2$ complexes exist as a mixture of two tautomers in rapid equilibrium; the $\eta^2$-dihydrogen ($\eta^2\text{-H}_2$) form shown in structure A, and the dihydride ($(\text{H})_2$) form shown in structure B or C. The size and the basicity of the bidentate phosphine determines which tautomer predominates at 25 °C as indicated by the $K_1$ values in Table III.\textsuperscript{26a} However, when both tautomers are observed simultaneously, the $pK_a'$ values measured for each tautomer

![Chemical structures A, B, and C](image)

(Table III) are within 0.3 ± 0.2 units of each other. Thus, trends in acidity can be obtained with use of the averaged $pK_a'$ values.

When chelate size is held constant the average $pK_a'$ values increase as the R substituents of the bidentate phosphine $(R_2P(CH_2)_2PR_2)$ become more electron donating (eq 8).\textsuperscript{26a}

$$\text{[CpRuH}_2\text{(dtfpe)}]^+ (4.8) < \text{[CpRuH}_2\text{(dppe)}]^+ (7.3) < \text{[CpRuH}_2\text{(dape)}]^+ (8.8) < \text{CpRuH}_2\text{(dmpe)}]^+ (9.8)$$ (8)

The $pK_a'$ value of $\text{[CpRuH}_2\text{(dmpe)}]^+$ was estimated by taking the $pK_a\text{MeCN}$ value (17.6)\textsuperscript{27} and converting it to the aqueous scale.\textsuperscript{26b}

For the complexes in eq 8 the $\eta^2\text{-H}_2$ triplet $^1\text{H}$ NMR resonance shifts upfield as the electron density on the metal center increases
from -8.78 ppm for the dtfpe complex to -10.07 ppm for the dmpe complex. Also, as $pK_a'$ values increase, the $^1J_{(HD)}$ coupling constants decrease from 25.3 Hz for the dtfpe complex to 22 Hz for the dmpe complex. The increasing electron density at the metal center is thought\textsuperscript{26a} to increase Ru $\rightarrow$ H$_2$ backbonding, probably lengthening the H-D bond, thus, lowering the $^1J_{(HD)}$ value.

Only the trans-dihydride tautomer is observed for [CpRu(H)$_2$-(dppp)]BF$_4$ (B) and [CpRu(H)$_2$(PPh$_3$)$_2$]BF$_4$ (C) complexes.\textsuperscript{26} Their $pK_a'$ values are (Table III) about one order of magnitude greater than that of the pure $\eta^2$-dihydrogen complex, [CpRu($\eta^2$-H$_2$)(dppm)]BF$_4$ ($pK_a' = 7.3$). Also, the average $pK_a'$ value of [CpRuH$_2$(dppe)]BF$_4$ is 7.5 for both the tautomer (B), and the $\eta^2$-dihydrogen tautomer (A). Thus, when the equilibrium constant ($K_1$) between the dihydride and $\eta^2$-dihydrogen tautomers is large the dihydride complexes are less acidic.

As the electron density of the Ru metal center increases it also becomes easier to oxidize, and there is an inverse linear correlation (eq 9) between the $pK_a'$ values and the respective aniodic peak

$$pK_a'(\text{RuH}_2^+) = -10.6E_{\text{oxy}}(\text{MH}^+/\text{MH}) + 12.9 \quad (9)$$

potentials ($E_{\text{oxy}}$) in THF. However, the oxidation potentials are irreversible and it is possible that the difference between the true $E_{\text{oxy}}^*$ value and the irreversible $E_{\text{oxy}}$ potential vary systematically with $pK_a'$.\textsuperscript{26a} Nevertheless, a link between Ru-H acidity and electrochemical potential has been established (eq 9) and is very
useful in predicting $pK_a'$ values for [CpRuH$_2$(L^L)]BF$_4$ complexes. Furthermore, a method for predicting electrochemical potentials for the Ru$_{III}$/Ru$_{II}$ couple from additive ligand parameters ($\Sigma E_L$) developed by Lever$^{28}$ enables $pK_a'$ values to be calculated from eq 9 with use of calculated oxidation potentials. The examples in Table III indicate that the method works well for [Cp'RuH$_2$(L)(L')] and [CpRuH$_2$(L^L)]$^+$ complexes but not for other Ru complexes.

**CO, Olefin, Cp, and Cp* Ligand Effects**

Replacing the three CO ligands in Mn(H)(CO)$_5$ by the 6-electron donor C$_6$H$_6$ ligand$^{17b}$ to give ($\eta^6$-C$_6$H$_6$)Mn(H)(CO)$_2$ (D), Scheme I, increases the $pK_a^{MeCN}$ value by 11.5 units, which is ~ 4 units per CO ligand. Even though replacement of two CO groups in Mn(H)(CO)$_5$ by 1,3-cyclohexadiene gives the agostic ($\eta^4$-cyclohexadienyl)Mn(CO)$_3$ complex (E) the $pK_a^{MeCN}$ value increases 7.1 units, still about 4 $pK_a^{MeCN}$ units per CO ligand.$^{17b}$ This surprising result suggests that the basicity of a metal complex that forms an agostic hydride upon protonation may not differ appreciably from that expected for an analogous complex where protonation occurs only at the metal center.$^{17b}$

The basicity of Re is increased by 1.9 $pK_a^{MeCN}$ units by replacing the three CO ligands in Re(H)(CO)$_5$ (21.1) with Cp and H (eq 10) to give CpRe(H)$_2$(CO)$_2$ (23.0).$^{17b}$ In addition, the $pK_a^{MeCN}$ values of FeH$_2$(CO)$_4$ (11.4), CpFe(H)(CO)$_2$ (19.4) and RuH$_2$(CO)$_4$ (18.7), CpRu(H)(CO)$_2$ (20.2) suggest that replacement of CO by Cp
$\text{Mn(H)(CO)₅}$

$\text{pK}^\text{MeCN} = 15.1$

- $3 \text{CO} + C₆H₆$
- $2 \text{CO} + C₆H₆$

$\text{D}$

$\text{pK}^\text{MeCN} = 26.6$

$\text{E}$

$\text{pK}^\text{MeCN} = 22.2$

Scheme I
20

\[
\begin{align*}
\text{Re}({\text{H}})(\text{CO})_5 & \quad + \quad \text{Cp} \cdot \text{H} \quad - \quad 3 \text{CO} \quad \Rightarrow \quad \text{CpReH}_2(\text{CO})_2 \\
& \quad 1.9 \text{ kcal mol}^{-1}
\end{align*}
\]

generally increases metal basicity.\textsuperscript{17b}

The metal center in complexes containing the Cp\textsuperscript{*} ligand are generally more basic than the corresponding Cp complexes because of the inductive effect of the methyl groups on Cp\textsuperscript{*}.\textsuperscript{29} Thus, the Mn-H bond in Cp\textsuperscript{*}Mo(H)(CO)\textsubscript{3} is 3.2 pK\textsubscript{a}\textsuperscript{MeCN} units less acidic than that of CpMo(H)(CO)\textsubscript{3}, and Cp\textsuperscript{*}Fe(H)(CO)\textsubscript{3} is less acidic than CpFe(H)(CO)\textsubscript{3} by 6.9 pK\textsubscript{a}\textsuperscript{MeCN} units.\textsuperscript{17a} Also, the average pK\textsubscript{a}\textsuperscript{'} value of [Cp\textsuperscript{*}RuH\textsubscript{2}(dppm)]BF\textsubscript{4} (9.0) is 1.5 units larger than that of [CpRu(\eta\textsuperscript{2}-H\textsubscript{2})(dppm)]BF\textsubscript{4} (7.5).\textsuperscript{26a} The Cp-Cp\textsuperscript{*} replacement does not, however, increase the pK\textsubscript{a}\textsuperscript{8} values in all of the above metal complexes by the same amount.

Radical Cation Hydrides

Ryan and coworkers\textsuperscript{13a,b} have recently generated radical cation metal hydrides by chemical and electrochemical methods in MeCN solvent (Scheme II). All of the M-H\textsuperscript{+} species were short-lived, their major mode of decomposition being proton transfer to the neutral parent hydride (Scheme II) or deprotonation by the reaction medium (MeCN or adventitious H\textsubscript{2}O).\textsuperscript{13a,b}

Since the pK\textsubscript{a}\textsuperscript{MeCN} values for the neutral metal hydrides (Table I)\textsuperscript{17a} and oxidation potentials for the metal anions\textsuperscript{9} are known, the
Scheme II
thermodynamic acidities \( p\text{Ka}^{\text{MeCN}(M-H^+)} \) of the radical cation hydrides are calculated from the following thermodynamic cycle:\textsuperscript{13a}

\[
\begin{align*}
\text{M-H} & \rightleftharpoons \text{M}^- + \text{H}^+ & \text{pKa}(M-H) \\
\text{M}^- & \rightleftharpoons \text{M}^0 + \text{e}^- & E_{\text{ox}}^*(M^-) \\
\text{M-H}^+ + \text{e}^- & \rightleftharpoons \text{M-H} & E_{\text{ox}}^*(M-H) \\
\text{M-H}^+ & \rightleftharpoons \text{M}^0 + \text{H}^+ & \text{pKa}(M-H^+) 
\end{align*}
\]

\[
p\text{Ka}(M-H^+) = p\text{Ka}(M-H) + \left( F/2.303 \, \text{RT} \right) [E_{\text{ox}}^*(M^-) - E_{\text{ox}}^*(M-H)] \quad (11)
\]

The accuracy of the \( p\text{Ka}^{\text{MeCN}(M-H^+)} \) values in eq 11 depends on the ability to obtain good values of oxidation potentials for \( M^- \) and \( M-H \) compounds both of which exhibit full or partial electrochemical irreversibility.\textsuperscript{9,13a,b} Therefore, the \( p\text{Ka}^{\text{MeCN}(M-H^+)} \) values (Table IV) are considered to be estimated for which relative acidities should at least be reliable. This approach has been demonstrated in several organic systems.\textsuperscript{30}

The radical cation hydride acidities \( p\text{Ka}^{\text{MeCN}} \) range from -9.5 for \([\text{CpCr(H)(CO)\text{3}}]^{+} \) to 5.1 for \([\text{CpW(H)(CO)\text{3}}]^{+} \) (Table IV) and they are about 20.6 ± 1.5 units less than the respective \( p\text{Ka}^{\text{MeCN}(M-H)} \textsuperscript{17a} \) values (Table I). Even though they are the most acidic metal hydrides yet determined in MeCN, periodic trends and the magnitude of ligand effects parallel those obtained for the neutral metal hydrides.
Table IV. $pK_a^{MeCN}$ values for radical cation hydrides$^{13}$

<table>
<thead>
<tr>
<th>[M-H.]$^+$</th>
<th>$pK_a^{MeCN}(M-H.\text{+})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpCr(H)(CO)$_3$]+</td>
<td>-9.5</td>
</tr>
<tr>
<td>[CpMo(H)(CO)$_3$]+</td>
<td>-6.0</td>
</tr>
<tr>
<td>[Cp*Mo(H)(CO)$_3$]+</td>
<td>-2.5</td>
</tr>
<tr>
<td>[CpW(H)(CO)$_3$]+</td>
<td>-3.0</td>
</tr>
<tr>
<td>[CpW(H)(CO)$_3$]+</td>
<td>5.1</td>
</tr>
<tr>
<td>[CpRu(H)(CO)(PPh$_3$)$_3$]+</td>
<td>~4.5</td>
</tr>
</tbody>
</table>
Monodentate Anionic Ligands

Hammett constants \( \sigma_p \)\(^{31} \) indicate that \( \text{Me}^- (-0.17) \) is a better donor than \( \text{H}^- (0.00) \), thus, the \( \text{Os} \) in \( \text{OsH}_2\text{(Me)}\text{(CO)}_4 \) (\( \text{pK}_a^{\text{MeCN}} = 23.0 \)) is more basic than that in \( \text{OsH}_2\text{(CO)}_4 \) (\( \text{pK}_a^{\text{MeCN}} = 20.8 \)).\(^{32} \) However, the trend in the basicities of \( \text{IrY(CO)(PR}_3)_2 \) (\( \text{Y} = \text{Cl}, \text{Br}, \text{I} \)) complexes (see also, eq 5 and Table II)\(^{11} \) increases in the following order (eq 12):

\[
\text{IrCl}(\text{CO})(\text{PPh}_3)_2 < \text{IrBr}(\text{CO})(\text{PPh}_3)_2 < \text{IrI}(\text{CO})(\text{PPh}_3)_2 \quad (2.85) \quad (12)
\]

This is consistent with the trend in electronegativities (in parentheses) of the halides: \( \text{Cl}^- (3.16) > \text{Br}^- (2.96) > \text{I}^- (2.66) \).\(^{33} \) Also, Pearson has suggested\(^{2b} \) that the effects of halides and other anionic ligands on metal basicity should follow their relative trans directing abilities. Since the \( \text{I}^- \) ligand is a better trans directing group than the \( \text{Cl}^- \) ligand, its affinity for \( \text{H}^+ \) should also be greater. However, the order of \( \text{Me}^- \) and \( \text{H}^- \) above does not follow the same trend in the trans-effect series.\(^{2b} \) Clearly more studies of the behavior of anionic ligands on the basicities of metal complexes are needed.

Periodic Trends

The following order in \( \text{pK}_a^{\text{MeCN}} \) values indicates that metal basicity increases as one goes down a column of the periodic table:

\( \text{CpCrH(CO)}_3 \) (13.3) < \( \text{CpMoH(CO)}_3 \) (13.9) < \( \text{CpW(H(CO)}_3 \) (16.1).\(^{32} \) In group 8, there is a much larger difference in the \( \text{pK}_a^{\text{MeCN}} \) values.
between the first and second row elements: FeH₂(CO)₄ (11.4) < RuH₂(CO)₄ (18.7) < OsH₂(CO)₄ (20.8). Also, the Re in Re(H)(CO)₅ (pKₐ MeCN = 21.1) is more basic than the Mn in Mn(H)(CO)₅ (pKₐ MeCN = 15.1), and Cp₂Ru (H₀ = -5.7) is more basic than Cp₂Fe (H₀ = -7.7). Pearson and Kresge have shown a greater basicity for Ir than Rh in MY(CO)(L)₂ complexes (M = Ir, Rh; Y = Cl, Br, I; L = PPh₃, AsPh₃) in Table II (see also eq 5). The greater basicity of the heavier elements may be due to greater M-H bond strengths.

A few studies suggest that there are exceptions in the above trends as unpublished pKₐ MeOH values of M[P(OEt)₃]₄ show (see eq 4) that metal basicity increases in the order: M = Pd (0.7) < Ni (1.5) < Pt (10.2). Semiquantitative studies of group 9 complexes gave the following order listed by increasing metal basicity: Rh(H)(L)₄ < Co(H)(L)₄ < Ir(H)(L)₄, L = CO, PF₃. However, that Co(H)(dmgH)(P-n-Bu₃)₃ (pKₐ = 10.5, s = 50% aqueous MeOH/hexanes) has a higher pKₐ value than Rh(H)(dmgH)(PPh₃) (pKₐ = 9.5, s = 50% aqueous MeOH) is probably due to a combination of the stronger σ-donor ability of P-n-Bu₃ and the different solvent conditions in which pKₐ was measured.

On going across a row from left to right the trends in metal basicity are more difficult to discern as the molecular structures, number of ligands, and the metal's oxidation states often change. These trends do not appear to be well understood.
POLYMETALLIC HYDRIDE COMPLEXES

The few data available (Table V) indicate that the thermodynamic acidity of polynuclear hydrides are not much different from the monometallic complexes. Some of the trends parallel those for the mononuclear species. Thus, replacing the p-MeOC₆H₄ substituent (R) on the phosphorus in (µ-H)₂Fe₃(CO)₉(µ₃-PR) with the better donating t-Bu group raises the pKₐ MeCN value from 9.0 to 11.4.¹⁷b The isoelectronic cyclohexylthio-capped monohydride cluster, (µ-H)Fe₃(CO)₉(µ₃-SCy) is considerably less acidic (pKₐ MeCN = 16.9).¹⁷b Replacing a CO group with the stronger σ-donating and weaker π-accepting P(OMe)₃ group results in an increase in the pKₐ MeCN of H₄Ru₄(CO)₁₀[P(OMe)₃]ₙ (L = CO, P(OMe)₃) by 3.0 units.¹⁷b The relative increase in the pKₐ MeCN value for Co(H)(CO)₃(L) (L = CO, P(OPh)₃) was 3.0 units; since the P(OPh)₃ group is less electron donating than P(OMe)₃, this suggests that relative ligand effect in clusters are less than those observed in monometallic complexes. Caution is advised when interpreting the pKₐ MeOH values of H₄Ru(CO)₁₀(L)₂ (L = CO, P(OMe)₃),¹⁰b that were determined by a stopped-flow kinetic method, because Kristjándóttir¹⁷b and co-workers have shown that it is likely that the reaction being measured was that of a carbomethoxy anion formation (eq 13). The values listed in Table V are those redetermined by Kristjándóttir and co-workers.¹⁷b
\[ H_4Ru(CO)_{11}[P(OMe)_3] + MeO^- \rightleftharpoons H_4Ru_4(CO)_{10}(CO_2Me)[P(OMe)_3]^- \] (13)

Going down a column causes little change in the pK_a^{MeOH} values of H_4M_4(CO)_{12} complexes. Substitution of one Ru atom in H_4Ru_4(CO)_{12} (pK_a^{MeOH} = \sim 11.7)^{17b} by Fe to give H_4FeRu_3(CO)_{12} (pK_a^{MeOH} = 11.8)^{10b} has essentially no effect on cluster acidity. The pK_a^{MeOH} value of H_4Os_4(CO)_{12} (12.0)^{10b} is also similar.

The pK_a^{MeCN} values of H_2Os_2(CO)_{4} (20.8) and H_2Os_2(CO)_{8} (20.4) are approximately the same;^{32} however, the difference between the pK_a^{MeOH} values of H_2Os_3(CO)_{12} (14.7) and H_4Os_4(CO)_{12} (12.0) is large.^{10b} Although there are other substantial differences in the structures of these complexes only the Os_4 cluster has bridging hydride ligands. Walker suggested^{10b} that the Os_4 cluster is more acidic than the Os_3 cluster because the bridging hydride ligands leave a symmetrically delocalized polynuclear anion.

It is surprising that the anionic Rh cluster \([H_3Rh_{13}(CO)_{24}](PPN)_2\) which contains interstitial hydrides^{10a} is actually one of the most acidic polymetallic complexes (pK_a^{MeCN} = 11.0)^{10a}. The pK_a^{MeCN} value is comparable to that of FeH_2(CO)_{4} (11.4)^{17a}. However, the rate of deprotonation of one of the interstitial hydrides (1.2 x 10^{-3} M^{-1}s^{-1}) is 7 orders of magnitude slower than that of FeH_2(CO)_{4} (5.4 x 10^{4} M^{-1}s^{-1})^{10a}.

Removal of a second proton from the Rh_{13} cluster, above, is thermodynamically more difficult (pK_a^{MeCN} = 16.5) than the first.
This is also observed in the pK\textsubscript{a} values of H\textsubscript{3}Re\textsubscript{3}(CO)\textsubscript{12} (Table V) which are 3 for pK\textsubscript{a1}, 10 for pK\textsubscript{a2}, and 25 for pK\textsubscript{a3}.\textsuperscript{16a}
Table V. pKₐ values of polymetallic hydride complexes in various solvents

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<tr>
<th>complex</th>
<th>MeOH</th>
<th>MeCN</th>
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<th>ref</th>
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<tr>
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<td>16ᵃ</td>
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<tr>
<td>[H₂Re₃(CO)₁₂]⁻</td>
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<td>10ᵃ</td>
<td>16ᵃ</td>
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<td></td>
<td>25ᵃ</td>
<td>16ᵃ</td>
</tr>
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<td>(μ-H)₂Fe₃(CO)₉[μ₃-P(p-OMeC₆H₄)]</td>
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<td>17ᵇ</td>
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<tr>
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<td>17ᵇ</td>
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<td></td>
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</tbody>
</table>

ᵃSolvent not specified.
SECTION II. CALORIMETRIC DETERMINATION OF THE HEATS OF PROTONATION OF THE METAL IN (METHYL-SUBSTITUTED CYCLOPENTADIENYL)IRIDIUM COMPLEXES, Cp'\text{Ir}(1,5-COD)
ABSTRACT

Titration calorimetry has been used to determine the enthalpies of protonation ($\Delta H_{\text{HM}}$) of the iridium in the Cp'Ir(1,5-COD) (Cp' = C$_5$Me$_x$H$_{5-x}$, $x$ = 0, 1, 3-5) complexes according to the reactions, Cp'Ir(1,5-COD) + CF$_3$SO$_3$H (0.1 M) $\rightarrow$ [Cp'Ir(1,5-COD)]$^+$CF$_3$SO$_3^-$, at 25.0 °C in 1,2-dichloroethane. The $\Delta H_{\text{HM}}$ values become more exothermic from -22.8 ± 0.2 kcal mol$^{-1}$ for Cp' = C$_5$H$_5$ to -28.5 ± 0.2 kcal mol$^{-1}$ for C$_5$Me$_5$. A plot of $\Delta H_{\text{HM}}$ vs the number of Me groups on Cp' is linear; this result has been interpreted to indicate that the bulkiness of the Me group, even in the C$_5$Me$_5$ ligand probably does not affect the $\Delta H_{\text{HM}}$ values. Each Me group contributes -1.1 kcal mol$^{-1}$ to $\Delta H_{\text{HM}}$. Correlations between $\Delta H_{\text{HM}}$ and the COD olefin $^1$H NMR chemical shift of the protonated species are also made. Equilibrium studies for the protonation of Cp'Ir(1,5-COD) show that the effect of each added Me group on $\Delta G^\theta$ is -0.89 kcal mol$^{-1}$ and on $\Delta S^\theta$ is -0.7 eu. Thus, $\Delta S^\theta$ contributes little to the differences in equilibrium constants for protonation of the Cp'Ir(1,5-COD) complexes. A comparison of the common C$_5$H$_5$ and C$_5$Me$_5$ ligands shows that the replacement of C$_5$H$_5$ by C$_5$Me$_5$ increases the equilibrium constant for the protonation of Cp'Ir(1,5-COD) by 1900, makes $\Delta G^\theta$ more favorable by -4.5 kcal mol$^{-1}$, causes $\Delta H_{\text{HM}}$ to be more exothermic by -5.7 kcal mol$^{-1}$, and reduces $\Delta S^\theta$ slightly by ~-4 eu.
INTRODUCTION

Currently there is much interest in quantitative measures of the basicities of metals in transition metal complexes.¹ Yet few data are available for neutral complexes in which the ligands are systematically varied.¹⁺⁻ In this paper, we report the first of a series of such determinations by titration calorimetry in which the basicity is given as the enthalpy of protonation of the transition metal complex (ΔH<sub>HM</sub>) with triflic acid (CF<sub>3</sub>SO<sub>3</sub>H) in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1). Previously, Bush and Angelici reported

\[
\text{ML}_x + \text{CF}_3\text{SO}_3\text{H} \xrightarrow{\text{DCE}, 25.0 \degree \text{C}} H\cdot\text{ML}_x^+ \cdot \text{CF}_3\text{SO}_3^- \text{, } \Delta H_{\text{HM}} \quad (1)
\]

enthalpies of protonation (ΔH<sub>HP</sub>) of several organophosphines using this method.²

Among the types of ligands that are of special interest in organotransition metal chemistry are the cyclopentadienyl ligand (C<sub>5</sub>H<sub>5</sub>) and its methyl-substituted analogs (C<sub>5</sub>Me<sub>x</sub>H<sub>5-x</sub>, x=1-5). Elschenbroich and Salzer³ summarized some special properties of the pentamethylcyclopentadienyl ligand (C<sub>5</sub>Me<sub>5</sub>) as compared with C<sub>5</sub>H<sub>5</sub>. Properties that may affect the basicity of C<sub>5</sub>Me<sub>5</sub> complexes relative to their C<sub>5</sub>H<sub>5</sub> analogs are "stronger π-donor, weaker π-acceptor properties, increased covalent character of the cyclopentadienyl-metal bond, and kinetic stabilization effected by steric shielding of the metal center." Equilibrium acidities⁴ of
uncoordinated $\text{C}_5\text{Me}_5\text{H}$ and $\text{C}_5\text{H}_6$ in dimethyl sulfoxide solution show $\text{C}_5\text{Me}_5\text{H}$ ($pK_{HA} = 26.1$) to be considerably less acidic than $\text{C}_5\text{H}_6$ ($pK_{HA} = 18.0$). Differences in the donor abilities of coordinated $\text{C}_5\text{H}_5$ and $\text{C}_5\text{Me}_5$ ligands have been explored by a variety of techniques.$^{1,5,6}$ Gassman and co-workers$^5a$ showed by ESCA studies that the substitution of $\text{C}_5\text{H}_5$ by $\text{C}_5\text{Me}_5$ results in a "dramatic" lowering of the binding energies of the inner shell electrons of the metal. They found that the substitution of the two $\text{C}_5\text{H}_5$ ligands by two $\text{C}_5\text{Me}_5$ ligands results in an effective one electron reduction of the metal.$^5b$ Lowering of the core and valence ionization energies of the metal's electrons is attributed to an increase in electron density at the metal center caused primarily by the inductive effect of the methyl group on the Cp' ring.$^5c$ Miller and co-workers,$^5d$ however, studied the effect of $\text{C}_5\text{H}_5$ vs $\text{C}_5\text{Me}_5$ by $^{59}\text{Co}$ nuclear quadrupole resonance spectroscopy and concluded that the inductive effect of the permethylated ligand was small.

Perhaps the best available comparison of the effect of $\text{C}_5\text{H}_5$ vs $\text{C}_5\text{Me}_5$ on the basicity of a metal center is provided by Moore and co-workers.$^5e$ They determined $pK_a$'s of $\text{Cp'}\text{Mo(CO)}_3\text{H}$ and $\text{Cp'}\text{Fe(CO)}_2\text{H}$ ($\text{Cp'} = \text{C}_5\text{H}_5$, $\text{C}_5\text{Me}_5$) by deprotonation with organic bases for which the $pK_a$ values of the conjugate acids are known in acetonitrile solution. For the $\text{Cp'}\text{Mo(CO)}_3\text{H}$ complexes, the $\text{C}_5\text{Me}_5$ derivative was less acidic by 3.2 $pK_a$ units than the $\text{C}_5\text{H}_5$ analog. In the iron series ($\text{C}_5\text{Me}_5)$Fe(CO)$_2$H was 6.9 $pK_a$ units less acidic than ($\text{C}_5\text{H}_5$)Fe(CO)$_2$H.
No studies that investigate systematically the effect of methyl substitution in the cyclopentadienyl ligand on the proton basicity of a neutral metal center have been reported. In this paper we describe an investigation of the effects of methyl-substituted cyclopentadienyl ligands on the basicity of the iridium center in Cp'Ir(1,5-COD) complexes (Cp' = C₅H₅, C₅MeH₄, 1,2,3-C₅Me₃H₂, C₅Me₄H, C₅Me₅) by measuring heats of protonation (ΔH_HM) of the reactions shown in eq 2.

\[ \text{CF}_3\text{SO}_3^- + \text{Cp'Ir(1,5-COD)} \rightarrow \text{Cp'Ir}^{+} \text{CF}_3\text{SO}_3^- \]

\begin{align*}
1, \text{Cp'} & = \text{C}_5\text{H}_5 \\
2, \text{Cp'} & = \text{C}_5\text{MeH}_4 \\
3, \text{Cp'} & = 1,2,3-\text{C}_5\text{Me}_3\text{H}_2 \\
4, \text{Cp'} & = \text{C}_5\text{Me}_4\text{H} \\
5, \text{Cp'} & = \text{C}_5\text{Me}_5
\end{align*}

Also, competitive equilibrium studies for proton transfer between methyl-substituted Cp'Ir(1,5-COD) complexes have yielded values of \( K_{eq}, \Delta G^\circ \) and \( \Delta S^\circ \) for the reaction in eq 3. Comparisons of these thermodynamic quantities for the C₅H₅ and C₅Me₅ complexes permit a detailed discussion of their ligand properties as they affect the basicity of the metal.
In addition, protonation reactions of (indenyl)Ir(1,5-COD) (6), (HBPz₃*)Ir(1,5-COD) (7) (Pz* = 3,5-dimethyl-1-pyrazolyl), and (Me₃SiC₅H₄)Ir(1,5-COD) are reported.
EXPERIMENTAL

Argon and nitrogen gases were purified by passing them through a deoxygenation column containing a supported, activated Cu metal catalyst (R3-11, Chemical Dynamics Corporation) thermostated at 100 °C. This column was followed by a drying column (45 x 4.5 cm) packed with molecular sieves (Davison Type 4A, Fisher Scientific) which were treated at 350 °C at 10^-2 mm Hg for 12 hours prior to loading. All preparative reactions and manipulations (except as stated otherwise) were carried out under an atmosphere of nitrogen using Schlenk techniques similar to those described by McNally and co-workers. Hexanes and petroleum ether "A" (b.p. 28 °C) were refluxed over CaH2 and then distilled. The petroleum ether was stored over molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Deuteriochloroform was stored over molecular sieves in air or distilled from P4O10 under nitrogen. Neutral Al2O3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under high vacuum for 9 h, deactivated with 5% (w/w) N2-saturated water, and stored under N2.

The 1H, 2-D COSY 1H and 13C NMR spectra were recorded in CDCl3 on a Nicolet-NT 300 MHz spectrometer (except as stated otherwise) using TMS (δ = 0.00 ppm) and CDCl3 (δ = 77.0 ppm), respectively, as the internal references. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.
The preparations of \( \text{C}_5\text{Me}_5\text{Ir}(1,5\text{-COD}) \)\(^{11} \) (5) and \( \text{indenyl} \text{Ir}(1,5\text{-COD}) \)\(^{12} \) (6) have been described previously. Even though the synthesis of \( \text{C}_5\text{H}_5\text{Ir}(1,5\text{-COD}) \) (1) has been described elsewhere\(^{13} \) the route given below resulted in higher yields. The preparation is given in detail and serves as an example of the procedure for the synthesis of related new \( \text{Cp}^\prime\text{Ir}(1,5\text{-COD}) \) compounds, \( \text{HBPz}^*\text{Ir}(1,5\text{-COD}) \) (7) (Pz* is 3,5-dimethyl-1-pyrazolyl) and \( \text{Me}_3\text{SiC}_5\text{H}_4\text{Ir}(1,5\text{-COD}) \) (8).

**Preparation of \( \text{C}_5\text{H}_5\text{Ir}(1,5\text{-COD}) \) (1)**

Freshly cracked cyclopentadiene\(^{14} \) (0.22 mL, 2.7 mmol) was added to a suspension of freshly cut potassium metal (~0.1 g, ~3 mmol) in 30 mL of THF. The mixture was heated to reflux until all of the potassium reacted (~1 h). After cooling to room temperature \( \text{CllIr}(1,5\text{-COD}) \)\(^{15} \) (0.53 g, 0.79 mmol) was added, and the solution was heated to reflux for 1 h. The THF was then evaporated under vacuum, and the residue was extracted with 2 x 10 mL of hexanes. The hexanes solution was then passed through a 15 x 1.5 cm column of neutral alumina by eluting with hexanes. The colorless eluent was evaporated and the residue was dissolved in 10 mL of petroleum ether. After cooling to -40 °C (dry ice/acetonitrile) for 2 h, the resulting white precipitate was filtered and washed twice with 2 mL of petroleum ether (at -40 °C) and dried under vacuum for 10 minutes. The filtrate was evaporated further and cooled to -40 °C to give a second crop of the product 1; yield: 0.38 g, 66\%. The
compound was further purified by recrystallization from petroleum ether at -40 °C or sublimation at 60-80 °C, 10^-2 mm Hg. \(^1\)H NMR:\(^{13b}\) \(\delta\) 3.78 (br s, 4 H, \(=\text{CH, COD}\)), 2.03 (m, 4 H, exo-\(\text{CH}_2\), COD), 1.78 (pseudo-q, 4 H, endo-\(\text{CH}_2\), COD), 5.18 (s, 5 H, Cp). \(^{13}\)C(H) NMR: \(\delta\) 45.51 (\(=\text{CH, COD}\)), 33.85 (\(\text{CH}_2\), COD), 81.56 (Cp).

**Preparations of 2-4, 7, 8**

These previously unreported compounds were prepared by the stated modifications of the above procedure. Compounds 2-4, and 8 are white, but 7 is orange in color. They are all air-stable as solids and in solution.

\((\text{C}_5\text{MeH}_4)\text{Ir}(1,5\text{-COD})\) (2)

Methylcyclopentadiene was obtained by cracking the dimer.\(^{16}\) Sublimation of 2 was performed at 30 °C, 10^-2 mm Hg. Yield: 84%. Anal. Calcd for \(\text{C}_{14}\text{H}_{19}\text{Ir}\): C, 44.31; H, 5.05. Found: C, 44.04; H, 5.09. \(^1\)H NMR:\(^{17}\) \(\delta\) 3.56 (br s, 4 H, \(=\text{CH, COD}\)), 2.05 (m, 4 H, exo-\(\text{CH}_2\), COD), 1.80 (pseudo-q, 4 H, endo-\(\text{CH}_2\), COD), 5.18 (m, 2 H, H2, H5, Cp), 4.97 (t, \(2J = 3J = 1.9\) Hz, 2 H, H3, H4, Cp), 1.90 (s, 3 H, MeCp).

\((1,2,3\text{-C}_5\text{Me}_3\text{H}_2)\text{Ir}(1,5\text{-COD})\) (3)

The synthesis of 1,2,3-trimethylcyclopentadiene (9) involved a modification of a previously reported procedure.\(^{18a}\) The products of the reactions were determined by GC, IR and \(^1\)H NMR and their spectra can be found in the references cited. Oxidative coupling of
methylethylketone to form 3,4-dimethylhexane-2,5-dione (10) was performed as previously described.\textsuperscript{18b} The formation of 2,3,4-trimethylcyclopent-2-enone (11)\textsuperscript{18a} by intramolecular aldol condensation of 10 was performed using the same conditions employed in the preparation of 3-methylcyclopent-2-enone.\textsuperscript{18c} Finally, reduction of 11 with LiAlH\textsubscript{4} in Et\textsubscript{2}O by the procedure described for the reduction of cyclopent-2-enone\textsuperscript{18d} (excess LiAlH\textsubscript{4} was quenched by careful, dropwise addition of saturated, aqueous Na\textsubscript{2}SO\textsubscript{4}) followed by treatment with I\textsubscript{2} (see, for example, ref 18e) gave 9. It was isolated by vacuum transfer at room temperature, 10\textsuperscript{-2} mm Hg, with a liq. N\textsubscript{2}-cooled receiver in 9\% overall yield. The organometallic product 3 was sublimed at 60-80 °C, 10\textsuperscript{-2} mm Hg. Yield: 60\%. Anal. Calcd for C\textsubscript{16}H\textsubscript{23}Ir: C, 47.15; H, 5.68. Found: C, 47.19; H, 5.80. \textsuperscript{1}H NMR: \( \delta \) 3.16 (br s, 4 H, \(-\text{CH, COD})\), 2.03 (m, 4 H, exo-\text{CH\textsubscript{2}, COD}), 1.80 (pseudo-\text{q, 4 H, endo-CH\textsubscript{2}, COD}), 4.87 (s, 2 H, H\textsubscript{4}, H\textsubscript{5}, Cp), 1.91 (s, 3 H, 2-MeCp), 1.84 (s, 6 H, 1,3-Me\textsubscript{2}Cp). \textsuperscript{13}C\textsubscript{(H)} NMR: \( \delta \) 50.44 (\(-\text{CH, COD})\), 34.07 (CH\textsubscript{2}, COD), 96.76 (C2, Cp ring), 9.18 (2-MeCp), 95.14 (C1, C3, Cp ring), 10.84 (1,3-Me\textsubscript{2}Cp), 78.18 (C4, C5, Cp ring).

\((\text{C}_5\text{Me}_4\text{H})\text{Ir(1,5-COD)}\) (4)

The tetramethylcyclopentadiene was prepared from 2,3,4,5-tetramethylcyclopent-2-enone (Aldrich), as previously described.\textsuperscript{19} It was metalated with 1 equiv of \textit{n}-BuLi in THF. Sublimation of 4 at 60-80 °C (10\textsuperscript{-2} mm Hg) gave a 45\% yield. Anal. Calcd for C\textsubscript{17}H\textsubscript{25}Ir:
C, 48.43; H, 5.98. Found: C, 48.20; H, 5.99. $^1$H NMR: $\delta$ 2.90 (br s, 4 H, =CH, COD), 2.10 (m, 4 H, exo-CH$_2$, COD), 1.81 (pseudo-q, 4 H, endo-CH$_2$, COD), 5.06 (s, 1 H, Cp), 1.88 (s, 6 H, Me$_2$Cp), 1.73 (s, 6 H, Me$_2$Cp).

(C$_5$Me$_5$)Ir(l,5-COD) (5)

$^1$H NMR: $\delta$ 2.73 (m, 4 H, =CH, COD), 2.04 (m, 4 H, exo-CH$_2$, COD), 1.76 (pseudo-q, 4 H, endo-CH$_2$, COD), 1.83 (s, 15 H, Me$_5$Cp).
$^{13}$C(H) NMR: d 53.09 (=CH, COD), 34.16 (CH$_2$, COD), 92.10 (Cp ring), 9.20 (Me$_5$Cp).

(HBPz$^*$$_3$)Ir(l,5-COD) (7)

Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate, K(HBPz$^*$$_3$), was purchased from Columbia Organic Chemical. Compound 7 was obtained by chromatography on neutral alumina (15 x 1.5 cm) as an orange band eluting with Et$_2$O/hexanes (1:5). It was recrystallized from CH$_2$Cl$_2$/hexanes (1:10) at -40 °C. Yield: 60%. $^1$H NMR: $\delta$ 3.83 (br s, 4 H, =CH, COD), 1.95 (m, 4 H, exo-CH$_2$, COD), 1.35 (pseudo-q, 4 H, endo-CH$_2$, COD), 5.82 (s, 3 H, Pz$^*$H), 2.35 (s, 9 H, 3-MePz$^*$), 2.14 (s, 9 H, 5-MePz$^*$).

(Me$_3$SiC$_5$H$_4$)Ir(l,5-COD) (8)

Trimethylsilylcyclopentadiene was prepared using a literature procedure and was metalated with n-BuLi in THF. Yield of 8: 58%. $^1$H NMR: $\delta$ 3.74 (br s, 4 H, =CH, COD), 2.01 (m, 4 H, exo-CH$_2$,
COD), 1.76 (pseudo-\(q\), 4 H, endo-CH\(_2\), COD), 5.43 (t, \(2J = 3J = 1.8\) Hz, 2 H, Cp), 4.74 (t, \(2J = 3J = 1.8\) Hz, 2 H, Cp), 0.50 (s, 9 H, Me\(_3\)Si).

**Protonation Reactions**

Compounds 1-5 were protonated by dissolving approximately 50 mg of each compound in Et\(_2\)O (0 °C) and adding 1 equiv of CF\(_3\)SO\(_3\)H; a white precipitate formed immediately. Filtering the white precipitate and washing once with Et\(_2\)O (2 mL) and once with petroleum ether (2 mL) gave 1H\(^+\) - 5H\(^+\) as the CF\(_3\)SO\(_3\)\(^-\) salts. Only complex 1H\(^+\)PF\(_6\)\(^-\) was reported previously.\(^{23}\) The white powders can be handled in the air for short periods except for 4H\(^+\)CF\(_3\)SO\(_3\)\(^-\) which decomposes readily. Samples were stored under nitrogen or preferably under vacuum. Solutions of the salts in undried, non-de-aerated solvents discolored after ~1 h; therefore, all solvents used with the protonated complexes were de-aerated and dried. The compounds were characterized by NMR spectroscopy (refer to text for explanation of assignments for 1H\(^+\) - 5H\(^+\)). A 3-5 second pulse delay was used while obtaining proton spectra in order to ensure complete relaxation of all protons and accurate integrations. An elemental analysis was performed on 1H\(^+\)CF\(_3\)SO\(_3\)\(^-\). The data for each of these complexes are as follows:

\[
[(C_5H_5)Ir(H)(1.5-COD)](CF_3SO_3)(1H^+CF_3SO_3^-)
\]

Yield: 78%. Anal. Calcd for C\(_{14}\)H\(_{18}\)F\(_3\)IrO\(_3\)S: C, 32.59; H, 3.52. Found: C, 32.63; H, 3.42. ¹H NMR: δ 5.43 (m, 2 H, H\(_B\), COD), 4.52 (m, 2 H, H\(_A\), COD), 2.5 (m, 4 H, H\(_Y\), H\(_X\), COD), 2.39 (m, 2 H, H\(_X\)′,
COD), 2.27 (pseudo-q, 2 H, H_2 COD), 6.02 (s, 5 H, Cp), -11.79 (s, 1 H, Ir-H).  
^{13}\text{C}(\text{H}) \text{NMR}: \delta 71.27 (=\text{CH}, \text{COD}), 69.17 (=\text{CH}, \text{COD}), 32.85 (\text{CH}_2, \text{COD}), 31.61 (\text{CH}_2, \text{COD}), 88.35 (\text{Cp}).

[[\text{C}_5\text{Me}_4\text{H}]\text{Ir(H)(1,5-COD)}][\text{(CF}_3\text{SO}_3)] (2\text{H}^+\text{CF}_3\text{SO}_3^-)

Yield: 86%. \text{^1H NMR:} \delta 5.01 (m, 2 H, H_B, COD), 4.43 (m, 2 H, H_A, COD), 2.50 (m, 6 H, H_Y, H_X, H_X', COD), 2.26 (pseudo-q, 2 H, H_Y', COD), 5.81 (s, 2 H, H_2, H_5, Cp), 5.73 (s, 2 H, H_3, H_4, Cp), 2.21 (s, 3 H, MeCp), -11.89 (s, 1 H, Ir-H). \text{^{13}C NMR (proton coupled):} \delta 73.32 \text{ (d, } J_{\text{CH}} = 159 \text{ Hz, } =\text{CH, COD}), 69.66 \text{ (d, } J_{\text{CH}} = 166 \text{ Hz, } =\text{CH, COD}), 32.60 \text{ (t, } J_{\text{CH}} = 132 \text{ Hz, CH}_2, \text{COD}), 31.80 \text{ (t, } J_{\text{CH}} = 134 \text{ Hz, CH}_2, \text{COD}), 109.46 \text{ (s, C1, Cp ring)}, 12.47 \text{ (q, } J_{\text{CH}} = 129 \text{ Hz, MeCp), 87.71 \text{ (dm, } 1^\text{J_{CH}} = 186 \text{ Hz, C2, C5, Cp ring) 86.44 (dd, } 1^\text{J_{CH}} = 186 \text{ Hz, } 2^\text{J_{CH}} = 6.5 \text{ Hz, C3, C4, Cp ring).}

[[\text{1,2,3-C}_5\text{Me}_3\text{H}_2]\text{Ir(H)(1,5-COD)}][\text{(CF}_3\text{SO}_3)] (3\text{H}^+\text{CF}_3\text{SO}_3^-)

Yield: 58%. \text{^1H NMR:} \delta 4.47 (m, 2 H, H_B, COD), 4.32 (m, 2 H, H_A, COD), 2.55 (m, 2 H, H_Y, COD), 2.41 (m, 4 H, H_Y', H_X, COD), 2.21 (pseudo-q, 2 H, H_X', COD), 5.76 (s, 2 H, H_4, H_5, Cp), 2.17 (s, 6 H, 1,3-Me_2Cp), 2.07 (s, 3 H, 2-MeCp), -12.04 (s, 1 H, Ir-H).

[[\text{C}_5\text{Me}_4\text{H}]\text{Ir(H)(1,5-COD)}][\text{(CF}_3\text{SO}_3)] (4\text{H}^+\text{CF}_3\text{SO}_3^-)

Yield: 86%. \text{^1H NMR:} \delta 4.27 (m, 2 H, H_B, COD), 4.16 (m, 2 H, H_A, COD), 2.55 (m, 2 H, H_Y, COD), 2.41 (m, 4 H, H_Y', H_X, COD), 2.20 (pseudo-q, 2 H, H_X', COD), 5.88 (s, 1 H, Cp), 2.11 (s, 6 H, Me_2Cp), 2.07 (s, 6 H, Me_2Cp), -12.02 (s, 1 H, Ir-H).
[(C₅Me₅)Ir(H)(1,5-COD)][(CF₃SO₃) (5H⁺CF₃SO₃⁻)]

Yield: 66%. ¹H NMR: δ 4.04 (br m, 4 H, H₂, H₆, COD), 2.54 (m, 2 H, H₆, COD), 2.36 (m, 4 H, H₆, H₆, COD), 2.17 (pseudo-q, 2 H, H₆, COD), 2.02 (s, 15 H, Me₅Cp), -12.09 (s, 1 H, Ir-H). ¹³C{H} NMR: δ 78.34 (=CH, COD), 71.28 (=CH, COD), 32.14 (CH₂, COD), 31.49 (CH₂, COD), 100.87 (Cp ring), 9.48 (Me₅Cp).

The following protonation reactions proceeded differently from those for compounds 1-5.

Reaction of 6 with CF₃SO₃H

An excess of triflic acid (~2 equiv) was added to a solution of 6 (4.7 mg) in 0.5 mL of CDCl₃ or CD₂Cl₂ yielding a bright red solution. The ¹H NMR spectrum revealed a transient Ir-H resonance (-13.3 ppm in CDCl₃) which disappeared after 15 min. The final product, [(η⁶-indene)Ir(1,5-COD)][(CF₃SO₃), was characterized spectroscopically; however, no attempt was made to isolate it. Assignment of the η⁶-indene resonances are based on those made for [(η⁶-indene)Rh(C₂H₄)₂]BF₄²⁵a (see eq 5 for numbering scheme). ¹H NMR (CD₂Cl₂): δ 6.73 (d, J₁₂ = 5.2 Hz, 1 H, H₁), 7.03 (br s, 1 H, H₁), 3.21 (d, J₃₄ = 24.3 Hz, 1 H, H₃), 2.64 (d, 1 H, H₃'), 7.32 (d, J₄₅ = 6 Hz, 1 H, H₄), 6.24 (t, J₅₄ = J₅₆ = 6 Hz, 1 H, H₅), 6.50 (t, J₅₆ = J₆₇ = 6 Hz, 1 H, H₆), 7.23 (d, 1 H, H₇), η⁶-indene; 4.18 (m, 2 H, =CH, COD), 3.95 (m, 2 H, =CH, COD), 2.21-1.99 (br m, 8 H, CH₂, COD).
Reaction of 7 with CF$_3$SO$_3$H

The protonation was performed in CDCl$_3$ but no hydride resonance was detected; however, a resonance at 12.92 ppm was attributed to protonation of a pyrazolyl nitrogen to give \[\{[(\eta^2-\text{HBPz}^*)_2(\text{Pz}^*)\text{H}]\text{Ir}(1,5-\text{COD})\}(\text{CF}_3\text{SO}_3).\] $^1$H NMR: $^{20a} \delta$ 12.92 (s, 1 H, Pz-H), 6.19 (s, 1 H, Pz*, H4), 5.96 (s, 2 H, $\eta^2$-Pz*, H4), 2.54 (s, 3 H, 3-Pz*Me), 2.47 (s, 3 H, 5-Pz*Me), 2.41 (s, 6 H, $\eta^2$-3-Pz*Me), 2.36 (s, 6 H, $\eta^2$-5-Pz*Me), 4.31 (m, 2 H, =CH, COD), 3.62 (m, 2 H, =CH, COD), 2.2-1.9 (br m, 8 H, CH$_2$, COD).

Reaction of 8 with CF$_3$SO$_3$H

The protonation was done in Et$_2$O as described for compounds 1-5. The product was identified by its $^1$H NMR spectrum as $^1$H$^+$CF$_3$SO$_3^-$ (40% yield) by comparison with an authentic sample.

Calorimetry Studies

The determinations of the heats of protonation of the Cp'Ir(1,5-COD) compounds were performed using a Tronac Model 458 isoperibol calorimeter as previously described.$^2$ The only modifications of the procedure were that triflic acid was purchased from 3M Co. and both triflic acid and 1,2-dichloroethane (DCE) were distilled under argon instead of nitrogen. The preparation and standardization of the acid solution were also performed under an argon atmosphere.
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 standardized 0.1 M (± 0.2 mM) CF₃SO₃H solution in DCE at a constant rate during 3 minutes time to 50 mL of a 2.6 mM solution of Cp'Ir(1,5-COD) (~10% excess) in DCE. The Cp'Ir(1,5-COD) solutions were prepared by adding solid compound to an argon-filled Dewar flask. The flask was then attached to the calorimeter's insert assembly, flushed with argon, and 50 mL of DCE was added by syringe. The reaction enthalpies were corrected for the heat of dilution (ΔH_dil) of the acid in DCE (-0.2 kcal mol⁻¹), see below.

Readers interested in further experimental details and data analysis should refer to reference 2.

The value for ΔH_dil has been redetermined. The previous measurement of this quantity was complicated by traces of H₂O in the reaction vessel. This was remedied by turning the buret on for 1 minute prior to data collection, in effect, neutralizing the adventitious H₂O base. The time of the titration period was reduced to 2 minutes instead of 3 minutes. Three determinations with 2 different acid solutions (0.1059 M and 0.1047 M) were done giving an average ΔH_dil value of -0.24 ± 0.02 kcal mol⁻¹ which compares with -0.32 kcal mol⁻¹ reported earlier. Note that this value is very close to the experimental error in the titrations.
To ensure reproducibility of the determined $\Delta H_{HM}$ values, at least two different standardized acid solutions were used for titrations of each compound. The $\Delta H_{HM}$ values are reported as the average of at least 4 titrations, and as many as 8, for each compound. The error is reported as the average deviation from the mean of all the determinations.

The accuracy of the calorimeter was monitored periodically by titration of 1,3-diphenylguanidine (GFS Chemicals) with CF$_3$SO$_3$H in DCE (-36.9 ± 0.2 kcal mol$^{-1}$, 24 measurements; literature value$^2$ -37.2 ± 0.4 kcal mol$^{-1}$) or tris(hydroxymethyl)aminomethane (THAM, Fisher Scientific) with HCl in water (-11.6 ± 0.1 kcal mol$^{-1}$; literature value$^{26}$ -11.33 kcal mol$^{-1}$).

**Equilibrium Studies**

In a typical experiment, 21.4 mg (0.0384 mmol) of 3H$^+\text{CF}_3\text{SO}_3^-$, 11.3 mg (0.0268 mmol) of 4 (eq 3b) and 10.4 mg (0.0426 mmol) of the internal standard Ph$_3$CH were added to an NMR tube. Deuteriochloroform (~0.6 mL) was condensed into the tube using a liquid N$_2$ trap, and the tube was flame sealed under vacuum. The $^1$H NMR spectrum was taken at 298 K with a Bruker WM 200 NMR spectrometer using the methyl proton of Ph$_3$CH (5.55 ppm) as the internal reference. We observed that no changes in the spectrum occurred with time indicating that equilibrium was readily achieved, at least within 5 minutes. A 10 second pulse delay was
used to ensure complete relaxation of all the protons and 128 scans were taken.

The expression (eq 4) used for the calculation of the equilibrium constant, $K_{eq}$, is based on the reactions given in eq 3. The relative concentrations of the

$$K_{eq} = \frac{[\text{Cp}'\text{Ir(COD)}][\text{Cp}''\text{Ir(H)(COD)}^+]}{[\text{Cp}'\text{Ir(H)(COD)}^+][\text{Cp}''\text{Ir(COD)}]} \quad (4)$$

species present at equilibrium were calculated based on integrations of the COD olefin, Ir-H, and the Cp' ring proton NMR resonances of each particular species. Proton transfer is sufficiently slow that $^1\text{H}$ NMR signals for all four complexes are present in the spectrum. Only those resonances that were well separated from other resonances were integrated. When more than one resonance attributable to a single species was integrated, the calculated concentrations were averaged. For each experiment the mass balance was checked against the internal reference. We estimate that there is a possible 10% error in the equilibrium constants.

The equilibrium for eq 3b ($3\text{H}^+\text{CF}_3\text{SO}_3^-$, 20.9 mg, 0.0375 mmol; 4, 11.7 mg, 0.0278 mmol) was also performed in d$_4$-DCE (MSD Isotopes) but because of changes in the chemical shifts of the species present Ph$_3$CH was an ineffective standard. Therefore, the relative concentrations of the species present could be calculated but the mass balance could not be checked. For the equilibrium in eq 3a ($1\text{H}^+\text{CF}_3\text{SO}_3^-$, 25.1 mg, 0.0487 mmol; 2, 13.8 mg, 0.0364
mmol) the standard used was ferrocene (4.14 ppm, 2.3 mg, 0.012 mmol). For eq 3c the equilibrium experiment was performed by mixing known quantities of $5H^+\text{CF}_3\text{SO}_3^-$ (29.1 mg, 0.0497 mmol) and 4 (15.6 mg, 0.0370 mmol) with the Ph$_3$CH (11.7 mg, 0.0479 mmol) standard.
RESULTS

Characterization of Reactants and Products in Equation 2

Several preparations of 1 have been reported previously including the synthesis from NaC₅H₅ and [ClIr(1,5-COD)]₂. However, no experimental details for the latter preparation are given. We describe the synthesis of 1 from KC₅H₅ and [ClIr(1,5-COD)]₂ in 66% yield which is higher than yields (< 50%) previously reported. Analogous Cp'Ir(1,5-COD) complexes, 2-4, 7, 8, are also prepared in 45-84% yields by reaction of [ClIr(1,5-COD)]₂ with the respective cyclopentadienide salt in refluxing THF. The use of potassium metal or n-BuLi as the metallating agent (see Experimental) circumvents the inconvenience of preparing finely dispersed sodium metal. (Note, potassium melts in refluxing THF; therefore, a clean reaction surface is constantly obtained.) The products are characterized by their ¹H NMR and in some cases ¹³C NMR spectra (see Experimental). The assignments of the 1,5-COD ligand resonances are based on assignments made for [Rh(1,5-COD)(CH₂(Pz)₂)]ClO₄ (Pz = pyrazolyl). In particular, it is shown for the methylene backbone of the ligand that the downfield multiplet corresponds to the exo methylene protons (shown as X and Y, Figure 1A for the related [Cp'Ir(H)(1,5-COD)]⁺ derivative) and the upfield pseudo-quartet corresponds to the endo methylene protons (X' and Y' in Figure 1A).
The reaction of 1-5 with CF$_3$SO$_3$H in diethyl ether results in precipitation of the white protonated products 1H$^+$CF$_3$SO$_3^-$ - 5H$^+$CF$_3$SO$_3^-$ . Resonances are observed in the $^1$H NMR spectra between -11.79 ppm for 1H$^+$ and -12.09 ppm for 5H$^+$, typical of a metal hydride.$^{29}$ The protonated species are isolated in 58-86% yields; however, when the protonation reactions are carried out in CDCl$_3$ solution (~0.5 mL) by addition of one equiv of CF$_3$SO$_3$H to the neutral complexes, quantitative formation of 1H$^+$ - 5H$^+$ is observed by $^1$H NMR. When the CDCl$_3$ solutions are air-free, no changes in the $^1$H NMR spectra of the protonated species are observed over a period of at least 24 h. Quantitative deprotonation of 1H$^+$ - 5H$^+$ to form neutral compounds 1-5, respectively, is observed by $^1$H NMR when 1 equiv of 1,3-diphenylguanidinium base is added to the above CDCl$_3$ solutions.

It was important to establish that these complexes undergo protonation at the metal center forming Ir-H bonds with no subsequent proton transfer to the 1,5-COD ligand, formation of agostic C-H interactions, or isomerization of the 1,5-COD diene ligand. The structures of the protonated products 1H$^+$ - 5H$^+$ were investigated by various NMR methods. The Ir-H resonance integrates as 1H for each species. Previously,$^{23}$ the protonated product 1H$^+$ was formulated with an isomerized 1,3-COD diene ligand. Our $^1$H NMR data for 1H$^+$CF$_3$SO$_3^-$ are nearly identical to those previously reported; however, further consideration of the $^1$H, $^{13}$C NMR and a 2-D COSY $^1$H NMR experiment indicates that the
formulation is more likely $[(\text{C}_5\text{H}_5)\text{Ir}(\text{H})(1,5-\text{COD})]\text{CF}_3\text{SO}_3$, without an isomerized diene. Attempts to grow crystals of $1\text{H}^+\text{CF}_3\text{SO}_3^-$ suitable for X-ray diffraction studies were unsuccessful.

Distinction between the two types of COD coordination is not trivial because both coordinated ligands have a $\sigma_v$ plane of symmetry (Figure 1). Each type should exhibit six signals corresponding to $H_A$, $H_B$, $H_X$, $H_{X'}$, $H_Y$, and $H_{Y'}$, in the $^1\text{H}$ NMR spectrum and four signals for $C_A$, $C_B$, $C_X$, and $C_Y$ in the $^{13}\text{C}$ NMR spectrum. The previous authors$^{23}$ made the 1,3-COD structural assignment on the basis of double irradiation experiments which in our hands led to ambiguous results. The authors also claimed that "the isomerization of the octadiene ligand must occur without incorporation of D+".

![Figure 1](image)

Figure 1. (A) 1,5-COD coordination to Cp'lrH+ or (B) 1,3-COD coordination. Protons X and Y are exo; protons X' and Y' are endo.
when protonation was done with CF₃COOD. We find this hard to believe because if such an isomerization were to occur, it is likely that it would involve migration of D⁺ to an olefinic carbon; consequently, incorporation of deuterium should occur (for example, the protonation of (C₅H₅)Rh(1,5-COD) gives [(C₅H₅)Rh(1,3,4-η³-C₈H₁₃)]PF₆). Furthermore, protonation of Cp'Ir(1,3-diene) (Cp' = C₅H₅, C₅Me₅; 1,3-diene = butadiene, 2,3-dimethylbutadiene, 1,3-cyclohexadiene) at room temperature gives products with fluxional NMR spectra consistent with the formation of η³-allyl intermediates which are stabilized by an agostic C-H bond. Only upon cooling are the classical hydride structures seen in the NMR spectra. In view of this reactivity it is unlikely that a species such as [(C₅H₅)Ir(H)(1,3-COD)]⁺ would have a stable Ir-H bond at room temperature.

An examination of the differences in chemical shifts between ¹H and ¹³C NMR resonances at positions A and B (see Figure 1), given as ¹Δ⁵Hₐₕₜₑₜ and ¹Δ¹³Cₜ₁₂, usually show greater Δ values for 1,3-COD complexes than for asymmetric 1,5-COD complexes. Four 1,3-COD complexes found in the literature give ¹Δ⁵Hₐₜ values from 1.43 to 2.02, and three of these complexes give ¹Δ¹³Cₜ₁₂ values which range from 28.6 to 35.5. Kruczynski and Takats have also noted a significant difference between the ¹³C chemical shifts of outer carbons (Figure 1B, C_A) and inner carbons (Figure 1B, C_B) of conjugated diene complexes of iron. Consideration of a total of 33 asymmetric 1,5-COD complexes gives ¹Δ⁵Hₐₜ values in the range 0.2-1.7 (average = 0.77) and ¹Δ¹³Cₜ₁₂ values in the range 0.6-
28.2 (average = 4.5). The $|\Delta^{1} H_{AB}|$, $|\Delta^{13} C_{AB}|$ values for $1H^{+}$ are 0.91 and 2.1, respectively. In fact, for compounds $2H^{+} - 5H^{+}$ the $|\Delta^{1} H_{AB}|$ values are found between 0.58 and 0. The $|\Delta^{13} C_{AB}|$ values for $2H^{+}$ and $5H^{+}$ are 3.66 and 7.06, respectively. Furthermore, ($C_{5}H_{5})Ru(H)(1,5-COD)$, which is isoelectronic with $1H^{+}$, is known to have 1,5-COD coordination and has a $|\Delta^{1} H_{AB}|$ value of 0.6 and a $|\Delta^{13} C_{AB}|$ value of 1.4. The crystal structure of ($C_{5}Me_{5})Ru(H)(1,5-COD)$ has been reported recently, the $|\Delta^{1} H_{AB}|$ and $|\Delta^{13} C_{AB}|$ values are 0.3 and 8, respectively. The $\Delta$ values for the ruthenium complexes are within the range for 1,5-COD complexes. Our results also suggest that $1H^{+}$ as well as $2H^{+} - 5H^{+}$ are 1,5-COD complexes because the $\Delta$ values clearly fall within the asymmetric 1,5-COD complex ranges but not in the higher ranges for 1,3-COD complexes.

Also the 2-D COSY $^{1}H$ NMR spectrum of $1H^{+}$ shows $^{1}H-^{1}H$ coupling more indicative of a 1,5-COD structure. One cross peak connects the 5.43 ppm ($H_{B}$) resonance to the left side of the broad multiplet at 2.5 ppm, and another cross peak connects the 4.52 ppm ($H_{A}$) resonance to the right side of the 2.5 ppm multiplet. This indicates that the multiplet at 2.5 ppm consists of two different types of protons coincidently overlapped. There is also a weak cross peak connecting 5.43 and 2.27 ppm. The pattern is typical for coordinated 1,5-COD; in particular, it has been shown that the olefin protons in 1,5-COD ligands couple strongly to the cis, exo methylene protons (assigned as $H_{Y}$ to the left side and $H_{X}$ to the right side of the resonance at 2.5 ppm) and weakly, if at all, to the
trans, endo methylene protons (assigned as H_Y and H_X' to 2.27 and 2.39 ppm, respectively). We note that 2.27 and 2.39 ppm share cross peaks with 2.5 ppm but they do not share a cross peak between themselves. This supports their assignment as H_Y and H_X' because they are separated by 5 bonds. We find these assignments for the 1,5-COD coordination more consistent than any probable assignments for the 1,3-COD coordination type. The CH_2 COD resonances of 2H^+ have been assigned analogously because of their similarity to 1H^+.

The ^1H NMR resonances of the CH_2 COD protons of 5H^+ are slightly different than those in 1H^+; therefore, a similar 2-D COSY experiment was performed with 5H^+. The broad multiplet at 4.04 ppm is assigned to olefin protons H_B (left side) and H_A (right side), see Figure 1A. The resonance at 2.54 ppm is connected to the left side of 4.04 (H_B) by a cross peak and thus assigned to H_Y. The multiplet at 2.36 ppm which integrates as 4 H shares a cross peak between its right side and the right side of 4.04 ppm (H_A) and thus 2 H's of the 4 H's are assigned to H_X. A cross peak between 2.54 and 2.36 ppm permits H_Y to be assigned to the remaining 2H's of 2.36 ppm. And the 2.17 ppm resonance is assigned to H_X' because there is a cross peak connecting that resonance with 2.36 ppm. However, there is no cross peak between the 2.17 ppm and 2.54 ppm signals. Again, we find these assignments for 1,5-COD coordination more consistent than any probable assignments for 1,3-COD coordination. Furthermore, because of the similarity between the CH_2 COD proton
resonances of $5\text{H}^+$ to those of $3\text{H}^+$ and $4\text{H}^+$ analogous assignments have been made.

We note that we cannot unequivocally assign the resonances of the olefin protons $H_A$ (and therefore, $H_X$, $H_X'$) or $H_B$ (and therefore, $H_Y$, $H_Y'$) to those up toward the cyclopentadienyl ring or those down and close to the hydride ligand as they are drawn in Figure 1A.

No evidence was found for the formation of an agostic type C-H interaction with the metal which may have resulted from protonation of the COD olefin.\textsuperscript{37} Normal chemical shifts are observed for the COD olefin and methylene groups in the $^1\text{H}$ NMR spectra of $1\text{H}^+ - 5\text{H}^+$ and in the $^{13}\text{C}$ NMR spectra of $2\text{H}^+$ and $5\text{H}^+$. In addition, the proton coupled $^{13}\text{C}$ NMR spectrum of $2\text{H}^+$ was investigated as low values for $J_{\text{CH}}$ are diagnostic of agostic CH interactions.\textsuperscript{38} However, normal coupling constants for the COD sp\textsuperscript{2} carbons ($J_{\text{CH}} = 159$ Hz and 166 Hz) and the sp\textsuperscript{3} carbons ($J_{\text{CH}} = 132$ Hz and 134 Hz) were found.\textsuperscript{39}

The protonation reactions of 6-8 proceed differently than those of compounds 1-5. Protonation of (indenyl)Ir(1,5-COD) (6) in CDCl\textsubscript{3} gives a transient Ir-H resonance at -13.3 ppm probably due to $[(\eta^5\text{-indenyl})\text{Ir(H)(1,5-COD)}]\text{CF}_3\text{SO}_3$ (see eq 5) but this resonance disappears within 15 minutes. The resulting product has $^1\text{H}$ resonances which are indicative of an $\eta^6$-indenene complex\textsuperscript{25} (see Experimental). A very similar reaction is reported by Clark and co-workers\textsuperscript{25a} for the protonation of $(\eta^5\text{-indenyl})\text{Rh(C}_2\text{H}_4)_2$ with HBF\textsubscript{4}•Et\textsubscript{2}O. Our data suggest that the proton is transferred from the
metal to the indenyl ligand resulting in an $\eta^5$ to $\eta^6$ haptotropic rearrangement forming $[(\eta^6\text{-indenyl})\text{Ir}(1,5\text{-COD})]\text{CF}_3\text{SO}_3$ (eq 5).

\[
\begin{align*}
6 & \xrightarrow{\text{CF}_3\text{SO}_3\text{H}} [\text{\begin{tikzpicture}[scale=0.5]
  \draw[thick, black] (0,0) -- (2,0) -- (2,2) -- (0,2) -- cycle;
  \draw[thick, black] (0,0) -- (0,2);
  \draw[thick, black] (2,0) -- (2,2);
  \draw[thick, black] (0,0) -- (2,0);
  \draw[thick, black] (0,2) -- (2,2);
  \node at (1,1) {H-Ir(COD)};
\end{tikzpicture}}] ^+ \\
& \rightarrow [\text{\begin{tikzpicture}[scale=0.5]
  \draw[thick, black] (0,0) -- (2,0) -- (2,2) -- (0,2) -- cycle;
  \draw[thick, black] (0,0) -- (2,2);
  \draw[thick, black] (0,0) -- (0,2);
  \draw[thick, black] (2,0) -- (2,2);
  \draw[thick, black] (0,0) -- (0,2);
  \node at (1,1) {Ir(COD)};
\end{tikzpicture}}] ^+ 
\end{align*}
\]

Protonation of $(\text{HBPz}^*3)\text{Ir}(1,5\text{-COD})$ (7) does not give a detectable Ir-H resonance in the $^1\text{H}$ NMR spectrum; however, a resonance which integrates as 1 H is found at 12.92 ppm. This is attributed to protonation of a pyrazolyl nitrogen yielding $[(\eta^2\text{-HBPz}^*2)(\text{Pz}^*\text{H})]\text{Ir}(1,5\text{-COD})]\text{CF}_3\text{SO}_3$. Ball and co-workers$^{20a}$ have obtained a similar rhodium complex by protonation of $(\eta^3\text{-HBPz}^*3)\text{Rh}(\text{CO})_2$ with $\text{HBF}_4\cdot\text{Et}_2\text{O}$. Surprisingly, they also observed that protonation of $(\eta^3\text{-HBPz}^*3)\text{Ir}(\text{CO})_2$ occurs at the Ir.$^{20a}$

Reaction of $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Ir}(1,5\text{-COD})$ (8) with $\text{CF}_3\text{SO}_3\text{H}$ in $\text{Et}_2\text{O}$ gives a white precipitate but the product is identified to be $1\text{H}^+\text{CF}_3\text{SO}_3^-$ (40% yield) by $^1\text{H}$ NMR. Apparently, the reaction occurs by protodesilylation$^{40}$ followed by protonation of iridium (or vice versa), which requires overall two equiv of acid per equiv of 8.

Compounds 6-8 were not studied calorimetrically because clean protonation at the metal center does not occur.
Calorimetric and Equilibrium Studies

Heats of protonation determined by calorimetric titration of the Cp'Ir(1,5-COD) complexes with CF$_3$SO$_3$H in 1,2-dichloroethane (DCE) at 25.0 °C according to eq 2 are presented in Table I. The titrations of the organometallic compounds went cleanly. We observed no side reactions prior to the start of the titration or after the titration was completed as evidenced by normal baseline slopes in these periods. As expected, the titrations displayed a linear increase in temperature with acid addition indicating stoichiometric reaction of the compounds with the acid. There was also an immediate temperature response upon addition of the acid indicating that the kinetics of the protonation reactions were fast. Usually the final titrated solutions of the iridium complexes were colorless; however, occasionally a slight tinge of brown or yellow was detected. The $\Delta H_{\text{HM}}$ values were the same within experimental error whether or not the product solution was slightly colored. Analysis of the resultant titrate solutions by $^1$H NMR spectroscopy after removal of the DCE solvent revealed only the protonated species, and a trace of the unprotonated species due to the presence of a slight excess of the starting material in the reaction.

Because DCE has a low dielectric constant ($\epsilon = 10.36$) the products formed in eq 1 probably occur as ion pairs. Dissociation of these ion pairs, and autoprotolysis and dimerization of the acid are other reactions which may occur in nonpolar solvents such as DCE.
An analysis of these factors was presented in the phosphine basicity study; it was concluded that they contribute less than 2% to the total $\Delta H_{HP}$ value. Presumably these reactions also contribute negligibly to $\Delta H_{HM}$ values in the current study.

The results of the competitive equilibrium studies at 25.0 °C between two methyl-substituted Cp'Ir(1,5-COD) complexes (eq 3) are given in Table II. The equilibria between $1H^+$ and 2 (eq 3a), and $5H^+$ and 4 (eq 3c) were studied in CDCl₃, while the $3H^+/4$ equilibrium (eq 3b) was studied in both CDCl₃ and d₄-DCE. An error of 10% is estimated for each $K_{eq}$; therefore, the $K_{eq}$ values in all four studies, including that in d₄-DCE, are approximately the same within experimental error. Values of $\Delta G^\circ$ were calculated ($\Delta G^\circ = -RT \ln K_{eq}$) from the $K_{eq}$ values. Because of the similarity of the $K_{eq}$ values for the $3H^+/4$ equilibrium (eq 3b) in CDCl₃ and d₄-DCE, we combined ($\delta \Delta H_{HM} = \Delta G^\circ + TAS^\circ$) relative $\Delta H_{HM}$ values ($\delta \Delta H_{HM} = -1.1$ kcal mol⁻¹) in DCE and $\Delta G^\circ$ values in CDCl₃ to obtain the $\Delta S^\circ$ of each reaction. An error of ± 0.06 kcal mol⁻¹ in $\Delta G^\circ$ is obtained from the corresponding estimated error in $K_{eq}$ and the error in $\delta \Delta H_{HM}$ is estimated to be ± 0.2 kcal mol⁻¹. Although the estimated error (±0.7 eu) in $\Delta S^\circ$ is as large as $\Delta S^\circ$ itself, values for the four reactions (Table II) are consistently negative. Thermodynamic constants for the equilibrium between $1H^+CF_3SO_3^-$ and 5 (eq 3d) are calculated from the average $K_{eq}$ values in Table II, and $\Delta H_{HM}$ values in Table I. This allows the effect of $C_5Me_5$ vs $C_5H_5$ on the basicity of iridium to be
discussed in terms of $\Delta H_{HM}$, $\Delta G^\circ$, and $\Delta S^\circ$; the data are summarized in Table II.
Table I. Heats of protonation ($\Delta H_{HM}$) of Cp'Ir(1,5-COD) complexes\(^a\)

<table>
<thead>
<tr>
<th>Cp'Ir(1,5-COD)</th>
<th>$-\Delta H_{HM}$ kcal mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_5H_5)Ir(COD)$, 1</td>
<td>22.8 (±0.2)(^b)</td>
</tr>
<tr>
<td>$(C_5MeH_4)Ir(COD)$, 2</td>
<td>24.1 (±0.1)</td>
</tr>
<tr>
<td>$(1,2,3-C_5Me_3H_2)Ir(COD)$, 3</td>
<td>26.4 (±0.2)</td>
</tr>
<tr>
<td>$(C_5Me_4H)Ir(COD)$, 4</td>
<td>27.5 (±0.2)</td>
</tr>
<tr>
<td>$(C_5Me_5)Ir(COD)$, 5</td>
<td>28.5 (±0.2)</td>
</tr>
</tbody>
</table>

\(^a\)For protonation with CF$_3$SO$_3$H (0.1 M) in DCE solvent at 25.0 °C.

\(^b\)Numbers in parentheses are average deviations.
Table II. Results of equilibrium studies (at 25.0 °C) for the reactions in eq 3.

<table>
<thead>
<tr>
<th>reactants</th>
<th>$K_{eq}^a$</th>
<th>$\Delta G^\circ$ kcal mol$^{-1}^a$</th>
<th>$\Delta S^\circ$ eu$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H$^+$/2$^c$</td>
<td>4.4</td>
<td>-0.88</td>
<td>-0.74</td>
</tr>
<tr>
<td>3H$^+$/4$^c$</td>
<td>5.0</td>
<td>-0.95</td>
<td>-0.50</td>
</tr>
<tr>
<td>3H$^+$/4$^d$</td>
<td>4.8</td>
<td>-0.93</td>
<td>-0.57</td>
</tr>
<tr>
<td>4H$^+$/5$^c$</td>
<td>3.9</td>
<td>-0.81</td>
<td>-0.97</td>
</tr>
<tr>
<td>1H$^+$/5$^e$</td>
<td>1900</td>
<td>-4.5</td>
<td>~-4</td>
</tr>
</tbody>
</table>

$^a$Estimated error in $K_{eq}$ is 10% and ± 0.06 for $\Delta G^\circ$.

$^b$Calculated using $\delta \Delta H_{HM} = -1.1$ kcal mol$^{-1}$ for eq 3.

Estimated error is ± 0.7 eu.

$^c$In CDCI$_3$.

$^d$In d$_4$-DCE.

$^e$Values for this unmeasured equilibrium were calculated from the average $K_{eq}$ value of 4.5 per methyl group. $\Delta G^\circ$ was calculated ($\Delta G^\circ = -RT \ln K_{eq}$) from $K_{eq}$, and $\Delta S^\circ$ was calculated ($\delta \Delta H_{HM} = \Delta G^\circ + T \Delta S^\circ$) with $\delta \Delta H_{HM} = -5.7$ kcal mol$^{-1}$. 
DISCUSSION

The data presented in Table I show an excellent correlation between the number of methyl groups on the Cp' ring ($N_{Me}$) and the basicity of the iridium metal center, as measured by $\Delta H_{HM}$. The $\Delta H_{HM}$ values are exothermic and become more negative as the number of methyl groups in the cyclopentadienyl ring increases. A linear correlation is obtained when $\Delta H_{HM}$ is plotted against $N_{Me}$ as shown in Figure 2. The line fits eq 6 (correlation coefficient, $r = 0.999$) as determined by linear least-squares regression analysis.

$$-\Delta H_{HM} = 22.9 + 1.1N_{Me} \quad (\text{kcal mol}^{-1})$$ (6)

Each methyl effectively increases the basicity of the metal center by -1.1 kcal mol$^{-1}$. The results are consistent with an increase of electron density at the metal center caused by the electron-donating effect of the methyl groups.$^{5c}$

As protonation occurs at the Ir, the Cp' and COD ligands are forced closer to each other (see, for example, the crystal structure of (C$_5$Me$_5$)Ru(H)(1,5-COD)$_3$Sg) to make room for the hydride ligand. It is conceivable that steric repulsion between the COD and a highly methylated Cp' would cause $\Delta H_{HM}$ for the reaction to be less exothermic than otherwise expected. The linearity of the plot (Figure 2), however, suggests that either there is no steric effect of the methyl groups or the steric effect of each Me group is the same.
Figure 2. Plot of $\Delta H_{HM}$ (kcal mol$^{-1}$) for the protonation (eq 2) of 
Cp'Ir(1,5-COD) (Cp' = C$_5$Me$_x$H$_{5-x}$, x = 0, 1, 3-5) vs the
number of methyl groups on Cp' ($N_{Me}$)
The latter possibility seems less likely because the Cp' ligand with, for example, only one Me could rotate out of the way in order to avoid steric repulsion with the COD; whereas, a Me group in C₅Me₅ would definitely contribute to steric repulsion. Thus, one would expect the steric effect of added methyl groups to be most important in the more highly methylated complexes. The observation that each Me has the same effect (-1.1 kcal mol⁻¹) suggests that there is no measurable steric effect on ΔH HM even in (C₅Me₅)Ir(1,5-COD).

It is useful to correlate the ΔH HM values with spectroscopic properties of the complexes, especially NMR data. As the basicity of the iridium increases an increase in shielding of the 1,5-COD olefin ¹H NMR resonances is observed. In fact, there is a linear correlation (r = -0.999) between ΔH HM and the olefin proton chemical shift (x) of the 1,5-COD ligand in complexes 1-5, eq 7. The results can be interpreted in terms of the Dewar-Chatt-Duncanson model for π-olefin bonding to a metal.⁴³ Increasing N Me increases the electron density on the metal center thereby enhancing M → olefin dπ-π* backbonding and decreasing olefin-to-metal σ bonding. There is, consequently, an increase of electron density on the olefin resulting in an upfield shift of the olefin resonance.

We observe a systematic upfield shift of the Ir-H resonance of the protonated products with increasing N Me. Deviating from this
trend is $3H^+$ whose hydride resonance is found at slightly higher field (-12.04 ppm) than that of $4H^+$ (-12.02 ppm). Perhaps the asymmetry in the 1,2,3-Me$_3$C$_5$H$_2$ ring and an unusual distribution of rotamers$^{44}$ contribute to the surprising Ir-H resonance of $3H^+$. Although Ir-H chemical shifts appear to follow the trend in $\Delta H_{HM}$ values in this series of compounds, it seems unlikely to be a general trend for a broader range of metal hydrides.$^{45}$

In order to determine equilibrium constants (and therefore $\Delta G^\circ$) which measure the relative basicities of the Cp'Ir(1,5-COD) complexes we studied the reactions in eq 3. The $K_{eq}$ studies support the calorimetry results; $K_{eq}$ values (Table II) consistently show that protonation of the more highly methyl-substituted complex is favored. For the reactions in Table II and eq 3, $K_{eq}$ ranges from 3.9 to 5.0; however, with an experimental error of $\sim$10%, all 4 $K_{eq}$ values are approximately the same (4.5 average). Thus each Me increases the equilibrium constant by a factor of 4.5. This average value gives an average $\Delta G^\circ$ of $-0.89 \pm 0.06$ kcal mol$^{-1}$ per methyl group. There is only a relatively small difference between $\Delta G^\circ$ ($-0.89 \pm 0.06$ kcal mol$^{-1}$) and $\delta \Delta H_{HM}$ ($-1.1 \pm 0.2$ kcal mol$^{-1}$), especially considering the estimated errors. It is likely, however, that there is a small decrease in $\Delta S^\circ$ ($-0.7 \pm 0.7$ eu average per methyl group, Table II) when a proton is transferred to a complex with more Me groups. Other thermochemical studies$^{46}$ suggest that the effect of Me on the entropy associated with substitution of C$_6$H$_6$ in ($\eta^6$-C$_6$H$_6$)Mo(CO)$_3$ with methyl-substituted
arennes is also small. This small decrease in entropy in the present system may be interpreted as arising from more restricted rotation of the more highly methylated Cp" ring in Cp"Ir(H)(COD)+ as compared with rotation in the less methyl-substituted ring in Cp'Ir(H)(COD)+ in eq 3. The effect appears to be relatively constant for each Me group.

The results of the above experiments permit one to compare the effects of C5H5 and C5Me5 on ΔH_{HM}, ΔG^θ, and ΔS^θ values for the proton transfer reaction between compounds 1 and 5 (eq 3d). From Table I it is found that ΔH_{HM} of 5 is -5.7 kcal mol⁻¹ more exothermic than ΔH_{HM} of 1. The estimated value of K_{eq} for reaction 3d is 1900 (Table II) which means that ΔG^θ for this reaction is -4.5 kcal mol⁻¹. From these ΔH_{HM} and ΔG^θ values, ΔS^θ is estimated to be ~-4 eu. The small value of ΔS^θ clearly indicates that K_{eq} for reaction 3d is largely determined by the ΔH_{HM} values of 1 and 5.

For comparison with the ΔG^θ difference (-4.5 kcal mol⁻¹) between (C5H5)Ir(COD) (1) and (C5Me5)Ir(COD) (5), one can choose other pairs of complexes containing C5H5 and C5Me5 ligands. Moore and co-workers⁵ determined K_{eq} values for the protonation of Cp'Mo(CO)₃⁻ and Cp'Fe(CO)₂⁻, where Cp' is C5H5 or C5Me5, in acetonitrile solution. After converting their K_{eq} values to ΔG^θ's, one finds that the ΔG^θ for protonation of the C5Me5 molybdenum complex is -4.4 kcal mol⁻¹ more favorable than for the corresponding C5H5 complex. Thus, replacing C5H5 by C5Me5 in either Cp'Ir(COD) or Cp'Mo(CO)₃⁻ causes essentially the same
increase in metal basicity ($\Delta G^\theta = \sim -4.5 \text{ kcal mol}^{-1}$). On the other hand, $\Delta G^\theta$ for the protonation of $\text{(C}_5\text{Me}_5\text{)}\text{Fe(CO)}_2^-$ is -9.4 kcal mol$^{-1}$ more favorable than for $\text{(C}_5\text{H}_5\text{)}\text{Fe(CO)}_2^-$. Thus, in the iron system, the replacement of $\text{C}_5\text{H}_5$ by $\text{C}_5\text{Me}_5$ produces a much larger increase in metal basicity than in the Ir and Mo complexes. So it is evident that the substitution of $\text{C}_5\text{Me}_5$ for $\text{C}_5\text{H}_5$ does not cause the same increase in metal basicity in all metal complex systems.
SUMMARY

These studies of methyl-substituted Cp'\text{Ir}(1,5-COD) complexes show that protonation with CF$_3$SO$_3$H definitely occurs at the metal center to form products formulated as [Cp'\text{Ir}(H)(1,5-COD)]CF$_3$SO$_3$. The basicity of the iridium center as determined by the heats of protonation ($\Delta H_{HM}$) of the complexes in 1,2-dichloroethane increases linearly with the number of methyl groups in Cp' (N$_{Me}$) from C$_5$H$_5$ to C$_5$Me$_5$. For each methyl group $\Delta H_{HM}$ changes by -1.1 kcal mol$^{-1}$ ($\delta\Delta H_{HM}$). The $\Delta H_{HM}$ values correlate with the chemical shift of the olefin $^1$H NMR resonance in the 1,5-COD ligand of the neutral complexes and the Ir-H $^1$H NMR resonance of the protonated products.

Equilibrium studies of the proton transfer reactions (eq 3) show that the successive addition of methyl groups to the Cp' ring changes $\Delta G^\circ$ -0.89 ± 0.06 kcal mol$^{-1}$ per methyl group and $\Delta S^\circ$ by -0.7 ± 0.7 eu per methyl. Thus, the differences in basicities (Keq or $\Delta G^\circ$) of the various methyl-substituted Cp'\text{Ir}(1,5-COD) complexes is largely determined by $\Delta H_{HM}$ values of the complexes, and $\Delta S^\circ$ makes a relatively small contribution. Comparing the common C$_5$H$_5$ and C$_5$Me$_5$ ligands, one finds that replacing C$_5$H$_5$ in (C$_5$H$_5$)\text{Ir}(1,5-COD) by C$_5$Me$_5$ increases the equilibrium constant, Keq, for the protonation of the complex by 1900; $\Delta G^\circ$ becomes more favorable by -4.5 kcal mol$^{-1}$; $\Delta H_{HM}$ becomes more favorable by -5.7 kcal mol$^{-1}$, while $\Delta S^\circ$ becomes slightly less favorable by --4 eu.
REFERENCES


(d) Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* 1985, 4, 533.


(6) Some studies not discussed in this paper are included in the following references:

(a) Green, J. C.; Powell, P.; van Tilborg, J. E. *Organometallics* 1984, 3, 211.


(20) The assignments of the 3,5-dimethyl-1-pyrazolyl ring position are based on assignments made in the references below:


(30) We repeated the deuteration experiment discussed in ref 23 by reacting 1 with one equiv of CF$_3$SO$_3$D in CH$_2$Cl$_2$ solution at room temperature. The reaction was monitored by $^2$H NMR spectroscopy (Bruker WM 300 MHz spectrometer, CD$_2$Cl$_2$ internal standard, $\delta = 5.32$ ppm); we observed initial deuteration at the iridium center ($\delta$ -11.6 ppm, Ir-D) followed by slow incorporation of deuterium into the 1,5-COD ligand ($\delta$ 2.5 ppm, exo-CH$_2$ COD). These changes correspond to those reported in ref 23; however, because we assign a 1,5-COD
geometry to $\text{CF}_3\text{SO}_3^-$; these data indicate that the deuterium exchange is with the exo-1,5-COD protons rather than the endo-1,3-COD protons previously reported. It was not noted in ref 23, but deuterium is also incorporated into the Cp ring ($\delta$ 6.0 ppm) after 3 days.

(31) Proton transfer from a M-H to the vinylic carbon of 1,5-COD has been shown to give $\eta^3$-cyclooctadienyl complexes.


(33) Unfortunately $\eta^4$-1,3-COD complexes are rare.
   (a) ($\eta^6$-toluene)Fe(1,3-COD): Ittel, S. D.; Tolman, C. A. *Organometallics* **1982**, *1*, 1432.


**(35)** The range listed does not cover a comprehensive search of all asymmetric 1,5-COD complexes.


(b) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199.


(37) Reaction of (C₅Me₅)Ir(η⁴-dicyclopentadiene) with HPF₆ gives a product where the olefin ligand is protonated but the metal is stabilized by an agostic C-H interaction. Bennett, M. A.; McMahon, I. J.; Pelling, S.; Robertson, G. B.; Wickramasinghe, W. A. Organometallics 1985, 4, 754.


(44) For example a novel temperature dependence of the chemical shift of the Cp' ring protons in (XC₅H₄)RhL₂ complexes has been attributed "to preferential population of a particular rotamer state" at low temperature. See ref 17.


SECTION III. HEATS OF PROTONATION OF TRANSITION METAL COMPLEXES: THE EFFECT OF PHOSPHINE BASICITY ON METAL BASICITY IN CpIr(CO)(PR₃) AND Fe(CO)₃(PR₃)₂ COMPLEXES
ABSTRACT

Titration calorimetry has been used to determine the effects of phosphine basicity on the heats of protonation ($\Delta H_H M$) of the metal in the CpIr(CO)(PR$_3$) and Fe(CO)$_3$(PR$_3$)$_2$ complexes (PR$_3$ = P(p-C$_6$H$_4$)$_3$, PPh$_3$, P(p-MeOC$_6$H$_4$)$_3$, PMePh$_2$, PMe$_2$Ph, PMe$_3$) with CF$_3$SO$_3$H at 25.0 °C in 1,2-dichloroethane solvent. The $\Delta H_H M$ values of the CpIr(CO)(PR$_3$) compounds range from -29.2 kcal mol$^{-1}$ (PR$_3$ = P(p-C$_6$H$_4$)$_3$) 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 kcal mol$^{-1}$ (PR$_3$ = PPh$_3$) to -23.3 kcal mol$^{-1}$ (PR$_3$ = PMe$_3$). Linear correlations of metal basicity ($\Delta H_H M$) with phosphine basicity ($\Delta H_P$ 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 $\Delta H_H M$ values are inversely proportional to the $\nu$(CO) values. The effect of the indenyl, CS, and CO ligands on the basicities ($\Delta H_H M$) of (indenyl)Ir(CO)(PPh$_3$), CpIr(CS)(PPh$_3$), and Cp$^*$Ir(CO)$_2$ are also discussed.
INTRODUCTION

There is considerable interest in proton basicities of the metals in transition metal complexes\(^1,2,3\) because these basicities are indicators of other types of reactivity\(^4\) that depend upon electron-richness at the metal center. It is generally recognized that metal basicity is influenced by the basicity (e.g., \(pK_a\))\(^5,6,7\) of phosphine ligands bound to the metal. Numerous metal-phosphine complexes undergo protonation at the metal center,\(^8\) however, few quantitative data\(^2b,19-11\) are available concerning the relationship between phosphine basicity and metal basicity. Recently, Bush and Angelici\(^7\) reported heats of protonation (\(\Delta H_{HP}\) in eq 1) in 1,2-dichloroethane solvent as a measure of phosphine basicity.

\[
PR_3 + CF_3SO_3H \xrightleftharpoons{DCE, 25.0 \degree C} HPR_3 + CF_3SO_3^-; \quad \Delta H_{HP}
\]

In the present study, quantitative correlations between the basicities of these phosphines and their iridium and iron complexes are reported.

Heats of protonation (\(\Delta H_{HM}\)) are also used as a measure of the basicities of transition metal complexes; this method has been shown 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$_3$SO$_3$H) in 1,2-dichloroethane (DCE) solution (eq 2), the same conditions that were used to

$$\text{ML}_x + \text{CF}_3\text{SO}_3\text{H} \xrightarrow{\text{DCE} / 25.0 \, ^\circ\text{C}} \text{HML}_x^+ \text{CF}_3\text{SO}_3^-; \Delta H_{\text{HM}} \quad (2)$$

determine the heats of protonation ($\Delta H_{\text{HP}}$) of phosphines (eq 1).

Previously, it was established that the basicity ($\Delta H_{\text{HM}}$) of the iridium in Cp'Ir(1,5-COD) complexes (Cp' = C$_5$Me$_x$H$_{5-x}$, x = 0, 1, 3-5) increases linearly as the number of methyl groups in the cyclopentadienyl ring increases.$^3$

In this paper, studies of the basicities ($\Delta H_{\text{HM}}$) 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 are reported.

$$\text{Cp'Ir(CO)PR}_3 + \text{CF}_3\text{SO}_3\text{H} \xrightarrow{\text{DCE / 25.0 } ^\circ\text{C}} \text{CF}_3\text{SO}_3^-; \Delta H_{\text{HM}} \quad (3)$$

PR$_3$: P(p-ClC$_6$H$_4$)$_3$ (1, 1H$^+$), PPh$_3$ (2, 2H$^+$), PMe$_2$H$_3$ (3, 3H$^+$)
PMe$_2$Ph (4, 4H$^+$), PMe$_3$ (5, 5H$^+$)
In addition, we include protonation studies of (indenyl)Ir(CO)(PPh3) (11), CpIr(CS)(PPh3) (12), Cp*Ir(CO)2 (13), and (1,2,3-C5Me3H2)-Ir(CO)(PPh3) (14).
EXPERIMENTAL

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. Hexanes and CH\textsubscript{2}Cl\textsubscript{2} were refluxed over CaH\textsubscript{2} and then distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Benzene was distilled from LiAlH\textsubscript{4} and toluene from sodium metal. Deuteriochloroform (Aldrich) was stored over molecular sieves in air or distilled from P\textsubscript{2}O\textsubscript{5} under nitrogen. Anhydrous ethanol was obtained by distillation of absolute ethanol from Mg(OEt)\textsubscript{2} under nitrogen. Neutral Al\textsubscript{2}O\textsubscript{3} (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under high vacuum (10^{-5} \text{ mm Hg}) for 9 h, deactivated with 5% (w/w) N\textsubscript{2}-saturated water, and stored under N\textsubscript{2}.

The \textsuperscript{1}H NMR spectra were recorded in CDCl\textsubscript{3} on a Nicolet-NT 300 MHz spectrometer using TMS (\(\delta = 0.00 \text{ ppm}\)) as the internal reference. A Varian VXR-300 MHz instrument was used to obtain the \textsuperscript{13}C[\text{H}] NMR spectra in CDCl\textsubscript{3} solvent (internal reference, CDCl\textsubscript{3}, \(\delta = 77.0 \text{ ppm}\)). 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\textsuperscript{+}, 3H\textsuperscript{+}, 4H\textsuperscript{+}, 7H\textsuperscript{+}, 11H\textsuperscript{+}, 13H\textsuperscript{+}) 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-C1C6H4)3 and P(p-MeOC6H4)3 were purchased from Strem while PPh3, PMePh2, PMe2Ph, and PMe3 (1.0 M in toluene) were purchased from Aldrich. Vaska's complex, IrCl(CO)(PPh3)2, used in the preparation of 2, 11, and 14 was synthesized according to an updated procedure. The iridium complexes 2,14 12,15 1316 were prepared as previously reported. The compounds [CplrI2]n and Cplr(l)2(PMe3) 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 8,19b,20,21 9,21 and 1019a,22 have been previously reported by other methods.

Preparation of Iridium Complexes, Cp'Ir(L)(L'), 1-5, 11-14

Cplr(CO)[P(p-CIC6H4)3] (1)

The starting material, Cplr(l)2[P(p-CIC6H4)3]-CH2Cl2, was prepared using the same procedure described for the synthesis of Cplr(l)2(PMe3).17 It co-precipitated with one equiv of CH2Cl2 as a deep red powder in 92% yield [1H NMR: δ 5.44 (d, JPH = 1.3 Hz, 5H, Cp), 7.42 (m, 6H, Ph), 7.51 (m, 6H, Ph)]. A mixture of Cplr(l)2[P(p-CIC6H4)3]-CH2Cl2 (908 mg, 0.944 mmol), Na2CO3 (830
mg, 7.83 mmol) and anhydrous EtOH (30 mL) was heated to reflux under a slow stream of carbon monoxide (1 atm) for 24 h. The color of the mixture gradually turned from red to clear yellow. When monitoring the reaction by $^1$H NMR spectroscopy we observed a yellow intermediate [$^1$H NMR: $\delta$ 5.35 (d, $J_{PH} = 1.3$ Hz, 5H, Cp), 7.3-7.5 (m, 12H, 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 x 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 x 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: $\delta$ 5.13 (s, 5H, Cp), 7.36 (m, 6H, Ph), 7.48 (m, 6H, Ph). IR(CH$_2$Cl$_2$): $\nu$(CO) 1929 cm$^{-1}$.

CpIr(CO)(PPh$_3$) (2)

This compound was prepared in 56% yield from KCp$^3$ and IrCl(CO)(PPh$_3$)$_2$ according to the previously reported procedure. $^1$H NMR: $\delta$ 5.14 (d, $J_{PH} = 1.0$ Hz, 5H, Cp), 7.34-7.61 (m, 15H, Ph). IR(CH$_2$Cl$_2$): $\nu$(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, 0.35 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 and was added to a chromatography column of neutral alumina (10 x 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: \(\delta\) 2.30 (d, J\(_{PH}\) = 9.9 Hz, 3H, Me), 5.13 (s, 5H, Cp), 7.4-7.6 (m, 10H, Ph). IR(CH\(_2\)Cl\(_2\)): \(\nu\)(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 (7 x 3 cm) with a mixture of Et\(_2\)O/hexanes (1:5). An initial pale yellow band containing unreacted PMe\(_2\)Ph and 4 was discarded. A second 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 x 3 cm column of alumina. Recrystallization from Et\(_2\)O/hexanes at -20 °C gave yellow crystals of 4 (178 mg, 56%
yield). Anal. Calcd. for C₁₄H₁₆IrOP: C, 39.71; H, 3.81. Found: C, 39.61; H, 3.88. ¹H NMR: δ 2.02 (d, JₚH = 10.2 Hz, 6H, Me), 5.24 (s, 5H, Cp), 7.40-7.80 (m, 6H, Ph). IR(CH₂Cl₂): υ(CO) 1917 cm⁻¹.

CpIr(CO)(PMe₃) (5)

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

(Indenyl)Ir(CO)(PPh₃) (11)

This compound was prepared in 63% yield from K(indenide)³ and IrCl(CO)(PPh₃)₂ according to the procedure reported for the synthesis of 2.¹⁴ Anal. Calcd. for C₂₈H₂₂IrOP: C, 56.27; H, 3.71.
Found: C, 55.92; H, 3.69. $^1$H NMR: $\delta$ 5.18 (br s, 2H, H1, H3), 6.25 (m, 1H, H2), 6.81 (m, 4H, H4-H7), $\eta^5$-indenyl; $^2$H 7.0-7.4 (m, 15H, Ph). IR(CH₂Cl₂): v(CO) 1934 cm⁻¹.

CpIr(CS)(PPh₃) (12)

This complex was prepared from KCp³ and IrCl(CS)(PPh₃)₂$^{24}$ according to the previously reported procedure.$^{15}$ Yield: 45%. $^1$H NMR: $\delta$ 5.06 (s, 5H, Cp), 7.39-7.70 (m, 15H, Ph). IR(nujol mull): v(CS) 1291 cm⁻¹.

Cp*Ir(CO)₂ (13)

This complex was synthesized from [Cp*IrCl₂]₂$^{16b}$ and Fe₃(CO)₁₂$^{25}$ as previously reported.$^{16a}$ Yield: 64%. $^1$H NMR: $\delta$ 2.19 (s, 15H, Cp*). IR(CH₂Cl₂): v(CO) 2010 (s), 1938 (s) cm⁻¹.

(1,2,3-C₅Me₃H₂)Ir(CO)(PPh₃) (14)

Compound 14 was prepared using K(1,2,3-C₅Me₃H₂)$^3$ in the same manner as previously described for the synthesis of 2.$^{14}$ Yield of 14: 45%. Anal. Calcd. for C₂₇H₂₆IrOP: C, 54.99; H, 4.44. Found: C, 54.60; H, 4.61. $^1$H NMR: $\delta$ 1.85 (d, J₉H = 1.9 Hz, 6H, 1,3-Me₂Cp), 2.06 (d, J₉H = 1.1 Hz, 3H, 2-MeCp), 4.77 (s, 2H, Cp), 7.3-7.6 (m, 15H, Ph). IR(CH₂Cl₂): v(CO) 1914 cm⁻¹.
Preparation of Iron Complexes, Fe(CO)$_3$(PR$_3$)$_2$

**Method A**

To a solution of Fe(CO)$_3$(bda)$_{18a}$ (283 mg, 1.00 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 x 3 mL). Recrystallization by dissolution of the golden yellow solid in a minimum of CH$_2$Cl$_2$, layering this solution with Et$_2$O (10 x volume of CH$_2$Cl$_2$) and cooling to -20 °C gave the desired product.

**Method B**

A solution of Fe(CO)$_3$(bda)$_{18a}$ (424 mg, 1.50 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$_2$Cl$_2$ and added to a neutral alumina column (20 x 1.5 cm). Elution with CH$_2$Cl$_2$ gave a very pale yellow band. Evaporation of the eluent to dryness and recrystallization from CH$_2$Cl$_2$/hexanes (1:10) at -20 °C gave the desired product.
Fe(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2} (6)

Method A. Reaction time: 20 h. Yield: 82%. \textsuperscript{1}H NMR: \textdelta 7.40-7.60 (m, Ph). IR(CH\textsubscript{2}Cl\textsubscript{2}): \upsilon(CO) 1965(w), 1881(s) cm\textsuperscript{-1}.

Fe(CO)\textsubscript{3}[P(p-MeOC\textsubscript{6}H\textsubscript{4})\textsubscript{3}]\textsubscript{2} (7)

Method A. Reaction time: 15 h. Yield: 78%. \textsuperscript{1}H NMR: \textdelta 3.82 (s, 18H, Me), 6.91-7.51 (m, 24H, Ph). IR(CH\textsubscript{2}Cl\textsubscript{2}): \upsilon(CO) 1964(w), 1875(s) cm\textsuperscript{-1}.

Fe(CO)\textsubscript{3}(PM\textsubscript{e}Ph\textsubscript{2})\textsubscript{2} (8)

Method B. Reaction time: 15 h. Yield: 87%. \textsuperscript{1}H NMR: \textdelta 2.18 (d, J\textsubscript{PH} = 6.8 Hz, 6H, Me), 7.39-7.67 (m, 20H, Ph). IR(CH\textsubscript{2}Cl\textsubscript{2}): \upsilon(CO) 1965(w), 1876(s) cm\textsuperscript{-1}.

Fe(CO)\textsubscript{3}(PMe\textsubscript{2}Ph\textsubscript{2}) (9)

Method B. Reaction time: 24 h. Yield: 72%. \textsuperscript{1}H NMR: \textdelta 1.88 (s, 12H, Me), 7.42-7.78 (m, 10H, Ph). IR(CH\textsubscript{2}Cl\textsubscript{2}): \upsilon(CO) 1965(w), 1870(s) cm\textsuperscript{-1}.

Fe(CO)\textsubscript{3}(PMe\textsubscript{3})\textsubscript{2} (10)

Method B. Reaction time: 96 h. Yield: 74%. \textsuperscript{1}H NMR: \textdelta 1.59 (d, J\textsubscript{PH} = 8.3 Hz, Me). IR(CH\textsubscript{2}Cl\textsubscript{2}): \upsilon(CO) 1963(w), 1864(s) cm\textsuperscript{-1}.

Protonation Reactions of Iridium Complexes 1-5, 11-14

Compounds 1-5, 11-14 were protonated by dissolving ~30 mg of each compound in 3 mL of CH\textsubscript{2}Cl\textsubscript{2} under N\textsubscript{2}. To the solution was added 1 equiv of CF\textsubscript{3}SO\textsubscript{3}H by microliter syringe. Immediately, the
color of the solution was bleached. The IR spectra showed new 
$v$(CO) bands at higher frequency ($\sim$140 cm$^{-1}$, see below) and the 
complete disappearance of the bands corresponding to the neutral 
starting material (see above). Solutions of the protonated complexes 
are stable as long as they are kept under nitrogen or argon. By 
adding 1 equiv of 1,3-diphenylguanidine base the original color 
reappeared as did the IR bands corresponding to the unprotonated 
starting material. Protonated complexes $2H^+X^-$ ($X^- = BPh_4^-$, 
$BF_4^-)_14a,17$ $12H^+Cl^-$,15 and $13H^+BF_4^-$,26 have been reported 
previously.

Samples of $1H^+-5H^+$, $11H^+-14H^+$ for $^1H$ NMR spectroscopy 
were prepared by adding 1 equiv of CF$_3$SO$_3$H to solutions of the 
neutral complex ($\sim$10 mg) in CDCl$_3$ ($\sim$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$_3$SO$_3$H 
(1 equiv) in Et$_2$O (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) in 75% yield.

Spectroscopic data for compounds $1H^+CF_3SO_3^-$ - $5H^+CF_3SO_3^-$, 
$11H^+CF_3SO_3^-$ - $14H^+CF_3SO_3^-$ are presented below:
\[ \text{[CpIr(H)(CO)(P}p\text{-ClC}_6\text{H}_4\text{)\text{]}CF}_3\text{SO}_3 (1H+CF}_3\text{SO}_3^-) \]

\(^1\text{H NMR: } \delta 5.94 \text{ (s, 5H, Cp), 7.35 (d, } J_{\text{HH}} = 9.0 \text{ Hz, 6H, meta-Ph protons), 7.57 (dd, } J_{\text{PH}} = 12.3 \text{ Hz, 6H, ortho-Ph protons), -14.45 (d, } J_{\text{PH}} = 24.41 \text{ Hz, 1H, Ir-H). IR(CH}_2\text{Cl}_2): \nu(\text{CO}) 2063 \text{ cm}^{-1}.\]

\[ \text{[CpIr(H)(CO)(PPh}_3\text{)]CF}_3\text{SO}_3 (2H+CF}_3\text{SO}_3^-) \]

\(^1\text{H NMR: } \delta 5.88 \text{ (s, 5H, Cp), 7.56-7.40 (m, 15H, Ph), -14.44 (d, } J_{\text{PH}} = 24.10 \text{ Hz, 1H, Ir-H). IR(CH}_2\text{Cl}_2): \nu(\text{CO}) 2063 \text{ cm}^{-1}.\]

\[ \text{[CpIr(H)(CO)(PMePh}_2\text{)]CF}_3\text{SO}_3 (3H+CF}_3\text{SO}_3^-) \]

\(^1\text{H NMR: } \delta 5.90 \text{ (s, 5H, Cp), 2.70 (d, } J_{\text{PH}} = 12.3 \text{ Hz, 3H, Me), 7.5 (m, 10H, Ph), -14.66 (d, } J_{\text{PH}} = 23.21 \text{ Hz, 1H, Ir-H). IR(CH}_2\text{Cl}_2): \nu(\text{CO}) 2061 \text{ cm}^{-1}.\]

\[ \text{[CpIr(H)(CO)(PMe}_2\text{Ph)]CF}_3\text{SO}_3 (4H+CF}_3\text{SO}_3^-) \]

\(^1\text{H NMR: } \delta 5.89 \text{ (s, 5H, Cp), 2.36 (d, } J_{\text{PH}} = 11.6 \text{ Hz, 3H, Me), 2.39 (d, } J_{\text{PH}} = 11.4 \text{ Hz, 3H, Me), 7.27-7.62 (m, 5H, Ph), -15.03 (d, } J_{\text{PH}} = 25.11 \text{ Hz, 1H, Ir-H). IR(CH}_2\text{Cl}_2): \nu(\text{CO}) 2057 \text{ cm}^{-1}.\]

\[ \text{[CpIr(H)(CO)(PMe}_3\text{)]CF}_3\text{SO}_3 (5H+CF}_3\text{SO}_3^-) \]

\(^1\text{H NMR: } \delta 6.01 \text{ (s, 5H, Cp), 2.12 (d, } J_{\text{PH}} = 12.1 \text{ Hz, 9H, Me), -15.32 (d, } J_{\text{PH}} = 25.33 \text{ Hz, 1H, Ir-H). IR(CH}_2\text{Cl}_2): \nu(\text{CO}) 2052 \text{ cm}^{-1}.\]

\[ ((\text{Indenyl})\text{Ir(H)(CO)(PPh}_3\text{)]CF}_3\text{SO}_3 (11H+CF}_3\text{SO}_3^-) \]

\(^1\text{H NMR: } \delta 6.63 \text{ (br s, 2H, H1, H3), 7.19 (t, } J_{1,3-2} = 7.6 \text{ Hz, 1H, H2), 7.84 (d, } J_{5,6-4,7} = 8.4 \text{ Hz, 2H, H4, H7), 6.32 (d, 2H, H5, H6), } \eta^5\text{-indenyl; 23 7.00 (m, 6H, ortho-Ph protons), 7.51 (m, 9H,}
meta-, para-Ph protons), -17.14 (d, JPH = 21.6 Hz, 2H, Ir-H).
IR(CH2Cl2): υ(CO) 2058 cm⁻¹.

[CpIr(H)(CS)(PPh3)]CF3SO3 (12H+CF3SO3⁻)

1H NMR: δ 5.85 (s, 5H, Cp), 7.44-7.56 (m, 15H, Ph), -13.72 (d, JPH = 24.32 Hz, 1H, Ir-H). IR(CH2Cl2): υ(CS) 1372 cm⁻¹.

[(C5Me5)Ir(H)(CO)2]CF3SO3 (13H+CF3SO3⁻)

1H NMR: δ 2.43 (s, 15H, Me), -13.80 (br s, 1H, Ir-H).
IR(CH2Cl2): υ(CO) 2119 (s), 2080 (s) cm⁻¹.

[(1,2,3-C5Me3H2)Ir(H)(CO)(PPh3)]CF3SO3 (14H+CF3SO3⁻)

1H NMR: δ 1.93 (s, 3H, 2-Me), 2.13 (s, 3H, 1,3-Me2), 2.22 (s, 3H, 1,3-Me2), 5.59 (s, 2H, Cp), 7.56-7.38 (m, 15H, Ph), -14.43 (d, JPH = 25.5 Hz, 1H, Ir-H). IR(CH2Cl2): υ(CO) 2045 cm⁻¹.

Protonation Reactions of Iron Complexes 6-10

These complexes were protonated using the same procedure described above for that of the iridium complexes; however, we found that filtration of solutions of 6-10 in air-free CDCl3 through a short column of Celite (2 x 0.5 cm), under N2, resulted in better quality 1H NMR spectra of the protonated products 6H+CF3SO3⁻ - 10H+CF3SO3⁻. Yields of the protonated products as determined by IR and 1H NMR spectroscopy are quantitative. Only the protonation of 6 in H2SO4 solution was reported previously.27 Attempts to isolate the protonated complexes as solids were unsuccessful. However,
solutions are stable if kept under N₂ or Ar. The spectroscopic data for $6H^+\text{CF}_3\text{SO}_3^- - 10H^+\text{CF}_3\text{SO}_3^-$ are given below:

$[\text{Fe(H)(CO)}_3(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3 (6H^+\text{CF}_3\text{SO}_3^-)$

$^1H$ NMR: $\delta$ 7.45-7.61 (m, 30H, Ph), -7.90 (t, $J_{PH} = 30.7$ Hz, 1H, Fe-H). IR(CH₂Cl₂): $\nu$(CO) 2088(w), 2039 (m, sh), 2026 (s) cm⁻¹.

$[\text{Fe(H)(CO)}_3(\text{P}(p-\text{MeO}_2\text{C}_6\text{H}_4)_3)_2]\text{CF}_3\text{SO}_3 (7H^+\text{CF}_3\text{SO}_3^-)$

$^1H$ NMR: $\delta$ 3.88 (s, 18H, Me), 7.06-7.33 (m, 24H, Ph), -7.89 (t, $J_{PH} = 29.9$ Hz, 1H, Fe-H). IR(CH₂Cl₂): $\nu$(CO) 2080(vv), 2032 (m, sh), 2020(s) cm⁻¹.

$[\text{Fe(H)(CO)}_3(\text{PMePh}_2)_2]\text{CF}_3\text{SO}_3 (8H^+\text{CF}_3\text{SO}_3^-)$

$^1H$ NMR: $\delta$ 2.82 (s, 6H, Me), 7.6 (m, 20H, Ph), -8.27 (t, $J_{PH} = 34.2$ Hz, 1H, Fe-H). IR(CH₂Cl₂): $\nu$(CO) 2092(w), 2027(s) cm⁻¹.

$[\text{Fe(H)(CO)}_3(\text{PMe}_2\text{Ph})_2]\text{CF}_3\text{SO}_3 (9H^+\text{CF}_3\text{SO}_3^-)$

$^1H$ NMR: $\delta$ 2.07 (br, s, 12H, Me), 7.5 (m, 10H, Ph), -8.92 (t, $J_{PH} = 36.7$ Hz, 1H, Fe-H). IR(CH₂Cl₂): $\nu$(CO) 2090(w), 2023(s) cm⁻¹.

$[\text{Fe(H)(CO)}_3(\text{PMe}_3)_2]\text{CF}_3\text{SO}_3 (10H^+\text{CF}_3\text{SO}_3^-)$

$^1H$ NMR: $\delta$ 1.76 (d, $J_{PH} = 8.5$ Hz, 18H, Me), -9.49 (t, $J_{PH} = 36.6$ Hz, 1H, Fe-H). IR(CH₂Cl₂): $\nu$(CO) 2090(w), 2023(s) cm⁻¹.

Calorimetric Titrations

The calorimetric titration procedure was similar to that previously described.³⁷ 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 standardized 0.1 M (± 0.2 mM) CF$_3$SO$_3$H solution in DCE (under an argon atmosphere) at a constant rate during 3 minutes 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, 12) required, 2 minute titration periods were used. The reaction enthalpies were corrected for the heat of dilution ($\Delta H_{\text{dil}}$) of the acid in DCE (-0.2 kcal mol$^{-1}$).$^3$

The enthalpy values are reported as the average of usually 4 titrations and as many as 8. However, only 3 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, 14

In spite of the well-developed syntheses of CpM(CO)(PR₃) complexes where M = Co, Rh,⁴⁸ only the preparations of Ir complexes 2¹⁴ and 4²⁸ have been reported previously. However, 5 was recently identified spectroscopically in a solid CO matrix as a product from the photolysis of CpIr(C₂H₄)(PMē₃).²⁹ Compounds 1-5, 11-14 have the half-sandwich geometry shown in eq 3 as confirmed for 2 by an X-ray crystallographic determination.³⁰ The compounds were characterized by ¹H NMR and IR spectroscopy (see Experimental). Only 5 is air sensitive; even so, it can be handled in air for brief periods. As a precaution all compounds were stored under N₂ 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 2¹⁴ and 12¹⁵ were prepared from KCp and IrCl(CO)(PPh₃)₂ or IrCl(CS)(PPh₃)₂, respectively. Similarly, the previously unreported complexes 11 and 14 were prepared from KCp' (Cp' = indenyl, 1,2,3-C₅Me₃H₂)³ and IrCl(CO)(PPh₃)₂ (eq 5).

\[
\text{KCp'} + \text{IrCl(CO)(PPh₃)₂} \xrightarrow{\text{benzene reflux}} \text{Cp'Ir(CO)(PPh₃)}
\]

Cp' = indenyl, 11, 40%
Cp' = 1,2,3-C₅Me₃H₂, 14, 45%
Attempts to prepare 3 and 4 from KCp and IrCl(CO)(PR₃)₂ (PR₃ = PMePh₂, PMe₂Ph) resulted in only low yields of the desired products. But starting from 2, the PPh₃ ligand was easily replaced with PMePh₂ or PMe₂Ph (eq 6). The synthesis of complex 4 required less vigorous reaction conditions and a shorter reaction time (2 h) compared to that (5 h) for the synthesis of 3. The reactions were followed by ¹H NMR spectroscopy; in both cases the PPh₃ ligand was completely replaced.

Unfortunately, the reaction conditions used to prepare 3 and 4 (eq 6) were not successful for the synthesis of the PMe₃ derivative 5 as only decomposition of the starting material 2 was observed. However, reduction of CpIr(I)₂(PMe₃) in slightly basic alcoholic solution under an atmosphere of carbon monoxide gave 5 (eq 7) in variable yields (27-54%) which tended to be lower for prolonged reaction times. The P(p-ClC₆H₄)₃ derivative 1 was prepared similarly. The syntheses of 1 and 5 are best followed by ¹H NMR spectroscopy. An intermediate, which is observed in each reaction
(see Experimental), is tentatively assumed to be \( \text{CpIr(H(OEt)(PR}_3)_{33} \). Carbon monoxide induced reductive elimination of EtOH then produces the \( \text{CpIr(CO)(PR}_3) \) product.

**Protonation Reactions of the Iridium Complexes**

The protonated complexes \( 2H^+X^- (X^- = \text{BPh}_4^-, \text{BF}_4^-) \), \( 12H^+\text{Cl}^- \), \( 13H^+\text{BF}_4^- \) and \( 14H^+\text{BF}_4^- \) have been isolated and characterized previously. It was established that protonation occurred at the iridium metal center. We observe that the addition of one equiv of \( \text{CF}_3\text{SO}_3\text{H} \) to solutions of the neutral metal complexes \( (1-5, 11-14) \) in \( \text{CH}_2\text{Cl}_2 \) results in quantitative formation of \( 1H^+\text{CF}_3\text{SO}_3^- - 5H^+\text{CF}_3\text{SO}_3^- \) and \( 11H^+\text{CF}_3\text{SO}_3^- - 14H^+\text{CF}_3\text{SO}_3^- \) as indicated by IR spectroscopy. The \( \nu(\text{CO}) \) band moves by \( \sim 140 \text{ cm}^{-1} \) (or \( 81 \text{ cm}^{-1} \) for the \( \nu(\text{CS}) \) band of \( 12 \)) to higher frequency (see Experimental). Quantitative formation of \( 1H^+ - 5H^+ \) and \( 11H^+ - 14H^+ \) in \( \text{CDCl}_3 \) solution is also observed by \(^1\text{H} \) NMR spectroscopy. Hydride resonances for \( 1H^+ - 5H^+ \) occur as doublets between \( -14.45 \text{ ppm (1H}^+ \) and \( -15.32 \text{ ppm (5H}^+) \) with \( 2J_{\text{PH}} = 24-25 \text{ Hz} \) due to coupling with the phosphine phosphorus. The \( \text{Ir-H} \) resonances for \( 11H^+ - 14H^+ \) are found in a wider range, \( -13.72 \text{ for 12H}^+ \) to \( -17.14 \text{ ppm for 11H}^+ \). Complexes \( 11H^+\text{CF}_3\text{SO}_3^- \) and \( 14H^+\text{CF}_3\text{SO}_3^- \) were isolated as white solids in yields of 70% and 75%, respectively, from reactions of 11 and 14 with \( \text{CF}_3\text{SO}_3\text{H} \) in \( \text{Et}_2\text{O} \) solutions.

The structures of the protonated products are shown in eq 3. In \( 4H^+\text{CF}_3\text{SO}_3^- \) the Me groups in the \( \text{PMe}_2\text{Ph} \) ligand are
diastereotopic; thus, they are observed as two sets of doublets centered at 2.32 ppm ($^2J_{PH} = 11.6$ Hz) and 2.39 ppm ($^2J_{PH} = 11.4$ Hz) in the $^1H$ NMR spectrum. Also, the 1,3-Me groups in the 1,2,3-C$_5$Me$_3$H ligand of 14H$^+$CF$_3$SO$_3^-$ are diastereotopic which gives rise to separate signals for these Me groups at 2.13 ppm and 2.22 ppm. The resonance at 1.93 ppm because it is the most different from the other two was assigned to the 2-Me group. The chemical shifts of the 4,5-Cp' ring protons are indistinguishable; but in principle they could also give two distinct $^1H$ NMR resonances.

The protonated complexes are stable in solution as long as they are kept under an atmosphere of $N_2$ or Ar. However, solutions of 5H$^+$CF$_3$SO$_3^-$ decompose readily upon exposure to air. The isolated complexes 11H$^+$CF$_3$SO$_3^-$ and 14H$^+$CF$_3$SO$_3^-$ are stable in air long enough to be weighed out. Also, 11H$^+$CF$_3$SO$_3^-$ did not isomerize (vide infra) or decompose after 24 h in refluxing DCE (b.p. 83 °C) under $N_2$. The protonated compounds can be deprotonated with 1,3-diphenylguanidinium 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)$_3$(η$^4$-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-
The generality of this reaction and the ability to store Fe(CO)₃(bda) (under N₂) makes this an excellent synthetic method for these complexes.

\[
\begin{align*}
\text{Ph} & \quad \text{Fe} \quad \text{CO} \\
\text{O} & \quad \text{C} \quad \text{C} \quad \text{CO} \\
& \quad \text{O}
\end{align*}
\]

+ 2PR₃ \xrightarrow{\text{THF}} \text{Fe(CO)₃(PR₃)₂} \quad (8)

Complexes 6, 19-21, 8, 19b, 20, 21 9, 21 and 10¹⁹a, 22 were characterized by comparison of their ¹H NMR and IR spectra with those reported in the literature for these compounds. Spectroscopic studies, 22, 35a, 38b, c X-ray diffraction determinations, 35b, c and theoretical calculations, 35d indicate that the Fe(CO)₃(PR₃)₂ complexes prefer to adopt the trigonal bipyramidal geometry shown in eq 4. Complexes 6-9 are air-stable as solids but were normally stored under N₂ at 0 °C. Complex 10 is only moderately air-stable. However, solutions of 6-10 were handled under nitrogen or argon using Schlenk techniques.

**Protonation of Fe(CO)₃(PR₃)₂ Complexes**

It has been previously shown by ¹H NMR and IR spectroscopy that 6 protonates at the metal center in conc. H₂SO₄ solution.²⁷ With one equiv of CF₃SO₃H we observe quantitative protonation of 6 to give 6H⁺CF₃SO₃⁻ (eq 4). Three ν(CO) infrared bands (2088(w), 2039(m, sh), 2026(s) cm⁻¹) in CH₂Cl₂ solution are observed for 6H⁺CF₃SO₃⁻ shifted by >100 cm⁻¹ from the unprotonated 6 values.
A trace of unprotonated 6 is also detected in the spectrum. This is probably due to deprotonation of \(6H^+\text{CF}_3\text{SO}_3^-\) by adventitious water or even \(\text{Cl}^-\) in the \(\text{NaCl}\) IR cells since titration calorimetry, vide infra, establishes that protonation of 6 with \(\text{CF}_3\text{SO}_3\) is quantitative. The \(^1\text{H}\) NMR spectrum of \(6H^+\text{CF}_3\text{SO}_3^-\) in \(\text{CDCl}_3\) shows a high field triplet hydride resonance at \(-7.90\) ppm \((2J_{PH} = 30.7\) Hz\) which is coupled to two equiv phosphine ligands.

Compounds 7-10 are also quantitatively protonated at the metal center as determined by IR and \(^1\text{H}\) NMR spectroscopy with one equiv of \(\text{CF}_3\text{SO}_3\)H. The two \(\nu(\text{CO})\) bands of weak and strong intensity in \(7H^+\text{CF}_3\text{SO}_3^- - 10H^+\text{CF}_3\text{SO}_3^-\) are >100 cm\(^{-1}\) higher than those of their neutral precursors. The \(^1\text{H}\) 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 \(\text{PR}_3\) ligands are shifted downfield from those in the unprotonated complexes. The protonated complexes \(6H^+\text{CF}_3\text{SO}_3^- - 10H^+\text{CF}_3\text{SO}_3^-\) are stable in solution as long as they are kept under nitrogen or argon. Also, the solution \((\text{CH}_2\text{Cl}_2)\) IR spectra of \(6H^+\text{CF}_3\text{SO}_3^-\), \(8H^+\text{CF}_3\text{SO}_3^-\), and \(10H^+\text{CF}_3\text{SO}_3^-\) show no absorptions characteristic of coordinated \(\text{CF}_3\text{SO}_3^-.\)

There are three possible isomers for \(6H^+-10H^+\), structures A, B, and C. The triplet Fe-H resonances and the equivalence of the \(\text{PR}_3\) ligands in the \(^1\text{H}\) 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 $^1\text{H}$ NMR spectrum.

The number and relative intensities of the $\nu$(CO) bands in the IR spectra of $6\text{H}^+-10\text{H}^+$ 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 a $B_1$, vibrational modes, respectively. For $6\text{H}^+-10\text{H}^+$, 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 that are only partially resolved for $6\text{H}^+$ and $7\text{H}^+$ and unresolved for $8\text{H}^+-10\text{H}^+$ in CH$_2$Cl$_2$ solution. The following related complexes have also been assigned the mer geometry A based on their IR spectra in the $\nu$(CO) region:

$[\text{Fe}(\text{CH}_3)(\text{CO})_3(\text{PMe}_3)_2]^+$, $[\text{Ru}(\text{H})(\text{CO})_3(\text{PPh}_3)_2]\text{PF}_6$, $[\text{Os}(\text{H})(\text{CO})_3(\text{PPh}_3)_2]\text{PF}_6$, $\text{Mn}(\text{H})(\text{CO})_3(\text{PPh}_3)_2$, $\text{Mn}(\text{H})(\text{CO})_3(\text{PMePh}_2)_2$, $\text{Re}(\text{H})(\text{CO})_3(\text{PPh}_3)_2$, $\text{Re}(\text{H})(\text{CO})_3(\text{PET}_3)_2$, $\text{Mn}(\text{H})(\text{CO})_3(\text{PPh}_3)_2^+$ and $\text{Mn}(\text{H})(\text{CO})_3(\text{PMePh}_2)_2^+$ which are isoelectronic with $6\text{H}^+$ and $8\text{H}^+$, respectively, have been established by X-ray crystallography. The fac-geometry B for $6\text{H}^+-10\text{H}^+$ is
unlikely since this structure having $C_s$ symmetry is predicted to give three $\nu$(CO) bands of equal intensity ($2A' + A''$).\textsuperscript{38}

In principle, "virtual coupling"\textsuperscript{43} of the $\text{trans}$ phosphines in structure A should cause the Me resonances in $8H^+-10H^+$ to appear as triplets in the $^1H$ NMR spectrum. However, they occur as singlets in $8H^+$ and $9H^+$ and as a doublet ($J_{PH} = 8.5$ Hz) in $10H^+$. The Me resonances for $\text{mer-Mn(H)(CO)}_3[\text{P(OPh)}_2\text{Me}]_2$\textsuperscript{44} and $\text{mer-Mn(H)(CO)}_3[\text{PMePh}_2]_2$\textsuperscript{42} also occur as doublets in spite of their having $\text{trans}$-$\text{PR}_3$ groups. Thus, in these cases the $^1H$ NMR spectra do not distinguish between the $\text{mer}$ (A) and $\text{fac}$ (B) structures.

The $^{13}$C NMR for the CO ligands, however, are more conclusive in supporting the $\text{mer}$ (A) structure for $6H^+-10H^+$. For $8H^+$, two 1:2:1 triplets\textsuperscript{45} are observed at 204.71 ppm ($2J_{PC} = 23.65$ 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 $\text{trans}$ CO groups leaving the remaining triplet to the CO $\text{trans}$ to the hydride in A. A comparison of the $2J_{PC}$ values in $8H^+$ with those in $[\text{Fe(CH}_3\text{(CO)}_2(\text{PMe}_3)]^+$, D\textsuperscript{46}, also supports structure A for these complexes. In D, the $2J_{PC}$ values
for the cis CO and PMe₃ ligands ($^{2}J_{P1C1} = 27.3$ Hz, $^{2}J_{P2C2} = ^{2}J_{P1C2} = 18.4$ Hz) are much smaller than those for trans CO and PMe₃ ligands ($^{2}J_{P2C1} = 41.3$ Hz). The $J_{PC}$ values in $\mathbf{8H}^{+}$ (23.65 and 13.35 Hz) indicate that there are only cis CO and PR₃ groups as required by structure A; there are no coupling constants in the range of 41 Hz which should be observed if there were trans CO and PR₃ ligands as in structure B. Supporting the mer structure A for these cations is the $^{13}$C NMR spectrum of $\mathbf{6H}^{+}$CF₃SO₃⁻ which also gives small $^{2}J_{PC}$ values of 23.3 Hz (204.88 ppm, t, CO) 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).

**Calorimetric Studies**

Heats of protonation ($\Delta H_{HM}$) determined by calorimetric titration in DCE solvent at 25.0 °C of the complexes Cp’Ir(L)(L’) 1-5, 11-13 (eq 3), and Fe(CO)₃(PR₃)₂ 6-10 with 0.1 M CF₃SO₃H(eq 4) 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. The only exception to this behavior was that of Fe(CO)₃(PMePh₂)₂ 8 for which the plots were slightly curved; the curvature was probably due to a small amount of decomposition of the reactant. However, the $\Delta H_{HM}$ 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
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less basic Fe(CO)$_3$(PPh$_3$)$_2$ (6) (-14.1 kcal mol$^{-1}$) and the more basic Fe(CO)$_3$(PMe$_2$Ph)$_2$ (9) (-21.2 kcal mol$^{-1}$).

Infrared spectra were taken of the titrated solutions. Those of the iridium complexes 1-5, 11, 13 gave $\nu$(CO) bands corresponding to the protonated products 1H$^+$-5H$, 11H$, 13H$. The protonated iron complexes, 6H$^+$-10H$, which are much less basic than those of Ir, 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, 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 $\Delta H_{HM}$ value. For reasons which are not understood, we were unable to obtain a reproducible $\Delta H_{HM}$ value for 14 even though this complex and its protonated product 14H$^+$CF$_3$SO$_3^-$ appeared to be stable under the conditions of the titrations.
Table I. Heats of protonation ($\Delta H_{HM}$) of Cp'Ir(L)(L') and Fe(CO)$_3$(PR$_3$)$_2$ complexes

<table>
<thead>
<tr>
<th>Metal Complex</th>
<th>$-\Delta H_{HP}$, kcal mol$^{-1}$</th>
<th>$-\Delta H_{HM}$, kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpIr(CO)[P(p-ClC$_6$H$_4$)$_3$], 1</td>
<td>17.9 (±0.2)</td>
<td>29.2 (±0.2)</td>
</tr>
<tr>
<td>CpIr(CO)(PPh$_3$), 2</td>
<td>21.2 (±0.1)</td>
<td>30.1 (±0.2)</td>
</tr>
<tr>
<td>CpIr(CO)(PMePh$_2$), 3</td>
<td>24.7 (±0.0)</td>
<td>31.5 (±0.1)</td>
</tr>
<tr>
<td>CpIr(CO)(PMe$_2$Ph), 4</td>
<td>28.4 (±0.2)</td>
<td>32.4 (±0.3)</td>
</tr>
<tr>
<td>CpIr(CO)(PMe$_3$), 5</td>
<td>31.6 (±0.2)</td>
<td>33.2 (±0.5)</td>
</tr>
<tr>
<td>(indenyl)Ir(CO)(PPh$_3$), 11</td>
<td>21.2 (±0.1)</td>
<td>29.8 (±0.3)</td>
</tr>
<tr>
<td>CpIr(CS)(PPh$_3$), 12</td>
<td>21.2 (±0.1)</td>
<td>26.51 (±0.01)</td>
</tr>
<tr>
<td>Cp*Ir(CO)$_2$, 13</td>
<td>---</td>
<td>21.4 (±0.1)</td>
</tr>
<tr>
<td>CpIr(1,5-COD)$_2$, d</td>
<td>---</td>
<td>22.8 (±0.2)</td>
</tr>
<tr>
<td>Cp*Ir(1,5-COD)$_2$, d</td>
<td>---</td>
<td>28.5 (±0.2)</td>
</tr>
<tr>
<td>Fe(CO)$_3$(PPh$_3$)$_2$, 6</td>
<td>21.2 (±0.1)</td>
<td>14.1 (±0.1)</td>
</tr>
<tr>
<td>Fe(CO)$_3$[P(p-MeOC$_6$H$_4$)$_3$]$_2$, 7</td>
<td>24.1 (±0.2)</td>
<td>16.2 (±0.3)</td>
</tr>
<tr>
<td>Fe(CO)$_3$(PMePh$_2$)$_2$, 8</td>
<td>24.7 (±0.0)</td>
<td>17.6 (±0.3)</td>
</tr>
<tr>
<td>Fe(CO)$_3$(PMe$_2$Ph)$_2$, 9</td>
<td>28.4 (±0.2)</td>
<td>21.2 (±0.4)</td>
</tr>
<tr>
<td>Fe(CO)$_3$(PMe$_3$)$_2$, 10</td>
<td>31.6 (±0.2)</td>
<td>23.3 (±0.3)</td>
</tr>
</tbody>
</table>

aFor protonation with CF$_3$SO$_3$H in DCE solvent at 25.0 °C.

bRef 7.

cNumbers in parentheses are average deviations.

dRef 3.
DISCUSSION

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

**Basicities of the CpIr(CO)(PR₃) Complexes 1-5**

The basicity of the metal (ΔHₜ) in these complexes increases as the free phosphine basicity (ΔHₚ) increases (Table I). The basicities of the phosphines extend over a wide range from the weakly basic P(p-ClC₆H₄)₃ (ΔHₚ = -17.9 kcal mol⁻¹; pKₐ = 1.03) to the very basic PMes (ΔHₚ = -31.6 kcal mol⁻¹; pKₐ = 8.65). However, the ΔHₜ values only range from -29.2 kcal mol⁻¹ for CpIr(CO)[P(p-ClC₆H₄)₃] (1) to -33.2 kcal mol⁻¹ for CpIr(CO)(PMes) (5). A linear correlation (eq 9a) with a correlation coefficient (r) of 0.996 is obtained when ΔHₜ is plotted vs phosphine ΔHₚ (Figure 1).

\[-ΔHₜ = -0.298 \Delta Hₚ + 23.9; \text{ in kcal mol}^{-1}\]  
\[-ΔHₜ = 0.540 pKₐ + 28.7; \text{ in kcal mol}^{-1}\]
Figure 1. Correlations of metal basicity ($\Delta H_{HM}$) with phosphine basicity ($\Delta H_{HP}$) as determined by calorimetric titration with 0.1 M CF$_3$SO$_3$H 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.
The correlation between the $\Delta H_{HM}$ and $pK_a$ values (eq 9b) is also linear ($r = 0.992$). Eq 9a suggests that the overall basicity of a complex is made up of a phosphine contribution ($-0.298 \Delta H_{HP}$) and a metal fragment (CpIr(CO)) contribution (23.9). The 0.298 coefficient for $\Delta H_{HP}$ (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 $\Delta H_{HP}$ is a measure of the $\sigma$-donor ability of the phosphine, the linear correlation with $\Delta H_{HM}$ (Figure 1) suggests, but does not prove, that the phosphine ligands in 1-5 behave as primarily $\sigma$-donor ligands thus supporting previous assignments of these phosphines as $\sigma$-donor ligands. However, it is not possible to distinguish phosphine $\pi$-bonding if its contribution correlates linearly with $\sigma$-donor ability. Though cone angles ($\theta$) 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 ($\theta$) of the phosphine does not significantly affect the $\Delta H_{HM}$ values, as might be expected for these relatively uncrowded reactants and products.

The $\Delta H_{HM}$ values are inversely proportional (eq 10, $r = -0.969$) to the $\nu$(CO) values (Figure 2) of the CpIr(CO)(PR$_3$) compounds 1-5.
in CH$_2$Cl$_2$ solvent, indicating that increasing phosphine basicity causes the electron density on the iridium to increase. This results in an increase in iridium to CO d$\pi \rightarrow p\pi^*$ backbonding that decreases the CO stretching frequency.\textsuperscript{38b,c} It is apparent, however, that relatively small changes in $\nu$(CO) (15 cm$^{-1}$)

$$-\Delta H_{HM} = 0.274[2034-\nu(CO)]; \quad \text{in kcal mol}^{-1}$$

(10)

occurring from 1 to 5 indicate substantial changes in metal basicity (4.0 kcal mol$^{-1}$ on going from 1 to 5). Therefore, it is important that all of the $\nu$(CO) values be measured in one solvent since changing solvents from CH$_2$Cl$_2$ (for 2, $\nu$(CO) = 1923 cm$^{-1}$) to hexanes (for 2, $\nu$(CO) = 1946 cm$^{-1}$) affects the $\nu$(CO) value by $\sim$20 cm$^{-1}$.\textsuperscript{49}

A correlation ($r = 0.978$) (eq 11) of $\Delta H_{HM}$ with the Ir-H chemical shift ($\delta$) in the complexes 2H$^+$-5H$^+$ is also obtained.

$$-\Delta H_{HM} = -4.31(\delta) - 32.4; \quad \text{in kcal mol}^{-1}$$

(11)

However, it is of limited use since data for 1H$^+$, 11H$^+$, and 13H$^+$ deviate significantly from it.
Figure 2. Correlation of metal basicity ($\Delta H_{\text{HM}}$) with $\nu$(CO) stretching frequency of CpIr(CO)(PR$_3$) complexes (upper line) and Fe(CO)$_3$(PR$_3$)$_2$ complexes (lower line).
Basicities of the Fe(CO)$_3$(PR$_3$)$_2$ Complexes 6-10

The $\Delta H_{HM}$ 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 $\Delta H_{HM}$ with $\Delta H_{HP}$ (Figure 1). The corresponding pK$_a$ correlation ($r = 0.981$) is given in eq 12b. Equation 12a shows that as the basicity of the $\text{PR}_3$ 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$^{-1}$ towards the metal basicity as PR$_3$ is varied by 1.0 kcal mol$^{-1}$.

Also, as for the CpIr(CO)(PR$_3$) system, the linear correlation between $\Delta H_{HM}$ and $\Delta H_{HP}$ suggests the metal basicity is determined by the $\sigma$-donor ability of the phosphine. However, as noted in the iridium discussion, it is not possible to exclude unequivocally some contribution of phosphorus $\pi$-bonding; Mossbauer studies$^{50}$ of Fe(CO)$_3$(PR$_3$)$_2$ complexes have been interpreted to support such $\pi$-bonding.

There is also a linear correlation (eq 13, $r = -0.972$) of $\Delta H_{HM}$ with the broad low frequency band corresponding to the E mode CO stretching vibration in the $\nu$(CO) region of the infrared spectra of 6-10 (Figure 2).
\[-\Delta H_{HM} = 0.562[1907 - \nu(CO)]; \text{ in kcal mol}^{-1}\] (13)

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

\[-\Delta H_{HM} = -5.66(\delta) - 2.99; \text{ in kcal mol}^{-1}\] (14)

**Comparisons of the Basicities of the CpIr(CO)(PR₃) and Fe(CO)₃(PR₃)₂ Complexes**

The iridium complexes 1-5 are much more basic than the corresponding Fe(CO)₃(PR₃)₂ complexes 6-10 (Figure 1). Using the PPh₃ complexes for comparison, CpIr(CO)(PPh₃) (2) \((\Delta H_{HM} = -30.1\) kcal mol\(^{-1}\)) is 16.0 kcal mol\(^{-1}\) more basic than Fe(CO)₃(PPh₃)₂ (6) \((\Delta H_{HM} = -14.1\) kcal mol\(^{-1}\)). Assuming \(\Delta S^\circ = 0\) eu, the estimated equilibrium constant \((\Delta G^* = \Delta H_{HM} = -RT\ln K)\) for the reaction (eq 15), is \(5.4 \times 10^{11}\), which illustrates

\[
\text{CpIr(CO)(PPh₃)} + \text{HFe(CO)₃(PPh₃)₂}^+ \xrightarrow{K} \text{CpIr(H)(CO)(PPh₃)}^+ + \text{Fe(CO)₃(PPh₃)₂}
\]

(15)

this very large difference in basicities. The free phosphines, e.g., PPh₃ \((\Delta H_{HP} = -21.2\) kcal mol\(^{-1}\)) have basicities which are intermediate between those of their CpIr(CO)(PR₃) 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 $\Delta H_{HM}$ with $\Delta H_{HP}$ (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$_3$)$_2$ is the greater contribution of the CpIr(CO) fragment. That CpIr(CO) is more electron-rich than Fe(CO)$_3$ is reasonable since the CO ligands are less electron-donating than Cp$^-$.$^{2b}$ Also, the metal Ir is likely to be more basic than Fe.$^{1a,2d}$

As noted above, the contribution of phosphine ligand basicity to $\Delta H_{HM}$ is indicated by the coefficients of the $\Delta H_{HP}$ terms in eq 9a (0.298) for CpIr(CO)(PR$_3$) and in eq 12a (0.916) for Fe(CO)$_3$(PR$_3$)$_2$. If a change in phosphine basicity were to produce the same change in metal basicity in both series of complexes, one would expect the $\Delta H_{HP}$ 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 $\Delta H_{HP}$, 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 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 C$_2$H$_2$Ir(CO)(PR$_3$)$_2$. 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 $\Delta H_{HM}$ 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 $\Delta H_{HM}$ vs $\nu$(CO), it is evident that $\nu$(CO) values may be used to estimate $\Delta H_{HM}$ values of closely related compounds. However, it is also clear that $\nu$(CO) values are not of general use in predicting $\Delta H_{HM}$ 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.

$$\text{IrCl(CO)(PPh}_3)_2 + \text{CF}_3\text{SO}_3\text{H} \xrightarrow{\quad} \text{trans-Ir(H)Cl(CO)(PR}_3)_2(\text{O}_3\text{SCF}_3)$$

(That CF$_3$SO$_3^-$ or MeOH was coordinated in the product was not unequivocally established.) The $K_{H^+}$ values (in parentheses) increase with increasing basicity of the phosphine: PPh$_3$ (114 M$^{-1}$) < PMePh$_2$
While the trend is the same as the $\Delta H_{HM}$ values in the Cplr(CO)(PR$_3$) and Fe(CO)$_3$(PR$_3$)$_2$ complexes, the $K_{H^+}$ values change relatively little with different phosphines. This could be due to the fact that both protonation and CF$_3$SO$_3^-$ (or MeOH) coordination are involved, and the Ir-H and IrO$_3$SCF$_3$ bond energies are likely to change in opposite directions with changes in phosphine basicity.

Kristjándóttir 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 $\Delta H_{HP}$ values of -21.2 kcal mol$^{-1}$ for PPh$_3$ and -24.9 kcal mol$^{-1}$ for PEtPh$_2$,$^{52}$ one obtains equation 17 which is analogous to 9a and 12a for the Cplr(CO)(PR$_3$). Although this equation is based on only two points, the $\Delta H_{HP}$ coefficient

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

(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
isolectronic except for the substitution of a CO ligand by PR₃. In
order to establish the range and meaning of the ΔHₜₚ 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 (ΔHₚₚ = -30.1 ± 0.2 kcal
mol⁻¹) and Cp'Ir(1,5-COD) (ΔHₚₚ = -22.8 ± 0.3 kcal mol⁻¹)³ indicates
(CO)(PPh₃) ligand combination makes the metal 7.3 kcal mol⁻¹ more
basic than does the 1,5-COD ligand (eq 18).

\[
\begin{align*}
\text{CpIr(CO)(PPh₃)} & > \text{CpIr(1,5-COD)} \\
-30.1 & > -22.8 \\
7.3 \text{ kcal mol}^{-1} \\
\text{Cp*Ir(1,5-COD)} & > \text{Cp*Ir(CO)₂} \\
-28.5 & > -21.4 \\
7.1 \text{ kcal mol}^{-1}
\end{align*}
\]

(18)

However, the 1,5-COD ligand in Cp*Ir(1,5-COD) makes the iridium
7.1 kcal mol⁻¹ more basic than two CO ligands in Cp*Ir(CO)₂ (13) (eq
18). Thus, we can estimate that the (CO)(PPh₃) ligand combination
makes the iridium 14.4 kcal mol⁻¹ more basic than (CO)₂, if one
assumes that the Cp and Cp* contributions remain the same in the
two pairs of compounds in eq 18. Thus, the replacement of a CO
ligand on Ir by a PPh₃ produces a very large increase in the basicity
of the metal. This effect is also observed in the pKₐ values for the
following pairs of compounds determined in acetonitrile:²ᵇ,ᵈ

Co(H)(CO)₄ (8.3) vs Co(H)(CO)₃(PPh₃) (15.4), Mn(H)(CO)₅ (15.1) vs
Mn(H)(CO)₄(PPh₃) (20.4), CpW(H)(CO)₃ (16.1) vs
CpW(H)(CO)₂(PMe₃) (26.6). It is evident, however, from these data that substitution of CO by PR₃ does not cause the same magnitude of increase in metal basicity in all metal complexes.

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

Recently,³ we showed that (indenyl)Ir(1,5-COD) is initially protonated with CF₃SO₃H at the iridium but the proton migrates within 15 min to the indenyl ligand to form [(η⁶-indene)Ir(1,5-COD)]CF₃SO₃ (E) (Scheme 1).

![Scheme 1](image-url)
However, knowing that the \((\text{CO})(\text{PPh}_3)\) ligand combination in 2 increases the iridium basicity by 7.3 kcal mol\(^{-1}\) relative to the 1,5-COD ligand in the analogous \(\text{CpIr}(1,5\text{-COD})\) complex (vide supra) we predicted that the iridium in 11 would be sufficiently basic that proton transfer from it to the indenyl ligand probably would not occur (Scheme 1). Indeed, the protonated complex 11\(\text{H}^+\text{CF}_3\text{SO}_3^-\) is stable as we detect no proton migration upon reflux in DCE (b.p., 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 \(\Delta H_{\text{HM}}\) 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 analog \(\text{CpIr}(\text{CO})(\text{PPh}_3)\) (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\(_3\))\(_2\)]\(\text{SbF}_6\) shows the indenyl ligand to be substantially slipped toward \(\eta^3\)-coordination,\(^{23,56}\) the indenyl donor ability may be variable and depend upon the electronic structure of each complex.
CONCLUSION

These studies demonstrate several important properties of basic metal complexes that have not been previously reported. We observe linear correlations between metal basicity as determined by $\Delta H_{HM}$ and phosphine basicity ($\Delta H_{HP}$ or $pK_a$) for the CpIr(CO)(PR$_3$) and Fe(CO)$_3$(PR$_3$)$_2$ series of complexes, respectively. However, for each 1.0 kcal mol$^{-1}$ change in phosphine basicity ($\Delta H_{HP}$), 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 $\Delta H_{HM}$ 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 ($\Delta H_{HM}$) of other complexes in these series which contain different phosphines whose $\Delta H_{HP}$ (or $pK_a$) values or $\nu$(CO) stretching frequencies are known.

Comparisons of $\Delta H_{HM}$ 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 $\Delta H_{HM}$ values of
the complexes CpIr(CO)(PPh₃) and (indenyl)Ir(CO)(PPh₃) are the same. These studies provide a quantitative basis for understanding how systematic changes in ligands affect the proton basicity of transition metal complexes.
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(c) Parshall, G. W. Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes; Wiley: New York, 1980.


(8) For a few examples see:

(9) Some qualitative studies include:

(11) One may also wish to include comparisons between phosphines and phosphites: (a) Ni[P(OR)3], Ni(dppe)2, Tolman, C. A. *Inorg. Chem.* 1972, 11, 3128. (b) Co(H)(CO)3(PR3) (PR3 = PPh3, P(OPh)3), ref 2d and (c) Hieber, W.; Lindner, E. *Chem. Ber.* 1961, 94, 1417. (d) CpCo(dppe), CpCo[P(OMe)3]2, ref 2i.


(23) The assignments for the indenyl ligand and the PPh₃ ligand are based on those given in [(indenyl)Ir(H)(PPh₃)₂⁺]: Crabtree, R. H.; Parnell, C. Organometallics 1984, 3, 1727.


(33) Newman and Bergman have shown that reaction of 
Cp*Ir(Cl)2PPh3 with NaOEt in EtOH solution gives 
Cp*Ir(OEt)(H)PPh3 which eliminates EtOH in the presence of 


(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 v(CO) stretching frequencies see: Braterman, P. S. Struct. Bond. 1976, 26, 2 and references 38b, c.


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

(53) Broadhurst, P. V. *Polyhedron* 1985, 4, 1801.


SECTION IV. BIDENTATE PHOSPHINE BASICITIES AS DETERMINED BY ENTHALPIES OF PROTONATION
Enthalpies for both the first ($\Delta H_{HP_1}$) and the second ($\Delta H_{HP_2}$) protonations of the phosphorus donors in bidentate phosphines have been determined by titration calorimetry using CF$_3$SO$_3$H in 1,2-dichloroethane solvent. The $\Delta H_{HP_1}$ values for the series Ph$_2$P(CH$_2$)$_n$PPh$_2$, $n$ = 1-6, range from -22.0 ± 0.1 kcal mol$^{-1}$ for $n$ = 1 to -25.2 ± 0.1 kcal mol$^{-1}$ for $n$ = 6. The $\Delta H_{HP_2}$ values also become more exothermic from -14.9 ± 0.2 to -24.9 ± 0.1 kcal mol$^{-1}$ with increasing alkyl chain length. The $\Delta H_{HP_1}$ and $\Delta H_{HP_2}$ values for other bidentates, Ph$_2$P(bridge)EPh$_2$ (E = P, bridge = cis-CH=CH, trans-CH=CH, 1,2-C$_6$H$_4$; E = As, bridge = CH$_2$CH$_2$) and Me$_2$PCH$_2$PMe$_2$, have also been determined. Correlations of $\Delta H_{HP_1}$ and $\Delta H_{HP_2}$ with the corresponding pK$_{a1}$ and pK$_{a2}$ values taken from the literature are presented.
INTRODUCTION

Bidentate and monodentate phosphines are common ligands in organometallic and coordination chemistry. Much effort has been directed toward understanding the effects of monodentate phosphines on properties of metal complexes. For example, the research groups of Giering,2a and Pöe,2b have recently introduced an approach to the quantitative analysis of ligand effects (QALE) using the steric and electronic properties of phosphorus(III) ligands. Relatively few studies, however, have focussed on the relationship between the properties of bidentate ligands and the properties of their metal complexes.3,4

Previously,5 Bush and Angelici measured the enthalpies of protonation (ΔHₚ, eq 1) of several aryl, mixed alkyl/aryl and alkyl phosphines with 0.1 M CF₃SO₃H in 1,2-dichloroethane (DCE) solution.

\[ \text{PR}_3 + \text{CF}_3\text{SO}_3\text{H} \xrightarrow{\text{DCE}} \text{H-PR}_3^+\text{CF}_3\text{SO}_3^-; \quad \Delta H_{\text{HP}} \] (1)

These ΔHₚ values are a quantitative measure of the basicities or σ-donor abilities of these monodentate phosphines. In this paper, the basicities of several bidentate phosphines as determined by their enthalpies of protonation with 0.1M CF₃SO₃H in DCE are reported. For the dibasic phosphines, which are listed with their abbreviations in Table I, ΔHₚ₁ represents the heat liberated during the addition
of the first equivalent of acid, while $\Delta H_{HP2}$ is the enthalpy of reaction for the addition of a second equivalent of acid. The protonation reactions occurring in these solutions are given in eqs 2 and 3, but do not necessarily represent

$$\begin{align*}
P^P + CF_3SO_3H &\xrightarrow{DCE \ 25.0 ^\circ C} HP^P CF_3SO_3^- & \quad (2) \\
HP^P CF_3SO_3^- + CF_3SO_3H &\xrightarrow{DCE \ 25.0 ^\circ C} HP^P PH^2(CF_3SO_3)_2 & \quad (3)
\end{align*}$$

$\Delta H_{HP1}$ and $\Delta H_{HP2}$, respectively, as will be discussed. The results of these studies give a quantitative measure ($\Delta H_{HP1}$ and $\Delta H_{HP2}$) of the $\sigma$-donor properties of bidentate phosphine ligands.

The studies presented herein are part of a program aimed at determining the quantitative effects of ligands on the basicities of transition metal complexes (eq 4). We have already reported a study of the effect of

$$\begin{align*}
ML_x + CF_3SO_3H &\xrightarrow{DCE \ 25.0 ^\circ C} H-ML_x^+ CF_3SO_3^- ; \Delta H_{HM} & \quad (4)
\end{align*}$$

methyl groups in the cyclopentadienyl ligand in Cp'Ir(1,5-COD) (Cp' = C$_5$MExH$_5-x$, x = 0, 1, 3-5; COD = 1,5-cyclooctadiene) on the iridium metal basicity. Forthcoming results will describe the relative effects of bidentate and monodentate ligands on transition metal complex basicities.
EXPERIMENTAL

The phosphine ligands used in these studies and their abbreviations are given in Table I. The following were purchased from Aldrich: dppm, cis-dppv, trans-dppv, dppent, and dpph. Dppe, dppbz, dppp, dppb, dmpm, and tris(p-trifluoromethyl-phenyl)phosphine were purchased from Strem. Arphos was obtained from Pressure Chemical Co. Dppp was purified by dissolving ~1.2 g of the compound in 6 mL of CH₂Cl₂ and filtering through 1 cm of Celite on a medium porosity frit. The resulting solution was then evaporated to ~3 mL and 10 mL of EtOH (95%) was added. The mixture was evaporated under vacuum until crystallization occurred. Filtration followed by a 2 x 2 mL cold EtOH wash and drying under vacuum gave white crystalline needles. Arphos and dpph were recrystallized by dissolving the compound in a minimum of C₆H₆, filtering, and adding hexanes (~2 x volume). The solution was cooled to 10 °C for 12 h. The resulting precipitate was collected by filtration and washed with 2 x 2 mL cold hexanes and dried under vacuum. Dppe was recrystallized from hot EtOH (95%) and dried under vacuum. All other compounds were used as received.

The calorimetric titration procedure was similar to that previously described. The titrations were performed under an atmosphere of argon. 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. For the determination of $\Delta H_{\text{HP1}}$, the titration period involved the addition of $\sim 1.2 \text{ mL}$ of a standardized 0.1 M ($\pm 0.2 \text{ mM}$) CF$_3$SO$_3$H solution in DCE at a constant rate during 3 minutes time to 50 mL of a $\sim 2.6 \text{ mM}$ solution of the phosphine ($\sim 10\%$ excess) in DCE at 25.0 °C. To obtain $\Delta H_{\text{HP2}}$, slightly more than one equiv of CF$_3$SO$_3$H (0.1 M, $\sim 0.105 \text{ mmol}$) was added to a 50 mL solution of the bidentate phosphine ($\sim 0.100 \text{ mmol}$). The second equiv of acid was then added (0.095 mmol) at a constant rate during $\sim 2 \text{ min}$ time to titrate at 25.0 °C the remaining unprotonated phosphine. The reaction enthalpies were corrected for the heat of dilution ($\Delta H_{\text{dil}}$) of the acid in DCE (-0.2 kcal mol$^{-1}$).

The enthalpy values reported in Table I are averages of at least 4 titrations and as many as 8. 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

The $\Delta H_{HP1}$ values (Table I) range from -19.9 kcal mol$^{-1}$ for cis-dppv to -31.0 kcal mol$^{-1}$ for dmpm and are comparable to the range of $\Delta H_{HP}$ values for the monodentate PR$_3$ compounds presented previously (-17.9 kcal mol$^{-1}$ for (p-ClC$_6$H$_4$)$_3$P to -36.6 for (t-Bu)$_3$P). However, the $\Delta H_{HP2}$ values for the smaller chelates, for example, dppm (-14.9 kcal mol$^{-1}$), are much less exothermic than any $\Delta H_{HP}$ values have yet reported. Nevertheless, all titration curves were linear indicating stoichiometric reaction of the acid with the neutral and monoprotonated species.

The low dielectric constant ($\varepsilon = 10.36$) of DCE suggests that the products formed in eqs 2 and 3 probably occur as ion pairs. Dissociation of these ion pairs, and autoprotolysis and dimerization of the acid are other reactions which may occur in nonpolar solvents such as DCE. An analysis of these factors was presented in the monodentate phosphine basicity study; it was concluded that they contribute a total of ~0.3 kcal mol$^{-1}$ to the $\Delta H_{HP}$ value. Presumably these reactions also contribute negligibly to the $\Delta H_{HP1}$ and even the weakly exothermic $\Delta H_{HP2}$ values in this study.

The $\Delta H_{HP}$ value (eq 1) of the monodentate, weakly-basic (p-CF$_3$C$_6$H$_4$)$_3$P was determined to be -13.6 kcal mol$^{-1}$.
### Table I. ΔH₁, ΔH₂ and pKα₁, pKα₂ values for bidentate phosphines

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>ΔH₁ (\text{kJ mol}^{-1})</th>
<th>pKα₁</th>
<th>ΔH₂ (\text{kJ mol}^{-1})</th>
<th>pKα₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂PCH₂PPh₂ (dppm)</td>
<td>22.0 (±0.1)</td>
<td>3.81</td>
<td>14.9 (±0.2)</td>
<td>-2.73</td>
</tr>
<tr>
<td>Ph₂P(CH₂)₂PPh₂ (dppe)</td>
<td>22.8 (±0.2)</td>
<td>3.86</td>
<td>20.2 (±0.1)</td>
<td>0.99</td>
</tr>
<tr>
<td>Ph₂P(CH₂)₃PPh₂ (dppp)</td>
<td>23.4 (±0.1)</td>
<td>4.50</td>
<td>22.4 (±0.3)</td>
<td>2.53</td>
</tr>
<tr>
<td>Ph₂P(CH₂)₄PPh₂ (dppb)</td>
<td>24.6 (±0.1)</td>
<td>4.72</td>
<td>23.8 (±0.2)</td>
<td>4.28</td>
</tr>
<tr>
<td>Ph₂P(CH₂)₅PPh₂ (dppent)</td>
<td>24.8 (±0.2)</td>
<td>4.84</td>
<td>24.5 (±0.1)</td>
<td>4.67</td>
</tr>
<tr>
<td>Ph₂P(CH₂)₆PPh₂ (dpph)</td>
<td>25.2 (±0.1)</td>
<td>5.05</td>
<td>24.9 (±0.1)</td>
<td>4.89</td>
</tr>
<tr>
<td>cis-Ph₂P(CH=CH)PPh₂ (cis-dppv)</td>
<td>19.9 (±0.3)</td>
<td>2.27</td>
<td>10.0 (±0.2)</td>
<td>-6.20</td>
</tr>
<tr>
<td>trans-Ph₂P(CH=CH)PPh₂ (trans-dppv)</td>
<td>21.7 (±0.2)</td>
<td>2.74</td>
<td>12.7 (±0.1)</td>
<td>-4.30</td>
</tr>
<tr>
<td>Ph₂P(1,2-C₆H₄)PPh₂ (dppbz)</td>
<td>21.3 (±0.1)</td>
<td>2.91</td>
<td>10.7 (±0.3)</td>
<td>-5.70</td>
</tr>
<tr>
<td>Ph₂P(CH₂)₂AsPh₂ (arphos)</td>
<td>23.2 (±0.4)</td>
<td>3.96</td>
<td>8.2 (±0.1)</td>
<td>-7.46</td>
</tr>
<tr>
<td>Me₂PCH₂PMe₂ (dmpm)</td>
<td>31.0 (±0.3)</td>
<td>8.24</td>
<td>25.8 (±0.2)</td>
<td>4.93</td>
</tr>
<tr>
<td>Et₂P(CH₂)₂PET₂ (depe)</td>
<td>31.3 (±0.3)</td>
<td>8.41</td>
<td>26.0 (±0.2)</td>
<td>5.04</td>
</tr>
<tr>
<td>Compound</td>
<td>(\delta) (\pm 0.2)</td>
<td>(\delta)</td>
<td>(\Delta H_{HP})</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------</td>
<td>---------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>((p-CF_3C_6H_4)_3P)</td>
<td>13.6 (\pm 0.2)(^d)</td>
<td>-1.32(^f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh(_3)</td>
<td>21.2 (\pm 0.1)(^d,e)</td>
<td>2.73(^e)</td>
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<td></td>
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<tr>
<td>PPh(_2Me)</td>
<td>24.7 (\pm 0.0)(^d,e)</td>
<td>4.59(^e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMe(_3)</td>
<td>31.6 (\pm 0.2)(^d,e)</td>
<td>8.65(^e)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)For protonation with 1 equiv of CF\(_3\)SO\(_3\)H in DCE solvent at 25.0 °C.
\(^b\)Ref 10.
\(^c\)For addition of a second equiv of CF\(_3\)SO\(_3\)H in DCE solvent at 25.0 °C.
\(^d\)\(\Delta H_{HP}\), eq 1.
\(^e\)Selected from ref 5.
\(^f\)Calculated from eq 7.
\(^g\)Calculated from eq 8.
DISCUSSION

$\Delta H_{HP1}$ and $\Delta H_{HP2}$ Values for the Series Ph$_2$P(CH$_2$)$_n$PPh$_2$

The $-\Delta H_{HP1}$ values for the Ph$_2$P(CH$_2$)$_n$PPh$_2$ compounds ($n = 1$-6) increase with increasing chain length (Figure 1) but level off at a value of approximately 25.0 kcal mol$^{-1}$. This trend can be explained by assuming that the PPh$_2$ group is electron withdrawing relative to an alkyl chain. Linear free energy analyses further indicate the electron-withdrawing character of the PPh$_2$ group (Hammett constant, $\sigma_p$, for PPh$_2$ = 0.19 and for CH$_3$ = -0.17). Thus, as the alkyl chain is lengthened and the electron withdrawing PPh$_2$ group is moved away from the site of protonation, the phosphorus becomes more basic. Beyond approximately $n = 4$, an increase in the alkyl chain length does not change $\Delta H_{HP1}$. At this point, $\Delta H_{HP1}$ is about -25.0 kcal mol$^{-1}$ which is within experimental error the same as $\Delta H_{HP}$ (-24.7 kcal mol$^{-1}$) of PPh$_2$Me (Table 1).

The $-\Delta H_{HP2}$ values also increase as the alkyl chain length increases; they level off at about 24.7 kcal mol$^{-1}$ for the higher $n$ values (Figure 1). A comparison of $\Delta H_{HP1}$ (-22.0 kcal mol$^{-1}$) and $\Delta H_{HP2}$ (-14.9 kcal mol$^{-1}$) for dppm shows that PPh$_2$H$^+$ is a much stronger electron withdrawing group than PPh$_2$. However, the effect of the PPh$_2$H$^+$ is rapidly attenuated to the point that at large $n$ values both $\Delta H_{HP1}$ and $\Delta H_{HP2}$ reach the same limiting value of approximately -24.8 kcal mol$^{-1}$, which is essentially the same as the value for PPh$_2$Me (-24.7 kcal mol$^{-1}$).
Figure 1. Plot of $\Delta H_{HP}$ vs $n$ of $\text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2$ (upper two curves) and $\Delta H_{HN}$ vs $n$ of $\text{H}_2\text{N(}\text{CH}_2\text{)}_n\text{NH}_2$ (lower two curves). $\Delta H_{HN}$ values are taken from ref 11a.
Thus, for the \( n = 5 \) and 6 ligands, dpent and dpph, the basicities of the P-donors are the same regardless of whether the other end of the ligand is protonated or not. That is, the basicity of one end of the ligand is not influenced by the form of the other end, \( \text{PPh}_2 \) or \( \text{PPh}_2\text{H}^+ \).

A consequence of this is that during titration with the first equiv of acid, both mono- and diprotonated \( \text{P}^\square \text{P} \) are probably formed (eqs 2 and 3). Thus, \( \Delta H_{\text{HP}1} \) does not simply correspond to the enthalpy of eq 2. To determine to what extent \( \Delta H_{\text{HP}1} \) corresponds to eq 2 for the bidentate phosphines, the amounts of \( \text{P}^\square \text{P} \), \( \text{HP}^\square \text{P}^+ \), and \( \text{HP}^\square \text{PH}^2+ \) present in solution after the addition of one equiv of CF\(_3\)SO\(_3\)H were estimated. Assuming the relative \( pK_{a1} \) and \( pK_{a2} \) values (Table I)\(^{10} \) for dpdm, dppe, and dppp measured in CH\(_3\)NO\(_2\) to be the same in DCE, the concentrations of \( \text{P}^\square \text{P} \), \( \text{HP}^\square \text{P}^+ \), and \( \text{HP}^\square \text{PH}^2+ \) in the titration solutions after 1 equiv of CF\(_3\)SO\(_3\)H has been added are calculated with use of eq 5.

\[
K = \frac{K_{a1}}{K_{a2}} = \frac{[\text{P}^\square \text{P}][\text{HP}^\square \text{PH}^2+]}{[\text{HP}^\square \text{P}^+]^2}
\]  

For the addition of 1 equiv of CF\(_3\)SO\(_3\)H to 50 mL (the 1.2 mL volume change is negligible) of 2.6 mM \( \text{P}^\square \text{P} \) (1.2 x 10\(^{-4}\) mol), the percentage of the ligand in the monoprotonated form (\( \text{HP}^\square \text{P}^+ \)) is >99% for dpdm, 92% for dppe, and 75% for dppp. Thus, for these compounds and probably cis- and trans-dppv where \( pK_{a2} \) is too low to be measured\(^{10} \) in CH\(_3\)NO\(_2\) (< 0.0 \( pK_a \) units), the \( \Delta H_{\text{HP}1} \) values
correspond to protonations of \( P^\ominus \) to form primarily \( HP^\ominus P^+ \) (eq 2), and \( \Delta H_{HP2} \) values correspond primarily to protonations of \( HP^\ominus P^+ \) to form \( HP^\ominus PH^2+ \) (eq 3). The \( \Delta H_{HP1}, \Delta H_{HP2} \) values for dppbz and arphos probably also fall into this category; however, \( pK_{a1} \) and \( pK_{a2} \) values for these ligands have not been published. Because \( pK_{a1} \) (8.41) is substantially greater than \( pK_{a2} \) (5.04) for depe\(^10\) the same will almost certainly be true for dmpm as well. Values of \( pK_{a1} \) and \( pK_{a2} \) for dmpm calculated from eqs 7 and 8 (vide infra) are 8.24 and 4.94. These indicate (eq 5) that the \( \Delta H_{HP1} \) (-31.0 kcal mol\(^{-1}\)) and \( \Delta H_{HP2} \) (-25.8 kcal mol\(^{-1}\)) values of dmpm correspond to the formation of \( HP^\ominus P^+ \) and \( HP^\ominus PH^2+ \), respectively.

For the titrations of dppb, dppent and dpph, significant amounts of \( P^\ominus \) and \( HP^\ominus PH^2+ \) are likely to be present after the addition of one equiv of acid because \( pK_{a1} \) and \( pK_{a2} \) are probably very similar considering the \( pK_a \) trend for the dppm, dppe, and dppp series of ligands (Table I). Thus, titrations of these ligands give \( \Delta H_{HP1} \) values which correspond to the formation of a mixture of \( P^\ominus \), \( HP^\ominus P^+ \), and \( HP^\ominus PH^2+ \). However, since the P-donors in these ligands are separated so far, \( \Delta H_{HP1} \) and \( \Delta H_{HP2} \) are very similar anyway.

Previously\(^5\) it was shown that there is a linear correlation (eq 6) between the \( \Delta H_{HP} \) and \( pK_a \) values of monodentate phosphines. As noted

\[
-\Delta H_{HP} = 16.3 + 1.82 \, pK_a; \quad \text{in kcal mol}^{-1}
\]  

(6)
above and in Table I, $pK_{a1}$ and $pK_{a2}$ values for several bidentate phosphines have also been determined from glass electrode potentials ($\Delta HNP$'s) at half neutralization with $\text{HClO}_4$ in $\text{CH}_3\text{NO}_2$; these $\Delta HNP$'s were then converted to $pK_a$ values in water. As for the monodentate phosphines, there is a correlation between $\Delta H_{ HP1}$ and $pK_{a1}$ of bidentate phosphines. When plotted (Figure 2) on the same graph as the $\Delta H_{ HP}$ and $pK_a$ values for monodentate phosphines, $\Delta H_{ HP1}$ and $pK_{a1}$ values fall on the same line as that of the monodentate phosphines. A linear least-squares regression analysis of the data for both the mono- and bidentate ($\Delta H_{ HP1}$) phosphines gives a new equation (eq 7) (correlation coefficient $r = 0.982$) which is only slightly different from that in eq 6.

$$-\Delta H_{ HP} = 16.0 + 1.82 \ pK_a; \ \text{in kcal mol}^{-1}$$ (7)

Although there are only 3 points, the $\Delta H_{ HP2}$ values appear to deviate (Figure 2) somewhat from eq 7. A linear least squares analysis of the $\Delta H_{ HP2}$ vs $pK_{a2}$ data gives eq 8 ($r = 1.000$). The deviation of the $\Delta H_{ HP2}$ data from

$$-\Delta H_{ HP2} = 18.8 + 1.42 \ pK_{a2}; \ \text{in kcal mol}^{-1}$$ (8)

eq 7 is largest for dppm and dppe in which the charges in the diprotonated species, $\text{HP}^+\text{PH}_2^+$, are closest to each other and solvation may be different than in diprotonated phosphines in which the positive charges are separated by greater distances. For dppp and longer chain diphosphines, this separation of the $\text{PPh}_2\text{H}^+$ groups
makes each end behave as independent phosphonium ions. The
pK\(_{a2}\) values for these longer chain bidentate phosphines, e.g., dppb,
dppent, dpph, may be calculated from eq 7. We use eqs 7 and 8 to
predict pK\(_{a1}\) and pK\(_{a2}\) values for ligands in Table I for which \(\Delta H_{HP1}\)
and \(\Delta H_{HP2}\) values have been measured.

It is interesting to compare \(\Delta H_{HP1}\) and \(\Delta H_{HP2}\) data for the
bidentate phosphines with \(\Delta H_{HN1}\) and \(\Delta H_{HN2}\) values for the
protonation of the diamines, H\(_2\)N(CH\(_2\))\(_n\)NH\(_2\) (n = 2-6), with HNO\(_3\) in
water\(^{11}\) (eqs 9 and 10).

\[
\begin{align*}
N \, \text{N} + H^+ & \overset{\text{H}_2\text{O}}{\underset{25.0 \, ^\circ C}{\longrightarrow}} N \, \text{N}^+ \quad (9) \\
\text{HN} \, \text{N}^+ + H^+ & \overset{\text{H}_2\text{O}}{\underset{25.0 \, ^\circ C}{\longrightarrow}} \text{HN} \, \text{NH}^{2+} \quad (10)
\end{align*}
\]

As for the Ph\(_2\)P(CH\(_2\))\(_n\)PPh\(_2\) series, \(-\Delta H_{HN1}\) increases with the
number of CH\(_2\) groups until it levels off at \(n \approx 4\) (Figure 1). The
relative effect of alkyl chain length on phosphorus basicity vs
nitrogen basicity can be obtained by plotting \(\Delta H_{HP1}\) vs \(\Delta H_{HN1}\) and
\(\Delta H_{HP2}\) vs \(\Delta H_{HN2}\) (Figure 3) for ligands with the same number (n) of
CH\(_2\) groups. When plotted on the same graph, one line correlating
the \(\Delta H_{HP1}\), \(\Delta H_{HN1}\) and the \(\Delta H_{HP2}\), \(\Delta H_{HN2}\) data can be drawn (Figure
3). A linear-least squares analysis gives eq 11 (r = 0.979). The slope

\[
\begin{align*}
-\Delta H_{HPx} &= 2.64 + 1.61 (\Delta H_{HNy}) \, \text{in kcal mol}^{-1} \quad (11) \\
& \quad \text{for } x = 1, \ y = 1 \\
& \quad \text{for } x = 2, \ y = 2
\end{align*}
\]
Figure 2. Plot of $\Delta H_{HP1}$ vs $pK_{a1}$ (□) and $\Delta H_{HP2}$ vs $pK_{a2}$ (•) for bidentate and monodentate phosphines. Numbers refer to the following compounds: 1) cis-dppv, 2) trans-dppv, 3) dppm, 4) dppe, 5) dppp. Points (□) not labeled are monodentate (PR₃) $\Delta H_{HP}$ values from ref 5. The $pK_{a1}$ and $pK_{a2}$ values are taken from ref 10.
Figure 3. Plot of $\Delta H_{HP1}$ vs $\Delta H_{HN1}$ (■) and $\Delta H_{HP2}$ vs $\Delta H_{HN2}$ (△) for Ph$_2$P(CH$_2$)$_n$PPh$_2$ and H$_2$N(CH$_2$)$_n$NH$_2$ (n = 2-5). The $\Delta H_{HN1}$ and $\Delta H_{HN2}$ values are taken from ref 11a.
of 1.61 shows that the relative effect of the PPh₂ (or PPh₂H⁺) groups on phosphorus basicity drops off more rapidly than the effect of NH₂ (or NH₃⁺) on nitrogen basicity as the (CH₂)ₙ link is lengthened. It is not clear why this is true but NH-hydrogen bonding to the water solvent is likely to be an important factor.

\( \Delta H_{HP1} \) and \( \Delta H_{HP2} \) Values for Other Bidentate Phosphines

The less exothermic \( \Delta H_{HP1} \) value for dppbz (-21.3 kcal mol⁻¹) compared to dppe (-22.8 kcal mol⁻¹) demonstrates the electron withdrawing character of the unsaturated chelate backbone¹⁰ as compared with -CH₂CH₂-. The basicity of dppbz is more comparable to that of PPh₃ (-21.2 kcal mol⁻¹)⁵ than PPh₂Me (-24.7 kcal mol⁻¹)⁵ which suggests that the PPh₂ group in dppbz has the same electronic effect as the ortho H in PPh₃. Thus, while the PPh₂ group is electron-withdrawing⁹ in the Ph₂P(CH₂)ₙPPh₂ series of ligands, this is not the case in dppbz. That PPh₂ and H have similar electronic effects in aromatic systems is supported by the \( \sigma_p \) value (-0.01)¹² for PPh₂ obtained from measurements of dissociation constants of substituted phosphinic and benzoic acids in aqueous THF. However, others¹³ have suggested that the PPh₂ group is electron-withdrawing (\( \sigma_p = 0.19 \)) in aromatic systems. Our results support the former conclusion.

The difference between \( \Delta H_{HP1} \) and \( \Delta H_{HP2} \) is much larger for dppbz (10.6 kcal mol⁻¹) than for dppe (2.6 kcal mol⁻¹). This suggests that the positive charge on the adjacent PPh₂H⁺ group is
more effectively transferred through the unsaturated 1,2-phenylene bridge in dppbz than through the -CH₂CH₂- link in dppe. It is also possible that the rigid 1,2-phenylene bridge which maintains the two PPh₂H⁺ groups in the diprotonated dppbz species in close proximity, will also reduce ΔHₚ₂ as compared with that in the more flexible dppe ligand. However, the latter factor probably does not contribute more than 1 or 2 kcal mol⁻¹ since cis- and trans-dppv, which also have unsaturated bridges, both also have similar large differences (9.9 and 9.0 kcal mol⁻¹, respectively) between ΔHₚ₁ and ΔHₚ₂.

As for dppbz, the cis- and trans-dppv ligands are also less basic than dppe (Table I). The ΔHₚ₁ measurements show cis-dppv to be 1.8 kcal mol⁻¹ less basic than trans-dppv; the same trend is observed in their pKₐ values¹⁰ (2.27 and 2.74, respectively). In addition, the heats of reaction (ΔH₉)¹⁴ of these compounds with Lewis acids HgX₂ (X = Cl, Br, I), eq 12, follow the same trend with cis-dppv (ΔH₉ = -80 kcal mol⁻¹, X = Cl) being 7 kcal mol⁻¹ less basic towards these Lewis acids than trans-dppv (ΔH₉ = -87 kcal mol⁻¹, X = Cl).

(Cis- and trans-dppv behave only as monodentate ligands towards HgCl₂.)¹⁴ The greater ΔHₚ₁ basicity of the trans-dppv compound

\[
P^\bigcirc P + HgX₂ \rightarrow P^\bigcirc PHgX₂; \quad ΔH₉ \quad (12)\]

than cis-dppv may be due to better stabilization of the positive charge in the monoprotonated product by p-π-conjugation of the lone pair of electrons on the unprotonated :PPh₂ group. As :PPh₂ is
more free to rotate about the P-C(vinyl) bond in the trans-isomer than in the more sterically congested cis-isomer, the lone pair of electrons on phosphorus may better orient itself to allow conjugation with the π-orbitals of the vinyl group.

The ΔH_{HP2} values (-10.0 and -12.7 kcal mol\(^{-1}\)) for cis- and trans-dppv are substantially less negative than ΔH_{HP1} for these ligands. The pK\(_a\)\(_2\) values for cis- and trans-dppv could not be measured by the potentiometric method because their basicities were too low.\(^{10}\) The successful determinations of the ΔH_{HP2} values for cis-dppv and trans-dppv demonstrate the usefulness of the calorimetric technique for measuring basicities of weakly basic compounds. Using eq 8, pK\(_a\)\(_2\) values of -6.20 and -4.30 for cis- and trans-dppv, respectively, are estimated. The weak donor character of the second phosphorus in these compounds is also illustrated by the report that cis- and trans-dppv are known to form only 1:1 adducts with HgX\(_2\) (eq 12)\(^{14}\) even when two equiv of HgX\(_2\) are used. As for dppbz, the weakly exothermic ΔH_{HP2} values for cis- and trans-dppv compared to that (-20.2 kcal mol\(^{-1}\)) of dppe indicates that the electron withdrawing effect of the proton bound to one phosphorus atom is effectively transmitted through the unsaturated vinyl group in the dppv molecule to substantially lower the basicity of the second phosphorus atom. Electrostatic repulsion between the mutually cis PPh\(_2\)H\(^+\) groups in cis-dppvH\(_2\)\(^{2+}\) could account in part for the even lower ΔH_{HP2} basicity of cis-dppv than trans-dppv.
The similarity of the basicity of trans-dppv to that of PPh₃ as
determined by both ΔHₜₚ and pKₐ measurements (Table I) suggests
that the trans-CH=CHPPh₂ and Ph groups have essentially the same
effect on phosphorus basicity. This observation is supported¹⁴ by
ΔHₕg values (eq 12) for Lewis adduct formation of HgBr₂ with trans-
dppv (-79 ± 2 kcal mol⁻¹), PPh₃ (-77 ± 4 kcal mol⁻¹), and
PPh₂(CH=CH₂) (-78 ± 2 kcal mol⁻¹), which are the same within
experimental error.

For the arphos ligand the ΔHₜₚ₁ value (-23.2 ± 0.4 kcal mol⁻¹)
is comparable to ΔHₜₚ₁ of dppe (-22.8 ± 0.2 kcal mol⁻¹) which
indicates that protonation occurs at the phosphorus atom, and AsPh₂
is within experimental error as electron-withdrawing as PPh₂. The
much lower ΔHₜₚ₂ value (-8.2 kcal mol⁻¹) of arphos, as compared
with that (-20.2 kcal mol⁻¹) of dppe is consistent with protonation of
the As atom in the second step. These protonation assignments are
in accord with the lower basicity of AsPh₃ (pKₐ = 10.60) compared
with PPh₃ (pKₐ = 8.57), as determined in anhydrous acetic acid.¹⁵
It was, however, not possible to confirm the site of initial
protonation by ¹H NMR studies of arphos with CF₃SO₃H in CDCl₃
because of rapid proton exchange.

The greater basicity of the phosphorus in arphos is also
supported by calorimetric studies of its reaction with the Lewis acid
BH₃.¹⁶ The heat of adduct formation of BH₃(g) with the phosphorus
in Ph₂PCH₂CH₂AsPh₂ is -155.3 kcal mol⁻¹, while that for the
subsequent addition of BH₃ to the arsenic atom is -103.3 kcal mol⁻¹.
These values are very similar to those for BH$_3$ addition to PPh$_3$ (-153.4 kcal mol$^{-1}$) and AsPh$_3$ (-111.3 kcal mol$^{-1}$).$^{16}$

The $\Delta H_{HP1}$ value of dmpm (-31.0 kcal mol$^{-1}$) is notably similar to that of the very basic PMe$_3$ (-31.6 kcal mol$^{-1}$).$^5$ Thus, the PMe$_2$ group in dmpm may be considered about as electron donating as H and certainly more donating than a PPh$_2$ group in dppm. Using the previously determined $pK_a$ values$^{10}$ for depe and eqs 7 and 8, $\Delta H_{HP1}$ (-31.3 kcal mol$^{-1}$) and $\Delta H_{HP2}$ (-26.0 kcal mol$^{-1}$) values for depe are calculated; thus depe is slightly more basic than dmpm which is consistent with the greater basicity of PEt$_3$ (-33.7 kcal mol$^{-1}$) as compared with PMe$_3$ (-31.6 kcal mol$^{-1}$).

When the bidentate phosphine ligands in Table I are arranged according to their $\Delta H_{HP1}$ values, their basicities decrease in the following order:

\[
\text{depe} \geq \text{dmpm} \gg \text{dpph} > \text{dppent} > \text{dppb} > \text{dppp} > \text{dppe} > \\
\text{dppm} > \text{trans-dppv} > \text{dppbz} > \text{cis-dppv}
\]

The same trend is also observed in the $\Delta H_{HP2}$ values. Since this series summarizes the energetics of phosphine bond formation with H$^+$, it presumably also represents the relative $\sigma$-donating abilities of bidentate phosphines toward metals in their metal complexes. This property appears otherwise difficult to obtain as calorimetric studies of silver(I)$^{17}$ and HgX$_2$ (X = Cl, Br, I)$^{14}$ with dppm, dppe, and dppp give a complicated array of products where the bidentate phosphines behave as chelate,$^{14,17}$ bridging$^{17}$ and/or monodentate$^{14}$ ligands.
The heat of protonation of the monodentate phosphine \((p-\text{CF}_3\text{C}_6\text{H}_4)_3\text{P}\), which is presumed to be very weakly basic\(^{2a}\), has also been determined. The \(\Delta H_{\text{HP}}\) value of \(-13.6\text{ kcal mol}^{-1}\) corresponds to a \(pK_a\) value of \(-1.32\) by application of eq 7. Thus, in the isosteric series (i.e., cone angle = 145°) \((p-X\text{C}_6\text{H}_4)_3\text{P}\) (\(X = \text{CF}_3, \text{Cl}, \text{F}, \text{H}, \text{Me}, \text{OMe}, \text{NMe}_2\))\(^{2a}\), the trifluoromethyl-substituted compound is by far the weakest base.
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SECTION V. CALORIMETRIC STUDIES OF THE HEATS OF PROTONATION OF THE METAL IN Fe(BIDENTATE PHOSPHINE, ARSINE) COMPLEXES: EFFECT OF CHELATE LIGANDS ON METAL BASICITY
Titration calorimetry has been used to determine the heats of protonation ($\Delta H_{HM}$) of Fe(CO)$_3$(L$^\wedge$L) complexes (L$^\wedge$L = dppm, dppe, dppp, dppb, dppbz, cis-dppv, arphos, dmpm, dcpe, and diars) with CF$_3$SO$_3$H (0.1 M) in 1,2-dichloroethane solution. Spectroscopic studies show that protonation occurs at the metal center to form fac-[Fe(H)(CO)$_3$(L$^\wedge$L)]CF$_3$SO$_3$. For the series Fe(CO)$_3$[Ph$_2$P(CH$_2$)$_n$PPh$_2$], $n = 1$-4, $\Delta H_{HM}$ becomes less exothermic as the chelate size increases from $n = 1$ (-24.0 ± 0.2 kcal mol$^{-1}$) to $n = 4$ (-20.1 ± 0.2 kcal mol$^{-1}$). Moreover, the chelate complexes are substantially more basic than the related non-chelate complexes Fe(CO)$_3$(PPh$_2$Me)$_2$ ($\Delta H_{HM} = -17.6 ± 0.3$ kcal mol$^{-1}$). Likewise, Fe(CO)$_3$(dmpm) is much more basic ($\Delta H_{HM} = -30.2 ± 0.4$ kcal mol$^{-1}$) than Fe(CO)$_3$(PMe$_3$)$_2$ ($\Delta H_{HM} = -23.3 ± 0.3$ kcal mol$^{-1}$). The higher basicities of complexes with small chelate ligands is ascribed to distortions imposed on the Fe(CO)$_3$(L$^\wedge$L) complexes by the chelate ligand.
INTRODUCTION

Bidentate phosphines and arsines are commonly used chelating ligands in transition metal complex chemistry.¹ The effects of the chelates on the properties and reactivities of metal complexes have been the subject of several investigations.² However, little is known of the influence of bidentate phosphine and arsine ligands on the basicities of such metal complexes.³

In this paper, the effect of how chelate size and basicity control the basicities of Fe(CO)₃(L̸̈̊L) complexes, as measured by their heats of protonation (ΔH_{HM}) with CF₃SO₃H in 1,2-dichloroethane (DCE) solvent at 25.0 °C (eq 1) is examined. Comparisons are made with ΔH_{HM} values of analogous monodentate phosphine complexes, Fe(CO)₃(L)₂. In previous calorimetric studies of basicities, the heats of protonation of monophosphines (PR₃),⁴a diphosphines⁴b and a series of methyl-
cyclopentadienyl complexes \( \text{Cp}'\text{Ir}(1,5-\text{COD}) \) (\( \text{Cp}' = \text{C}_5\text{Me}_x\text{H}_{5-x}, x = 0, 1, 3-5 \)), in which protonation occurs at the \( \text{Ir}^5 \) were reported.
EXPERIMENTAL

All preparative reactions and manipulations were carried out under an atmosphere of nitrogen using Schlenk techniques similar to those described by McNally et al. Hexanes and CH₂Cl₂ were refluxed over CaH₂ and then distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Deuteriochloroform was stored over molecular sieves in air or distilled from P₂O₅ under nitrogen. The phosphine and arsine ligands were purchased from commercial sources.

The ¹H NMR spectra were recorded in CDCl₃ (except as stated otherwise) on a Nicolet-NT 300 MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. The ³¹P{H} NMR spectra were recorded in 10 mm tubes on a Brucker WM 200 NMR spectrometer in CDCl₃ using 85% H₃PO₄ (δ = 0.00 ppm) as the external standard. A Digilab FTS-7 FT-IR spectrophotometer was used for recording solution infrared spectra. Mass spectra were obtained on a Finnigan 4000 instrument, and the elemental microanalysis of ¹H+CF₃SO₃⁻ was performed by Galbraith Laboratories Inc., Knoxville, TN.

Synthesis of Fe(CO)₃(L⁻L)

Although complexes 1,² 2,⁸a,⁹ 3,¹⁰ 5,¹¹ 6,¹² and 10⁹e,f,¹³ have been prepared previously by other methods, all of the complexes in this study were synthesized in reactions of Fe(CO)₃(bda)¹⁴a (bda = benzylideneacetone) with the appropriate phosphine. The purity
and characterization of each compound were established by infrared and $^1$H NMR spectroscopies.

Samples for $^1$H and $^{31}$P($^1$H) NMR spectra were prepared by dissolving $\sim$10 mg of each compound in 0.5 mL of CDCl$_3$ under N$_2$. The solutions were filtered under a nitrogen flow through a short plug of Celite ($\sim$2 x 0.5 cm) directly into an NMR tube to remove paramagnetic impurities. An additional 0.5 mL of CDCl$_3$ for $^1$H NMR samples and 2 mL for $^{31}$P($^1$H) NMR samples was then passed through the column to elute any remaining compound.

Fe(CO)$_3$(dppbz) (5)

A solution of Fe(CO)$_3$(bda)$_{14a}$ (0.49 g, 1.7 mmol) in THF (35 mL) was treated with a slight excess of 1,2-bis(diphenylphosphino)benzene (0.85 g, 1.9 mmol). The mixture was stirred for 24 h at room temperature. At this time the IR spectrum showed three new bands ($\nu$(CO), cm$^{-1}$, THF: 1986 s, 1916 m(sh), 1903 s) for 5 and no bands corresponding to the starting material. The mixture was filtered and the solvent was removed under vacuum. The oily residue was dissolved in a minimum of CH$_2$Cl$_2$ and chromatographed on a column of neutral alumina (15 x 3 cm, $\sim$150 mesh) with a 1:3 mixture of CH$_2$Cl$_2$/hexanes. The first yellow-orange band was collected and the solvent was evaporated under vacuum. Recrystallization by dissolving the residue in a minimum amount of CH$_2$Cl$_2$ and layering with 10 x that volume with hexanes and then cooling to -20 °C for $\sim$24 h afforded orange crystals of 5 (0.63 g,
64%). $^1$H NMR: δ 7.56-7.40 (m, C$_6$H$_5$, C$_6$H$_4$). IR(CH$_2$Cl$_2$) ν(CO), cm$^{-1}$: 1985 s, 1913 m(sh), 1897 s.

Data for Compounds 1-4, 6-10

Below are given yields, reaction times and spectral data for the other Fe(CO)$_3$(L$^\text{O}$L) complexes prepared by the above method.

Fe(CO)$_3$(dppm) (1)

Reaction time: 16 h. Yield 81%. MS (70 eV): m/e 524 (M$^+$), 495 (M$^+$-CO), 468 (M$^+$-2CO), 440 (M$^+$-3CO). $^1$H NMR: δ 4.22 (t, 2 H, $^2$J$_{FH}$ = 10.8 Hz, CH$_2$), 7.55 (m, Ph), 7.37 (m, Ph). $^{31}$P{H} NMR: δ 14.87. IR(CH$_2$Cl$_2$) ν(CO), cm$^{-1}$: 1984 s, 1911 m(sh), 1901 s.

Fe(CO)$_3$(dppe) (2)

Reaction time: 16 h. Yield: 52%. MS (70 eV): m/e 538 (M$^+$), 510 (M$^+$-CO), 482 (M$^+$-2CO), 454 (M$^+$-3CO). $^1$H NMR: δ 2.44 (pseudo-t, J = 17.6 Hz, 4 H), 7.57-7.39 (m, Ph). $^{31}$P{H} NMR: δ 96.08. IR(CH$_2$Cl$_2$) ν(CO), cm$^{-1}$: 1982 s, 1913 m, 1892 s.

Fe(CO)$_3$(dppp) (3)

Reaction time: 16 h. Yield: 52%. MS (70 eV): m/e 552 (M$^+$), 524 (M$^+$-CO), 496 (M$^+$-2CO), 468 (M$^+$-3CO). $^1$H NMR: δ 1.93 (m, 2 H, CH$_2$), 2.43 (pseudo-quintet, $^2$J$_{HH}$ = $^2$J$_{PH}$ = 5.2 Hz, 4 H, P(CH$_2$)), 7.31 (m, Ph), 7.45 (m, Ph). $^{31}$P{H} NMR: δ 46.35. IR(CH$_2$Cl$_2$) ν(CO), cm$^{-1}$: 1982 s, 1909 m, 1881 s.
Fe(CO)₃(dppb) (4)

Reaction time: 16 h. Yield, 72%. MS (70 eV): 566 (M⁺), 538 (M⁺-CO), 510 (M⁺-2CO), 482 (M⁺-3CO). ¹H NMR: δ 1.73 (br s, 4 H, CH₂), 2.40 (br s, 4 H, P(CH₂)), 7.49 (m, Ph), 7.35 (m, Ph). ³¹P{H} NMR: δ 57.12. IR(CH₂Cl₂) ν(CO), cm⁻¹: 1981 s, 1908 m, 1879 s.

Fe(CO)₃(cis-dppv) (6)

Reaction time: 26 h. Yield: 67%. ¹H NMR: δ 7.50-7.38 (m, Ph), =CH not identified. IR(CH₂Cl₂) ν(CO), cm⁻¹: 1988 s, 1918 m(sh), 1897 s.

Fe(CO)₃(arphos) (7)

Reaction time: 16 h. Yield: 55%. ¹H NMR: δ 2.19 (dt, ²J₈H = 23.9 Hz, ²J₈H = 7.0 Hz, 2 H, P(CH₂)), 2.47 (q, ²J₈H = ²J₈H = 7.0 Hz, 2 H, As(CH₂)), 7.56-7.34 (m, Ph). IR(CH₂Cl₂) ν(CO), cm⁻¹: 1982 s, 1910 m, 1890 s.

Fe(CO)₃(dmpm) (8)

Reaction time: 16 h. Yield: 53%. ¹H NMR (CD₂Cl₂, decomposes in CDCl₃): δ 1.63 (t, ²J₈H = 5.1 Hz, 12 H, CH₃), 3.23 (t, J₈H = 11.0 Hz, 2 H, CH₂). IR(CH₂Cl₂) ν(CO), cm⁻¹: 1975 s, 1899 m(sh), 1884 s.

Fe(CO)₃(dcpe) (9)

Reaction time: 16 h. Yield: 20%. ¹H NMR: δ 1.24-1.93 (m, Cy and CH₂). IR(CH₂Cl₂) ν(CO), cm⁻¹: 1968 s, 1890 s(sh), 1871 s.
Fe(CO)$_3$(diars) (10)

Reaction time: 20 h. Yield: 38%. $^1$H NMR(CD$_2$Cl$_2$), decomposes in CDCl$_3$:$^1$H 7.67 (m, 4 H, C$_6$H$_4$), 1.67 (s, 12 H, Me). IR(CH$_2$Cl$_2$) $\nu$(CO), cm$^{-1}$: 1977 s, 1901 m(sh), 1884 s.

Protonation Reactions

Compounds 1-10 were protonated by dissolving approximately 30 mg of each compound in 3 mL of CH$_2$Cl$_2$ under N$_2$. To the solution was added 1 equiv of CF$_3$SO$_3$H by microliter syringe. Immediately the color of the solution was bleached from the yellow or orange color of the neutral complex to pale yellow or pale orange, respectively. The IR spectrum showed the complete disappearance of the bands corresponding to the starting material and appearance of new bands at higher frequency for the [Fe(H)(CO)$_3$(L$^\uparrow$L)]$^+$ products. Solutions of the protonated complexes are fairly stable as long as they are kept under N$_2$, but when exposed to air they readily decompose. Upon adding 1 equiv of 1,3-diphenylguanidine base in CH$_2$Cl$_2$ solvent the original color immediately reappeared as did the IR bands corresponding to the unprotonated starting material. Samples for $^1$H NMR spectra of 1H$^+$-10H$^+$ were prepared by adding 1 equiv of CF$_3$SO$_3$H to solutions of the neutral complexes in CDCl$_3$ which were prepared as described above.

Isolation of [Fe(H)(CO)$_3$(dppm)]CF$_3$SO$_3$ (1H$^+$CF$_3$SO$_3$)$^-$

To a stirred solution of 1 (0.18 g, 0.34 mmol) in CH$_2$Cl$_2$ (4.0 mL), one equiv of CF$_3$SO$_3$H was added. The solution was then
layered with Et₂O (15 mL) and cooled slowly to -78 °C. It was stored at that temperature for three days giving pale yellow air-sensitive crystals of 1H⁺CF₃SO₃⁻ (0.18 g, 79%). Anal. Calcd for C₂₉H₂₃F₃FeO₆P₂S: C, 51.65; H, 3.44. Found: C, 51.44; H, 3.85. ¹H NMR: δ 4.31 (dt, ²J₇₅₇ = 16.8 Hz, ²J₅₇ = 13.2 Hz, 1 H, H₇), 5.57 (m, 9 lines, ²J₅₉ = 10.5 Hz, 1 H, H₅), 7.59 (m, Ph), 7.80 (m, Ph), -6.53 (td, ²J₉₄ = 42.6 Hz, ⁴J₉₄ = 3.9 Hz, 1 H, Fe-H, H₄).

IR(CH₂Cl₂) ν(CO), cm⁻¹: 2090 s, 1939 s.

[Fe(H)(CO)₃(dppe)]CF₃SO₃ (2H⁺CF₃SO₃⁻)

¹H NMR: δ 2.68 (m, 2 H, CH₂), 3.46 (m, 2 H, CH₂), 8.0-7.5 (m, Ph), -8.97 (t, ²J₉₄ = 43.9 Hz, 1 H, Fe-H). IR(CH₂Cl₂) ν(CO), cm⁻¹: 2094 s, 2042 s.

[Fe(H)(CO)₃(dppp)]CF₃SO₃ (3H⁺CF₃SO₃⁻)

¹H NMR: δ 1.83 (br m, 1 H, CH₂), 2.95 (br m, 5 H, CH₂), 7.45 (m, Ph), 7.65 (m, Ph), -7.49 (5, ²J₉₄ = 40.4 Hz, 1 H, Fe-H).

IR(CH₂Cl₂) ν(CO), cm⁻¹: 2087 s, 2034 s.

[Fe(H)(CO)₃(dppb)]CF₃SO₃ (4H⁺CF₃SO₃⁻)

¹H NMR: δ 1.80 (br s, 4 H, CH₂), 2.80 (br s, 4 H, CH₂), 7.9 (m, Ph), -7.55 (5, ²J₉₄ = 45.4 Hz, 1 H, Fe-H). IR(CH₂Cl₂) ν(CO), cm⁻¹: 2091 s, 2033 s.

[Fe(H)(CO)₃(dpbpb)]CF₃SO₃ (5H⁺CF₃SO₃⁻)

¹H NMR: δ 8.0-7.4 (m, Ph), -8.76 (t, ²J₉₄ = 44.3 Hz, 1 H, Fe-H). IR(CH₂Cl₂) ν(CO), cm⁻¹: 2096 s, 2045 s.
[Fe(H)(CO)₃(cis-dppv)]CF₃SO₃ (6H⁺CF₃SO₃⁻)

¹H NMR: δ 7.69-7.39 (m, Ph), = CH not identified, -9.50 (t, 2J_ph = 45.5 Hz, 1 H, Fe-H). IR(CH₂Cl₂) v(CO), cm⁻¹: 2095 s, 2044 s.

[Fe(H)(CO)₃(arphos)]CF₃SO₃ (7H⁺CF₃SO₃⁻)

¹H NMR: δ 2.25 (m, 1 H, CH₂), 2.75 (br m, 1 H, CH₂), 3.5 (m, 2 H, CH₂), 7.4-8.0 (m, Ph), -9.28 (d, 2J_ph = 44.4 Hz, 1 H, Fe-H). IR(CH₂Cl₂) v(CO), cm⁻¹: 2089 s, 2038 s.

[Fe(H)(CO)₃(dmpm)]CF₃SO₃ (8H⁺CF₃SO₃⁻)

¹H NMR(CD₂Cl₂): δ 1.95 (t, J_ph = 6.5 Hz, 12 H, CH₃), 3.59 (m, 9 lines, 2J_phb = 10.0 Hz, 1 H, Hb), 3.82 (q, 2J_HbHc = 2J_phc = 14.5 Hz, Hc), -7.75 (td, 2J_ph = 45.6 Hz, 4J_HH = 4.3 Hz, 1 H, Fe-H, Ha). IR(CH₂Cl₂) v(CO), cm⁻¹: 2087 s, 2031 s.

[Fe(H)(CO)₃(dcpe)]CF₃SO₃ (9H⁺CF₃SO₃⁻)

¹H NMR: δ 1.25-1.95 (br m, Cy and CH₂), -9.95 (t, 2J_ph = 43.8 Hz, 1 H, Fe-H). IR(CH₂Cl₂) v(CO), cm⁻¹: 2079 s, 2023 s.

[Fe(H)(CO)₃(diars)]CF₃SO₃ (10H⁺CF₃SO₃⁻)

¹H NMR (CD₂Cl₂): δ 2.00 (s, 6 H, CH₃), 2.07 (s, 6 H, CH₃), 8.0-7.8 (m, 4 H, Ph), -10.64 (s, 1 H, Fe-H). IR(CH₂Cl₂) v(CO), cm⁻¹: 2089 s, 2034 s.

Calorimetry Studies

Determinations of the heats of protonation of the Fe(CO)₃(L⁻^L⁻) compounds were performed using a Tronac Model 458 isoperibol
calorimeter as previously described. 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 standardized 0.1 M (± 0.2 mM) CF₃SO₃H solution in 1,2-dichloroethane (DCE) at a constant rate during 3 minutes time to 50 mL of a 2.6 mM solution of Fe(CO)₃(L^L) (10% excess) in DCE. The Fe(CO)₃(L^L) solutions were prepared by adding solid compound to an argon-filled Dewar flask. The flask was then attached to the calorimeter's insert assembly, flushed with argon, and 50 mL of DCE was added by syringe. The reaction enthalpies were corrected for the heat of dilution (ΔH_dil) of the acid in DCE (-0.2 kcal mol⁻¹).

To ensure reproducibility of the determined ΔH_HM values, at least 2 different standardized acid solutions were used for the titrations of each compound. The ΔH_HM values are reported as the average of at least 4 titrations, and as many as 6 for each compound. The error is reported as the average deviation from the mean of all the determinations.
RESULTS

Synthesis of Fe(CO)\textsubscript{3}(L'^L)

Complexes 1-10, in this study are prepared from Fe(CO)\textsubscript{3}(bda)	extsuperscript{14a} (bda = benzylideneacetone) in yields ranging from 20% for 9 to 81% for 1 (eq 4). This method is of general use for the

\[ \text{MePh Fe(CO)3(L""')} \xrightarrow{\text{THF}} \text{Fe(CO)3(L""')} \]

synthesis of Fe(CO)\textsubscript{3}(L'^L) complexes.\textsuperscript{17,18} Complexes 1-10 should be stored under N\textsubscript{2} (or vacuum); 8-10 are especially air sensitive and can be handled only for brief periods in air. Solutions of 1-10 are stable as long as they are kept under N\textsubscript{2} or Ar.

The observation of three \(\nu(\text{CO})\) bands in the solution infrared spectra (CH\textsubscript{2}Cl\textsubscript{2}) of 1-10 is consistent with these complexes having approximately trigonal bipyramidal structures\textsuperscript{19} with a ligand donor coordinated in axial and equatorial sites. The structures of 1,\textsuperscript{8b} 2,\textsuperscript{9c} 5,\textsuperscript{11} and 10\textsuperscript{13} determined by X-ray crystallography have been described as having distorted trigonal bipyramidal or square pyramidal geometries.

Singlet resonances in the \(\text{^31P[H]}\) NMR spectra of 1-4 and 5\textsuperscript{11} at room temperature indicate that the PPh\textsubscript{2} groups in these
molecules are equivalent. This is probably due to the fluxionality\textsuperscript{10} of the Fe(CO)\textsubscript{3}(L\textsuperscript{2}L) molecules (L\textsuperscript{2}L = bidentate phosphine). This has been studied in detail previously\textsuperscript{10} and is probably accomplished by relatively slight twists and bends of the M-L groups.\textsuperscript{8b,9c,10} The $^{31}$P chemical shift of the $^{31}$P[H] NMR resonances in Fe(CO)\textsubscript{3}(L\textsuperscript{2}L) depends on the size of the L\textsuperscript{2}L chelate ring.\textsuperscript{20}

**Protonation reactions of Fe(CO)\textsubscript{3}(L\textsuperscript{2}L)**

Bidentate complexes 1-10 were protonated with 1 equiv of CF\textsubscript{3}SO\textsubscript{3}H in CH\textsubscript{2}Cl\textsubscript{2} solution as shown in eq 1. Only the protonation of 10 has been described previously and then only as a personal communication to the authors in reference 21. These reactions occur immediately as indicated by the bleaching of the solution color, the disappearance of the starting complex $\nu$(CO) bands and the appearance of new $\nu$(CO) bands at higher frequency than those of the corresponding neutral starting complexes. These shifts in the $\nu$(CO) bands are characteristic of protonation at the metal.\textsuperscript{22}

Solutions of 1H\textsuperscript{+}-10H\textsuperscript{+} are stable as long as they are kept under a nitrogen or argon atmosphere. Complex 1H\textsuperscript{+}CF\textsubscript{3}SO\textsubscript{3} was isolated (79\% yield) and fully characterized; however, the solid compound decomposes immediately upon exposure to air. No attempts were made to isolate the analogous complexes 2H\textsuperscript{+}-10H\textsuperscript{+}; they were characterized by their IR and NMR spectra.

The two possible geometries for the protonated products are the \textit{fac} (C) and \textit{mer} (D) isomers.
Infrared spectra of 1H+-10H+ show two strong bands in the \( v(\text{CO}) \) region suggesting that these complexes have the \textit{fac} geometry as discussed below. The symmetric band found at higher frequency (2096 - 2087 cm\(^{-1}\)) is sharp, but the asymmetric band at lower frequency (2045-1939 cm\(^{-1}\)) is broad. Ideally a \textit{fac} geometry would be expected to have 3 strong bands\(^{23}\) as is found for the analogous M(H)(CO)\(_3\)(dppe) (M = Mn, Re) complexes.\(^{24}\) On the other hand, Re(H)(CO)\(_3\)(dppm)\(^{24b}\) has only two bands but the lower frequency absorption in CH\(_2\)Cl\(_2\) solvent (1927 cm\(^{-1}\)) is reported to be about twice as broad as that at higher frequency (2011 cm\(^{-1}\)). The Raman spectrum of the Re dppm complex, however, shows three separate lines at 2002, 1921, and 1908 cm\(^{-1}\). Thus, the broad IR band at 1927 cm\(^{-1}\) for Re(H)(CO)\(_3\)(dppm) consists of two unresolved absorptions. There are also only 2 bands in the IR spectrum of Mn(H)(CO)\(_3\)(dppm)\(^{25}\) when taken in CH\(_2\)Cl\(_2\) (2000 cm\(^{-1}\), 1917 cm\(^{-1}\)), but three bands are found in n-hexane indicating poorer resolution of the IR bands in the more polar CH\(_2\)Cl\(_2\) solution.\(^{19}\) It is thus reasonable to consider that the broad band at lower frequency for 1H+-10H+ consists of two unresolved IR absorptions which would be consistent with the \textit{fac} (C) geometry for these protonated
complexes. The *mer*-isomer D is much less likely since the equiv *trans* CO groups would be expected to give a weak $\nu$(CO) absorption at high frequency for the symmetrical stretching vibrational mode. The absence of this weak band indicates these [Fe(H)(CO)(L\(^{-}\)L)]\(^{+}\) complexes do not have structure D.

The \(^{1}\)H NMR spectra of \(1\text{H}^{+}\) to \(10\text{H}^{+}\) show one resonance in the high field region typical of metal hydrides,\(^{21,26}\) which indicates that only one isomer is present. The occurrence of this resonance as a triplet, due to coupling to the equivalent phosphorus atoms in the bidentate phosphine complexes \(1\text{H}^{+}\), \(6\text{H}^{+}\), \(8\text{H}^{+}\), and \(9\text{H}^{+}\), supports the assignment of *fac* (C) geometry for these complexes. For complexes \(1\text{H}^{+}\) and \(8\text{H}^{+}\) each triplet is further split into a doublet. Selective decoupling experiments were performed to identify the source of the extra coupling. Irradiation of the CH\(_2\) multiplet resonance of the dppm ligand at 5.57 ppm for \(1\text{H}^{+}\) reduced the Fe-H triplet of doublets resonance at -6.53 ppm to a triplet. Similarly for \(8\text{H}^{+}\), irradiation of the CH\(_2\) multiplet of dmpm at 3.59 ppm resulted in a triplet for the Fe-H resonance at -7.75. Thus, the fine structure of these hydride resonances results from long range coupling of one of the methylene protons of the dppm \(^{4}\text{J}_{\text{HH}} = 3.9\ \text{Hz}\) or dmpm \(^{4}\text{J}_{\text{HH}} = 4.3\ \text{Hz}\) ligand (see structure E). The complexes Re(H)(CO)\(_{3}\)(dppm)\(^{24b}\), and \((\text{C}_{5}\text{Me}_{5})\text{Ru}(\text{H})(\text{dppm})\(^{3c}\) were also
reported to exhibit a similar type of long range coupling ($^4J_{HH} = 4.0$ and 3.5 Hz, respectively). It is likely that the coupling is between protons $H_a$ and $H_b$ in structure $E$ because of the "w-conformation" found between the two nuclei.$^{27}$

Previously, it was noted for Mn(CH$_3$)(CO)$_3$(dppm)$^{28}$ that the observed chemical shift inequivalence of the methylene protons in the dppm ligand ($H_b$ and $H_c$) indicated a static geometry at the Mn atom. The inequivalence of the methylene protons in $1H^+$ and $8H^+$ show that these complexes are also stereochemically non-fluxional in contrast to the neutral complexes.

The hydride resonance for the arphos complex $7H^+$ occurs as a doublet at -9.28 ppm, $^2J_{PH} = 44.4$ Hz. Because the $^2J_{PH}$ value is similar to those for the other bidentate phosphine complexes $7H^+$ presumably also has the fac geometry. Complex $10H^+$ has only a singlet hydride resonance (-10.64 ppm) because the diars ligand contains no phosphorus atoms. The Me groups on the ligand in $10H^+$ are split into two singlets, 2.00 and 2.07 ppm, presumably from two Me groups cis to the hydride ligand and two trans to Fe-H.
Calorimetric Studies

Heats of protonation ($\Delta H_{HM}$) of the bidentate complexes 1-10 determined by calorimetric titration are presented in Table I. The values range from -20.1 kcal mol$^{-1}$ for complex 4 to -30.2 kcal mol$^{-1}$ for 8. As expected for titrations of reactions which occur stoichiometrically, rapidly, and without significant decomposition of the reactant or product, titration plots of temperature vs amount of acid added are linear.$^{16}$ Titrations of the air sensitive 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 increase in baseline slope is only ~5% of the titration slope indicating the heat contributed by decomposition is relatively small, and the effect on the $\Delta H_{HM}$ values is probably within the experimental error.

Because DCE has a low dielectric constant ($\varepsilon = 10.36$)$^{29}$ the products formed in eq 1 probably occur as ion pairs. Dissociation of these ion pairs, and autoprotolysis and dimerization of the acid are other reactions which may occur in nonpolar solvents such as DCE. An analysis of these factors was presented in the monodentate phosphine basicity study,$^{4a}$ it was concluded that they contribute less than 2% to the total $\Delta H_{HP}$ value. Presumably these reactions also contribute negligibly to $\Delta H_{HM}$ values in the current study.

Also listed in Table I are the heats of protonation, $\Delta H_{HP1}$ and $\Delta H_{HP2}$, for the free bidentate ligands$^{4b,30}$ determined under the
The same conditions (25.0 °C, in DCE solution) with 1 and 2 equiv of CF$_3$SO$_3$H. The $\Delta$H$_{HP1}$ and $\Delta$H$_{HP2}$ values correspond predominantly to the reactions in eq 3 and 4 for ligands (e.g. dppm and dppe) where there is a substantial difference between $\Delta$H$_{HP1}$ and $\Delta$H$_{HP2}$.

When this difference is small as for dppb, both

$$\text{P}^\bigcirc\text{P} + \text{CF}_3\text{SO}_3\text{H} \xrightarrow{\text{DCE} \ 25.0 \ ^\circ\text{C}} \text{HP}^\bigcirc\text{P}^+\text{CF}_3\text{SO}_3^-$$

(3)

$$\text{HP}^\bigcirc\text{P}^+\text{CF}_3\text{SO}_3^- + \text{CF}_3\text{SO}_3\text{H} \xrightarrow{\text{DCE} \ 25.0 \ ^\circ\text{C}} \text{HP}^\bigcirc\text{PH}^{2+}(\text{CF}_3\text{SO}_3)_2$$

(4)

reaction 3 and 4 occur simultaneously, as discussed previously, and have essentially the same values of $\Delta$H$_{HP1}$ and $\Delta$H$_{HP2}$. 
Table I. Heats of protonation (ΔH<sub>HM</sub>) of Fe(CO)<sub>3</sub>(L'<L') and Fe(CO)<sub>3</sub>(L) complexes and the uncoordinated phosphines<sup>a</sup>

<table>
<thead>
<tr>
<th>Complex</th>
<th>ΔH&lt;sub&gt;HM&lt;/sub&gt;, kcal mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Chelate ring size</th>
<th>ΔH&lt;sub&gt;HP1&lt;/sub&gt;, kcal mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>ΔH&lt;sub&gt;HP2&lt;/sub&gt;, kcal mol&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(dppm) 1</td>
<td>24.0 (±0.2)&lt;sup&gt;ε&lt;/sup&gt;</td>
<td>4</td>
<td>22.0 (±0.1)</td>
<td>14.9 (±0.2)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(dppe) 2</td>
<td>23.2 (±0.1)</td>
<td>5</td>
<td>22.8 (±0.2)</td>
<td>20.2 (±0.1)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(dppm) 3</td>
<td>21.1 (±0.2)</td>
<td>6</td>
<td>23.4 (±0.1)</td>
<td>22.4 (±0.3)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(dppb) 4</td>
<td>20.1 (±0.2)</td>
<td>7</td>
<td>24.6 (±0.1)</td>
<td>23.8 (±0.2)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(dppbz) 5</td>
<td>23.4 (±0.2)</td>
<td>5</td>
<td>21.3 (±0.1)</td>
<td>10.7 (±0.3)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(cis-dppv) 6</td>
<td>23.1 (±0.3)</td>
<td>5</td>
<td>19.9 (±0.3)</td>
<td>10.0 (±0.2)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(arphos) 7</td>
<td>22.6 (±0.1)</td>
<td>5</td>
<td>23.2 (±0.4)</td>
<td>8.3 (±0.1)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(dpm) 8</td>
<td>30.2 (±0.4)</td>
<td>4</td>
<td>31.0 (±0.3)</td>
<td>25.8 (±0.2)</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(di) 9</td>
<td>28.4 (±0.2)</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(diars) 10</td>
<td>26.5 (±0.3)</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(PPh&lt;sub&gt;2&lt;/sub&gt;Me)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>17.6 (±0.3)&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td>24.7 (±0.0)&lt;sup&gt;g&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;3&lt;/sub&gt;(PMe&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>23.3 (±0.3)&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td>31.6 (±0.2)&lt;sup&gt;g&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>
For protonation with CF₃SO₃H (0.1M) in DCE solvent at 25.0 °C.

Ligand abbreviations: Ph₂P(CH₂)₂PPh₂ (dppm), Ph₂P(CH₂)₃PPh₂ (dppp), Ph₂P(CH₂)₄PPh₂ (dppb), Ph₂P(1,2-C₆H₄)PPh₂ (dppb2), cis-Ph₂P(CH=CH)PPh₂ (cis-dppv), Ph₂P(CH₂)₂AsPh₂ (arphos), Me₂P(CH₂)₂PMe₂ (dmpm), (Cy)₂P(CH₂)₂P(Cy)₂ (dcpe), Me₂As(1,2-C₆H₄)AsMe₂ (diars).

Represents the addition of 1 equiv of CF₃SO₃H to 1 equiv of the free phosphine, see ref 4b.

Represents the addition of a second equiv of CF₃SO₃H to 1 equiv of the free phosphine, see ref 4b.

Numbers in parentheses are average deviations.

Ref 31.

ΔHₚₚ, ref 4a.
DISCUSSION

Dependence of $\Delta H_{HM}$ on Chelate Size in Fe(CO)$_3$[Ph$_2$P(CH$_2$)$_n$PPh$_2$]

A series of protonation reactions (eq 1) of the Fe(CO)$_3$-
[Ph$_2$P(CH$_2$)$_n$PPh$_2$], 1-4, complexes where $n$ in the bidentate ligand
backbone varies from 1 to 4 have been examined; the structures of
reactants and products as established by spectroscopic and in a few
cases X-ray diffraction studies are also shown in eq 1. As seen from
the data in Table I, the basicity of the metal in these complexes is
greatest ($\Delta H_{HM} = -24.0$ kcal mol$^{-1}$) for the smallest chelate ($n = 1$)
and smallest for the largest chelate ($n = 4$, $\Delta H_{HM} = -20.1$ kcal
mol$^{-1}$); in terms of equilibrium constants $K$ for protonation,
assuming $\Delta S^o$ is the same for both reactions, Fe(CO)$_3$(dppm) (1) is
723 times more basic than Fe(CO)$_3$(dppb) (4). A plot (Figure 1) of
$\Delta H_{HM}$ vs the chelate ring size in 1-4 shows the trend of decreasing
basicity of the complex with increasing chelate ring size.

In attempting to explain this trend, one might consider
differences in donor abilities of the Ph$_2$P(CH$_2$)$_n$PPh$_2$ which lead to
differences in the basicities of their complexes. In a study$^{31}$ of
monodentate phosphine complexes Fe(CO)$_3$(PR$_3$)$_2$, it was shown that
increasing the basicity of the phosphine increases the basicity of the
complex. In the present situation, however, increasing the basicity of
the Ph$_2$P(CH$_2$)$_n$PPh$_2$$^{4b,30}$ from -22.0 kcal mol$^{-1}$ ($\Delta H_{HP_1}$, Table I) for $n$
= 1 (dppm) to -24.6 kcal mol$^{-1}$ for $n = 4$ (dppb) decreases the basicity
of the complex. Since ligand basicity does not
Figure 1. Effect of chelate ring size on the basicity ($\Delta H_{HM}$) of the iron center in the Fe(CO)$_3$(L$^\wedge$L) complexes
explain the effect of chelate ring size on complex basicity, we suggest that it is the distortion of the complex imposed by the chelate which most affects the basicity of the Fe(CO)₃[Ph₂P(CH₂)ₙPPh₂] complexes. The structure adopted and predicted by theoretical calculations by all Fe(CO)₃(PR₃)₂ complexes containing monodentate phosphines has both phosphines in the axial positions of a trigonal bipyramid (eq 5). Since this is the most stable geometry, any distortion imposed on it by a bidentate ligand would make it less stable; this higher energy geometry apparently is also more basic. From X-ray diffraction studies reported in the literature, it is evident that the structures of Fe(CO)₃(P<sup>2</sup>P) complexes change substantially depending on the chelate ring size. Thus, the P-Fe-P angle in 1<sup>b</sup> (chelate ring size = 4) is only 73.5° as compared with 84.1° in the dppe complex (2)<sup>c</sup> (chelate ring size = 5). For Fe(CO)₃(trans-1,2-bis((diphenylphosphino)methyl)cyclopropane) (F),<sup>17</sup> which has the same chelate ring size (7) as 4, the P-Fe-P angle is 123.9°. Increasing the chelate ring size to 8 in Fe(CO)₃[2,2'-bis((diphenylphosphino)methyl)-1,1'-biphenyl] (G)<sup>17</sup> increases the P-Fe-P angle to 152.0°. Thus, increasing the chelate ring size from 4-8 causes a dramatic increase in the P-Fe-P angle from 73.5° to 152.0°.
This increase in the P-Fe-P angle is accompanied by a decrease in the basicity of the complex. This trend suggests that the diaxial complex Fe(CO)₃(PPh₂Me)₂ will be less basic than any of the Fe(CO)₃[Ph₂P(CH₂)ₙPPh₂] complexes. This is indeed true as ΔH_{HM} for this complex (Table I) is only -17.6 kcal mol⁻¹. This value for Fe(CO)₃(PPh₂Me)₃ compares with -20.1 kcal mol⁻¹ for 4, which has the largest chelating ligand. (It should be noted that both the PPh₂Me and dppb ligands have the about same basicity, ΔH_{HP} = -24.7 kcal mol⁻¹ (Table I.).) If the complex is distorted even further as with the smaller dppm ligand, the complex becomes even more basic.

These interpretations of the data in Table I are based on structural differences in the Fe(CO)₃[Ph₂P(CH₂)ₙPPh₂] and Fe(CO)₃[PPh₂Me]₂ reactants. However, it is possible that there are differences in energy in the protonated products especially since the [Fe(H)(CO)₃[Ph₂P(CH₂)ₙPPh₂]]⁺ (eq 1) complexes have a fac geometry and [Fe(CO)₃(PPh₂Me)₂]⁺ has a mer structure (eq 5).
The *mer* structure is presumably more stable than the *fac* since
[Fe(CO)$_3$(PPh$_2$Me)$_2$]$^+$ with the unconstraining monodentate ligands
adopts this geometry. The *fac* geometry of the chelate complexes
{Fe(H)(CO)$_3$[Ph$_2$P(CH$_2$)$_n$PPh$_2$]}$^+$ would then be of higher energy.
Thus, if the relative basicities ($\Delta$H$_{HM}$) of the Fe(CO)$_3$(PPh$_2$Me)$_2$ and
Fe(CO)$_3$[Ph$_2$P(CH$_2$)$_n$PPh$_2$] complexes were determined by the
energies of the protonated products, Fe(CO)$_3$(PPh$_2$Me)$_2$ would be
more basic than the chelated complexes. Since this is not the case,
it appears that it is distortion by the chelate ligands of the reactants
which makes the Fe(CO)$_3$[Ph$_2$P(CH$_2$)$_n$PPh$_2$] complexes more basic
than Fe(CO)$_3$(PPh$_2$Me)$_2$.

These large chelate effects on metal complex basicity are
illustrated by the equilibrium in eq 6. The difference between $\Delta$H$_{HM}$
values for Fe(CO)$_3$(PPh$_2$Me)$_2$ and 1 gives a $\Delta$H value of -6.4 kcal mol$^{-1}$

$$\text{Fe(H)(CO)$_3$(PPh$_2$Me)$_2$}^+ + \text{Fe(CO)$_3$(dppm)} \rightleftharpoons \text{Fe(CO)$_3$(PPh$_2$Me)$_2$} + \text{[Fe(H)(CO)$_3$(dppm)]}^+$$

for this reaction. Assuming $\Delta S = 0$ e.u., the equilibrium constant for
eq 6 is $4.9 \times 10^4$. A very similar enhancement (-6.9 kcal mol$^{-1}$) in
metal basicity is seen in the comparison of $\Delta$H$_{HM}$ values (Table I) for
the chelate complex Fe(CO)₃(dmpm) (8) (-30.2 kcal mol⁻¹) and the monodentate analog Fe(CO)₃(PMe₃)₂ (-23.3 kcal mol⁻¹).

**Effects on ΔH₉₅ of Other Bidentate Ligands in Fe(CO)₃(L²L)**

The basicities of the free bidentate ligands₄ᵇ,₃⁰ in complexes 5-7 are somewhat weaker donor ligands than dppe, as measured by their ΔH₉₅ values (Table I). This results from the relatively electron-withdrawing bridging groups, 1,2-C₆H₄ in dppbz and cis-CH=CH in cis-dppv, and the poorer donor ability of the AsPh₂ group in arphos. Despite the weaker donating abilities of these ligands, complexes 5-7 have ΔH₉₅ values which are essentially the same as that (-23.2 kcal mol⁻¹) of Fe(CO)₃(dppe). It appears that it is the chelate ring size of 5 which is common to these complexes, and among complexes with similar ligand ΔH₉₅ values, it is the chelate ring size which is the most important factor controlling the ΔH₉₅ values of the complexes (Figure 1). As discussed above, the chelate ring size affects the amount of distortion in the complex and therefore the basicity of the metal. That the dppe and dppbz ligands induce similar degrees of distortion is supported by X-ray structures of 2⁹ᶜ and 5¹¹ which have P-Fe-P angles of 84.1° and 85.81°, respectively.

In complexes where the basicity of the ligand is changed more dramatically, this is reflected in the ΔH₉₅ values of the Fe(CO)₃(L²L) complexes. Thus, Fe(CO)₃(dmpm) (8) is 6.2 kcal mol⁻¹ more basic than Fe(CO)₃(dppm) (1); in terms of the equilibrium in eq 7,
\[ \text{[Fe(H)(CO)\textsubscript{3}(dppm)]}^+ + \text{Fe(CO)}\textsubscript{3}(\text{dmpm}) \rightarrow \text{Fe(CO)}\textsubscript{3}(\text{dppm}) + \text{[Fe(H)(CO)\textsubscript{3}(dmpm)]}^+ \] (7)

Compound 8 is 3.5 \times 10^4 times more basic than 1 (assuming $\Delta S^\circ = 0$ e.u.). Similarly, the cyclohexyl groups in dcpe make Fe(CO)\textsubscript{3}(dcpe) (9) 5.2 kcal mol\(^{-1}\) more basic than Fe(CO)\textsubscript{3}(dppe) (2). Jia and Morris\textsuperscript{c} recently reported a similar trend as $pK_a$ values of [CpRuH\textsubscript{2}(R\textsubscript{2}P(CH\textsubscript{2})\textsubscript{2}PR\textsubscript{2})]BF\textsubscript{4} complexes ($R = p$-CF\textsubscript{3}C\textsubscript{6}H\textsubscript{4}, Ph, $p$-MeOC\textsubscript{6}H\textsubscript{4}, Me) increase with increasing $\sigma$-donor ability of the chelate. The weaker basicity (-26.5 kcal mol\(^{-1}\)) of Fe(CO)\textsubscript{3}(diars) (10) as compared with Fe(CO)\textsubscript{3}(dcpe) (-28.4 kcal mol\(^{-1}\)) is presumably due to the weaker donor ability of arsines as compared to that of arsines.\textsuperscript{33}
CONCLUSION

The most important result of these studies is the observation that chelating ligands increase the basicity ($\Delta H_{\text{HM}}$) of the metal in the Fe(CO)$_3$[Ph$_2$(CH$_2$)$_n$PPh$_2$] complexes by 3.5-6.4 kcal mol$^{-1}$ as compared to the analogous monodentate complex Fe(CO)$_3$(PPh$_2$Me)$_2$. That these are substantial changes in basicity is illustrated by the factor of $4.9 \times 10^4$ difference in basicities of Fe(CO)$_3$(dppm) and Fe(CO)$_3$(PPh$_2$Me)$_2$. A chelate-imposed distortion of the complexes from the most stable diaxial geometry of Fe(CO)$_3$(PPh$_2$Me)$_2$ causes the metal in the chelate complexes to be more basic; the greater the distortion from this geometry the greater the basicity of the metal. These results suggest that structural effects of chelates in other metal complexes may influence the basicity of the metal.
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SUMMARY

This research illustrates several ways that the basicity of the metal center in organometallic complexes is regulated by changing the ligands. Thus, replacing the C₅H₅ ligand in (C₅H₅)Ir(1,5-COD) with C₅Me₅ increases the iridium basicity by -5.7 kcal mol⁻¹.

Systematic substitution of the methyl groups in Cp'lr(1,5-COD) (Cp' = C₅MeₓH₅₋ₓ, x=0, 1, 3-5) shows a linear increase in iridium basicity with the number of methyl groups. These data along with competitive equilibrium studies suggest that increasing the bulkiness of the Cp' ligand has no effect on metal basicity.

Increasing the basicity of the phosphine (ΔΗ_HP) in CpIr(CO)(PR₃) and Fe(CO)₃(PR₃)₂ complexes results in a linear increase in the basicity of the iridium or iron metal center (ΔΗ_HM). This quantitative trend has not been previously demonstrated. Also, linear correlations between ΔΗ_HM and the respective CO stretching frequencies of the iridium and iron complexes are obtained.

In the Fe(CO)₃[Ph₂P(CH₂)ₙPPh₂] (n=1-4) complexes the basicity (ΔΗ_HM) of the iron center increases as chelate size decreases. This trend is opposite the trend in free bidentate phosphine basicities, as determined by ΔΗ_HP, which increase with chelate size. However, the chelate complexes are more basic than their respective non-chelate derivatives Fe(CO)₃(PR₃)₂. The effects of chelate size on metal basicity are ascribed to the distortion the chelate imposes on the Fe(CO)₃(L'L) complex.
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