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Calorimetric studies of the basicities of organometallic compounds

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

Iowa State University, 1991

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Calorimetric studies of the basicities of organometallic compounds

by

John R. Sowa, Jr.

A Dissertation Submitted to the
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For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1991

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DEDICATION

to my father and the memory of my grandfather

PREFACE

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 $Fe(CO)_3(L^\frown L)$ compounds. Also in Section III, Valerio worked out the preparation of $CpIr(CO)(PMe_2Ph)$. Their expert collaboration is greatly appreciated.

SECTION I. SOLUTION ACID-BASE STRENGTHS OF ORGANOMETALLIC COMPLEXES: A REVIEW

INTRODUCTION

Quantitative data[1] 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.[2] 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[3] and nucleophilic reactions,[4] and catalytic reactions including hydrogenation, hydroformylation, and C-H activation.[5] 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.[6] Hydrogenation and hydroformylation are two important catalytic processes involving M-H intermediates.[7] Thermodynamic data on the acidity of organometallic hydrides may also distinguish between reactions of a transition-metal hydride or its conjugate base.[8] Recently, Tilset and Parker[9] have used metal-hydride pK_a 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.[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.[8a,b] In some cases the rates of kinetic acidities parallel trends in thermodynamic acidities.[8a] Rates of protonation and deprotonation of polymetallic complexes are slower than monometallic compounds even when the thermodynamic acid-base strengths are comparable.[10a] The many interesting studies of proton transfer rates are beyond the scope of this review but leading references are listed in the bibliography.[2a,c,8,10,11]

Transition-metal Brønsted acid-base strengths are usually expressed as pK_a values derived from eq 1. Thus, the simplest measure would be the determination of the pK_a of $[HML_x]^n$

$$[HML_x]^n \underset{K_b}{\overset{K_a}{\rightleftharpoons}} [ML_x]^{n-1} + H^+ \qquad (1)$$

in H_2O.[12] However, for reasons of stability, solubility, and that several metal hydrides are completely dissociated in H_2O, very few values have been determined in this solvent. Also, K_b values have been measured (eq 1); however, in this review, these are converted to K_a values ($K_a = 1/K_b$). Most pK_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]

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

$$pK_a^s = pK_{eq} + pK_a(BH^+) \quad (2b)$$

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'. 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, η^5-C_5H_5 ligand

Cp*, η^5-C_5Me_5 ligand

Cp', substituted cyclopentadienyl ligand

M-H, metal hydride

M-H$\cdot^+$, metal hydride cation radical

pK_a^s, proton dissociation constant in solvent s

pK_a', proton dissociation constant extrapolated to H_2O

H_2, dihydride or η^2-dihydrogen ligand

$(H)_2$, dihydride ligands

(η^2-H_2), η^2-dihydrogen ligand

dppm, $Ph_2PCH_2PPh_2$

dtfpe, $(p\text{-}CF_3C_6H_4)_2P(CH_2)_2P(p\text{-}CF_3C_6H_4)_2$

dppe, $Ph_2P(CH_2)_2PPh_2$

dape, $(p\text{-}MeOC_6H_4)_2P(CH_2)_2P(p\text{-}MeOC_6H_4)_2$

dmpe, $Me_2P(CH_2)_2PMe_2$

dppp, $Ph_2P(CH_2)_3PPh_2$

cis-dppv, cis-$Ph_2P(CH{=}CH)PPh_2$

dmgH, monoanion of dimethylglyoxime

Cy, cyclohexyl group

MONONUCLEAR COMPLEXES

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_2O but $Co(H)(CO)_3[P(OPh)_3]$ ($pK_a^{H_2O} = 4.95$) is more acidic than $Co(H)(CO)_3(PPh_3)$ ($pK_a^{H_2O} = 6.69$).[12a,c] In MeCN solvent, the pK_a^{MeCN} value of $Co(H)(CO)_4$ (8.3) is comparable to that estimated for HCl (8.9).[17a] 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).[17a]

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

Also, $Mn(H)(CO)_4(PPh_3)$ ($pK_a^{MeCN} = 20.4$) is less acidic by 5.3 pK_a^{MeCN} units than $Mn(H)(CO)_5$ ($pK_a^{MeCN} = 15.1$),[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_2O.[12b,18] The greater σ-donor and poorer π-acceptor ability of PPh_3[19] 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^s value. Thus, on going from PPh_3 ($pK_a' = 2.73$)[20] to $PEtPh_2$ ($pK_a' = 4.9$)[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

		pK_a, solvent =			
complex	H_2O	MeOH	MeCN	other	ref
$V(H)(CO)_6$	strong				12b,16a
$V(H)(CO)_5(PPh_3)$	6.8				12b
$CpCr(H)(CO)_3$		5.4^a	13.3		16b,32
$CpMo(H)(CO)_3$		6.2^a	13.9		16b,32
$Cp^*Mo(H)(CO)_3$			17.1		32
$CpW(H)(CO)_3$		8.0^a	16.1		16b,32
$Mn(H)(CO)_5$	7.1		15.1		12a,17a
$(\eta^6\text{-}C_6H_6)Mn(H)(CO)_2$			26.6		17b
$(\eta^4\text{-}C_6H_9)Mn(CO)_3{}^b$			22.2		17b
$Re(H)(CO)_5$			21.1		17a
$CpReH_2(CO)_2$			$23.0pK_{a1}$		17b
$[Cp_2ReH_2]^+$				8.5^c	16c
$[CpReH_2(CO)(NO)]^+$				$\sim\text{-}2^d$	16d
$FeH_2(CO)_4$	$4.00pK_{a1}$	$5.88pK_{a1}{}^a$	$11.4pK_{a1}$		
	$12.68pK_{a2}$	^{e}			16e,17b

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[a] In 70% aqueous MeOH extrapolated to H_2O.

[b] This is an agostic C-H complex. See text.

[c] In 60% aqueous dioxane. In this solvent the pK_a of NH_4^+ is 8.85.

[d] In CH_2Cl_2 with Et_2O base.

[e] Too weak to be measured.

Table I. Continued

complex	H_2O	MeOH	MeCN	other	ref
			pK$_a$, solvent =		
$CpFe(H)(CO)_2$			19.4		17b
$Cp^*Fe(H)(CO)_2$			26.3		17b
$CpFe(H)(CO)(SiCl_3)_2$			~2.6		16f
$Fe(H)(NO)(CO)_3$	~5				16g
$RuH_2(CO)_4$			18.7		17a
$CpRu(H)(CO)_2$			20.2		17a
$CpRu(H)(CO)(PPh_3)$			~27-28		13b
$OsH_2(CO)_4$		15.2	20.8		10b,32
$Os(H)(Me)(CO)_4$			23.0		32
$Co(H)(CO)_4$	strong	strong	8.4		16h, 17b
$Co(H)(CO)_3[P(OPh)_3]$	4.95		~11.4		12c, 17b
$Co(H)(CO)_3(PPh_3)$	6.96		15.4		12c, 17b
$Co(H)(CO)_3(PF_3)$	strong				16i
$Co(H)(dmgH)_2(P\text{-}n\text{-}Bu_3)$		~10.5[f]			35a
$[CpCo(H)(cis\text{-}dppv)]^+$				5.1[g]	13c
$\{CpCo(H)[P(OMe)_3)]\}^+$				6.5[g]	13c
$Rh(H)(dmgH)_2(PPh_3)$			~9.5[h]		35b,c

---

[f] 50% aqueous MeOH/hexanes.

[g] In CH_2Cl_2.

[h] 50% aqueous MeOH.

Table I. Continued

			pK_a, solvent =		
complex	H_2O	MeOH	MeCN	other	ref
$[Rh(H)(dppe)(MeOH)_2]_2^+$			1.0		16j
$[Ni(H)(dppe)_2]^+$			2.6		21
$\{Ni(H)[P(Ph(OEt)_2)]_4\}^+$			2.0		21
$\{Ni(H)[P(OEt)_3]_4\}^+$			1.5		21
$\{Ni(H)[P(OMe)_3]_4\}^+$			1.5		21
$\{Ni(H)[P(OCH_2CH_2Cl)_3]_4\}^+$			0.08		21
$\{Ni(H)[P(OCH_2CCl_3)_4]\}^+$			e		21
$\{Pd(H)[P(OMe)_3]_4\}^+$			0.7	8.0	16k,l
$\{Pt(H)[P(OMe)_3]_4\}^+$			10.2	18.5	16k,l

values (Table I) increase by 1.2 units.[17b] Above, it was shown that replacement of CO by PPh_3 increases the Mn-H or Co-H pK_a^{MeCN} value by 5.3-7.1 units, respectively. However, replacing a CO by the more basic PMe_3 ligand ($pK_a' = 8.65$)[20] in $CpW(H)(CO)_2(L)$ (L = CO, PMe_3)[17a] results in a larger 10.5 unit increase in the W-H pK_a^{MeCN} value (Table I).

Systematic substitution of phosphite ligands in NiL_4 complexes (L = $PPh(OEt)_2$, $P(OEt)_3$, $P(OCH_2CH_2Cl)_3$, $P(OCH_2CCl_3)_3$)[21] showed a linear correlation (eq 4) between the Ni-H pK_a^{MeOH} values

$$NiL_4 + H_2SO_4 \xrightleftharpoons{MeOH} HNiL_4^+ + HSO_4^- \qquad (4a)$$

$$-pK_a^{MeOH} = 0.16[2086 - \upsilon(CO)] \qquad (4b)$$

(Table I) and Tolman's $\upsilon(CO)$ values (for the A_1 band in $Ni(CO)_3L$).[22] The latter is a measure of the electronic properties of the phosphite ligands. Use of eq 4b permits the estimate of pK_a^{MeOH} values of NiL_4 complexes if Tolman's $\upsilon(CO)$ value for L is known.

Equilibrium constants for the protonation[11] of $IrCl(CO)(PR_3)_2$ complexes (eq 5) with CF_3SO_3H in MeOH solvent (given as pK_a^{MeOH} in Table II) increase, $IrCl(CO)(PPh_3)_2$ (2.06) < $IrCl(CO)(PMePh_2)_2$ (2.48) < $IrCl(CO)(PMe_2Ph)_2$ (2.80), with increasing phosphine basicity. However, this reaction is not a simple metal protonation because it was shown that either the $CF_3SO_3^-$ anion or a solvent molecule of MeOH (X) also coordinates to the square planar Ir center. Increases in PR_3 basicity should shift the

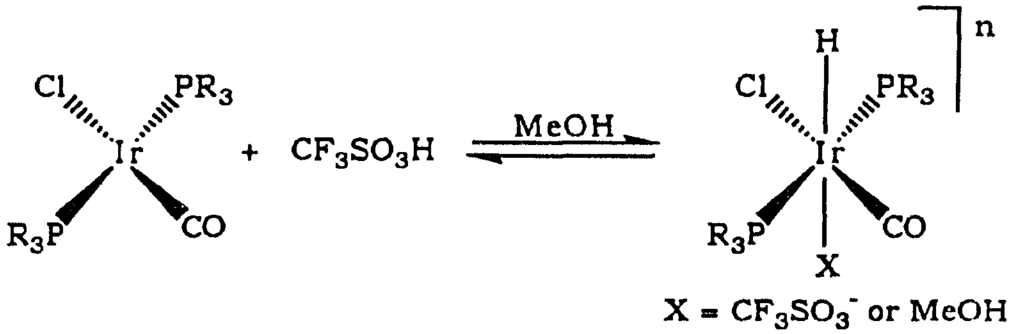
Table II. pK_a^{MeOH} values for the protonation[a] of $MY(CO)(L)_2$ complexes[b]

$MY(CO)(L)_2$	pK_a^{MeOH}
$IrCl(CO)(PPh_3)_2$	2.06
$IrBr(CO)(PPh_3)_2$	2.61
$IrI(CO)(PPh_3)_2$	2.85
$IrCl(CO)(PMePh_2)_2$	2.48
$IrBr(CO)(PMePh_2)_2$	2.93
$IrI(CO)(PMePh_2)_2$	3.21
$IrCl(CO)(PMe_2Ph)_2$	2.80
$IrBr(CO)(PMe_2Ph)_2$	3.27
$IrI(CO)(PMe_2Ph)_2$	3.58
$IrCl(CO)(AsPh_3)_2$	2.31
$IrCl(CO)(AsMePh_2)_2$	2.71
$IrCl(CO)(AsMe_2Ph)_2$	3.94
$IrCl(CO)[P(t\text{-}Bu)Me_2]_2$	2.78
$IrCl(CO)[P(t\text{-}Bu)Et_2]_2$	2.70
$IrCl(CO)[P(t\text{-}Bu)_2Me]_2$	2.66
$IrCl(CO)[P(t\text{-}Bu)_2Et]_2$	2.58
$RhCl(CO)(PPh_3)_2$	1.80
$RhBr(CO)(PPh_3)_2$	1.94
$RhI(CO)(PPh_3)_2$	2.01
$RhCl(CO)(AsPh_3)_2$	1.78
$RhBr(CO)(AsPh_3)_2$	2.00
$RhI(CO)(AsPh_3)_2$	2.04

[a] With CF_3SO_3H in MeOH solvent. There is evidence for coordination of $CF_3SO_3^-$ or 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 pK_a^{MeOH} values with PR_3 basicity are small.



(5)

Steric effects in the PR_3 ligands are indicated[11] by the decreasing pK_a^{MeOH} values (eq 6) of $IrCl(CO)(PR_3)_2$ as the bulkiness of the phosphine ligand is increased:

$$IrCl(CO)[P(t\text{-}Bu)Me_2]_2\ (2.78) > IrCl(CO)[P(t\text{-}Bu)Et_2]_2\ (2.70) >$$
$$IrCl(CO)[P(t\text{-}Bu)_2Me]_2\ (2.66) > IrCl(CO)[(t\text{-}Bu)_2Et_2]_2\ (2.58) \quad (6)$$

The pK_a^{MeOH} values (Table II) also indicates that $IrCl(CO)(AsR_3)_2$ complexes are slightly more basic than $IrCl(CO)(PR_3)_2$ complexes; e.g., the pK_a^{MeOH} value of $IrCl(CO)(AsPh_3)_2$ (2.31) is larger than that of $IrCl(CO)(PR_3)_2$ (2.06). This is surprising since PR_3 ligands are much stronger bases toward H^+[23a] and BH_3[23b] than are AsR_3 ligands. However, since As is softer than P, the AsR_3 ligand may induce more electron density on the Ir(I) center thereby increasing iridium's proton affinity.[24] Also, because of the larger As atom, the R substituents in metal complexes of AsR_3 are further from the metal than in PR_3 complexes; this reduces steric hindrance and may increase metal basicity.[24] 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[21] that Ni(dppe)$_2$ (pK_a^{MeOH} = 2.6) is more basic than Ni[P(OMe)$_3$]$_4$ (pK_a^{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) (p$K_a^{CH_2Cl_2}$ = 5.1) and CpCo[P(OMe)$_3$]$_2$ (p$K_a^{CH_2Cl_2}$ = 6.5) indicate

$$\mathrm{CpCo(L)_2} + \mathrm{H^+} \rightleftharpoons \mathrm{CpCo(H)(L)_2^+} \qquad (7a)$$

$$K_a = [\mathrm{CpCo(L_2)}][\mathrm{H^+}] / [\mathrm{CpCo(H)(L)_2^+}] \qquad (7b)$$

greater basicity for the bis(phosphite) complex.[13c]

The effects of chelate size and basicity on the coordination of dihydrogen and pKa' values of [Cp'RuH$_2$(L$\frown$L)]BF$_4$ complexes have been recently investigated by Jia and Morris.[26] 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)[20] 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 ^{31}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 III. Measured and calculated pK_a' values for $[Cp'RuH_2(L^\frown L)]^+$ and $[Cp'RuH_2(L)(L')]^+$ dihydride ($(H)_2$) and dihydrogen (η^2-H_2) complexes[a]

Ru complex	$(H)_2/(\eta^2\text{-}H_2)^b$ K_1	$pK_a'(H)_2{}^a$	$pK_a'(\eta^2\text{-}H_2)^a$	E_{pa} $(\Sigma E_L)^{c,d}$	$pK_a'(calc)^e$
$[CpRuH_2(dtfpe)]^+$	1.6	4.9	4.6	0.77 (0.72)	5.3
$[CpRuH_2(dppe)]^+$	2	7.5	7.2	0.51 (0.50	7.6
$[CpRuH_2(dppm)]^+$	$<10^{-3}$	-	7.5	0.56 (0.64)	6.1
$[CpRuH_2(PPh_3)_2]^+$	$>10^3$	8.0	-		
$[CpRuH_2(dppp)]^+$	$>10^3$	8.6	-		
$[CpRuH_2(dape)]^+$	2.6	9.0	8.6	0.38 (0.44)	9.2
$[Cp^*RuH_2(dppm)]^+$	0.5	8.8	9.2	0.35 (0.39)	6.8
$[CpRuH_2(dmpe)]^+$	0.17	-	9.8	(0.3)	10
$[Cp^*RuH_2(PMePh_2)_2]^+$	$>10^{-3}$	12.1	-		
$[Cp^*RuH_2(CO)_2]^+$		$<0^f$		(1.5)	-3
$[Cp^*RuH_2(dmpe)]^+$		unknown[f]		(0.1)	12
$[CpRuH_2(CO)_2]^+$		unknown[f]		(1.8)	-6
$[CpRuH_2(CO)(PMe_3)]^+$		unknown[f]		(1.1)	1

$[CpRuH_2(CO)(CNPh)]^+$	unknown[f]	(1.2)	0
$[Ru(H)H_2(dppe)_2]^+$	>10[f]	(0.8)	4
$[Ru(H)_2H_2(PPh_3)_3]^+$	~16[f]	(0.3)	10

[a] Measured in THF and extrapolated to H_2O. Ref 26.

[b] In CH_2Cl_2.

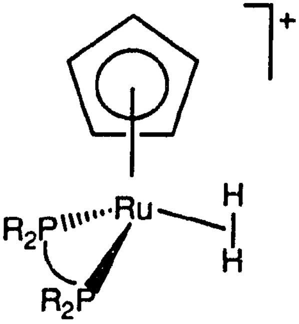
[c] Oxidation potential of Ru complexes vs NHE (V) in THF.

[d] Values in parentheses are calculated from Lever's electrochemical parameters (E_L), ref 28.

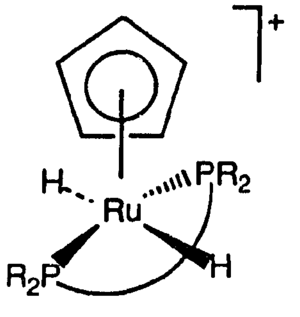
[e] Calculated from eq 9 independent of the form of the H_2 ligand.

[f] For these complexes the pKa values correspond to hydride or η^2-dihydrogen co-ordination.

Most of the H_2 complexes exist as a mixture of two tautomers in rapid equilibrium; the η^2-dihydrogen (η^2-H_2) form shown in structure **A**, and the dihydride ($(H)_2$) 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.[26a] However, when both tautomers are observed simultaneously, the pK_a' values measured for each tautomer (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.



A



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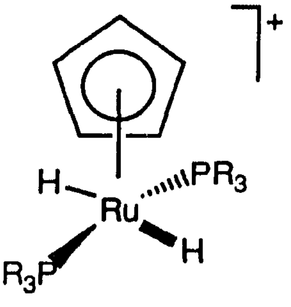


C

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).[26a]

$$\begin{aligned}&[CpRuH_2(dtfpe)]^+\ (4.8) < [CpRuH_2(dppe)]^+\ (7.3) <\\ &\qquad [CpRuH_2(dape)]^+\ (8.8) < [CpRuH_2(dmpe)]^+\ (9.8)\end{aligned} \tag{8}$$

The pK_a' value of $[CpRuH_2(dmpe)]^+$ was estimated by taking the pK_a^{MeCN} value (17.6)[27] and converting it to the aqueous scale.[26b]. For the complexes in eq 8 the η^2-H_2 triplet ^1H 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[26a] to increase Ru → 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.[26] Their pKa' values are (Table III) about one order of magnitude greater than that of the pure η^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 η^2-dihydrogen tautomer (A). Thus, when the equilibrium constant (K_1) between the dihydride and η^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

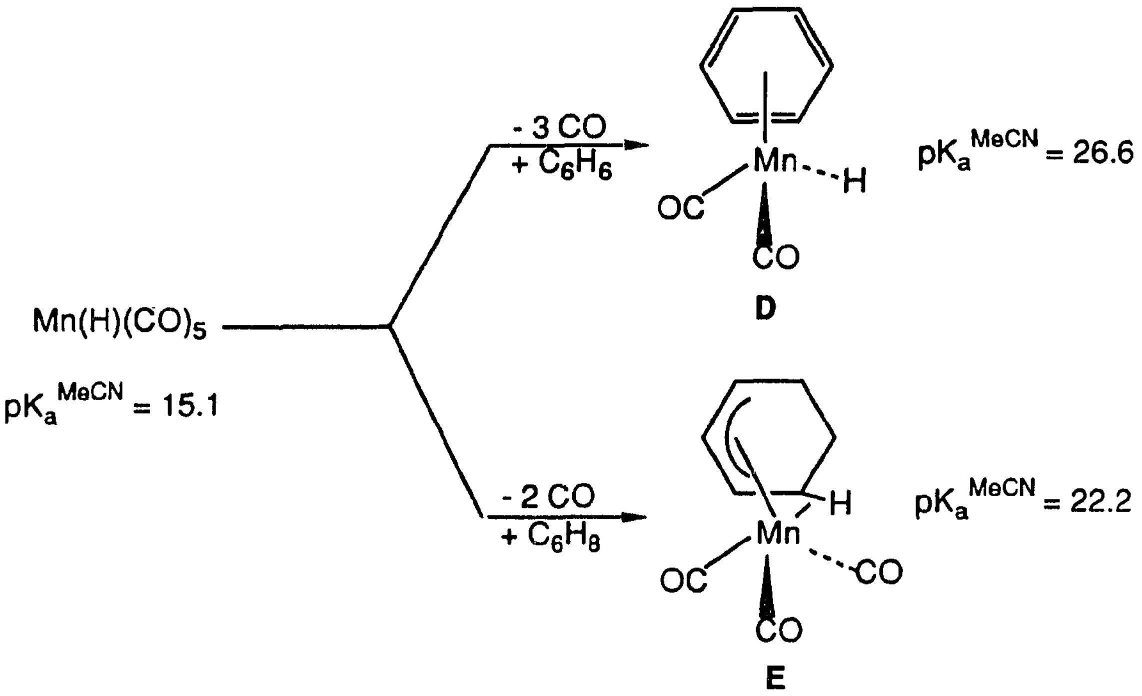
$$pK_a(RuH_2^+) = -10.6E_{ox}(MH^+/MH) + 12.9 \qquad (9)$$

potentials (E_{ox}) in THF. However, the oxidation potentials are irreversible and it is possible that the difference between the true E_{ox}° value and the irreversible E_{ox} potential vary systematically with pK_a'.[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 $[CpRuH_2(L^\frown L)]BF_4$ complexes. Furthermore, a method for predicting electrochemical potentials for the Ru_{III}/Ru_{II} couple from additive ligand parameters (ΣE_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 $[CpRuH_2(L^\frown L)]^+$ complexes but not for other Ru complexes.

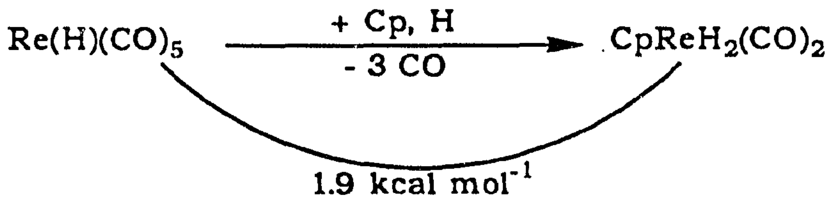
CO, Olefin, Cp, and Cp* Ligand Effects

Replacing the three CO ligands in $Mn(H)(CO)_5$ by the 6-electron donor C_6H_6 ligand[17b] to give $(\eta^6\text{-}C_6H_6)Mn(H)(CO)_2$ (**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 (η^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


Mn(H)(CO)5
pKa MeCN = 15.1
- 3 CO
+ C6H6
Mn
H
OC
CO
D
pKa MeCN = 26.6
- 2 CO
+ C6H8
H
Mn
OC
CO
CO
E
pKa MeCN = 22.2

Scheme I



(10)

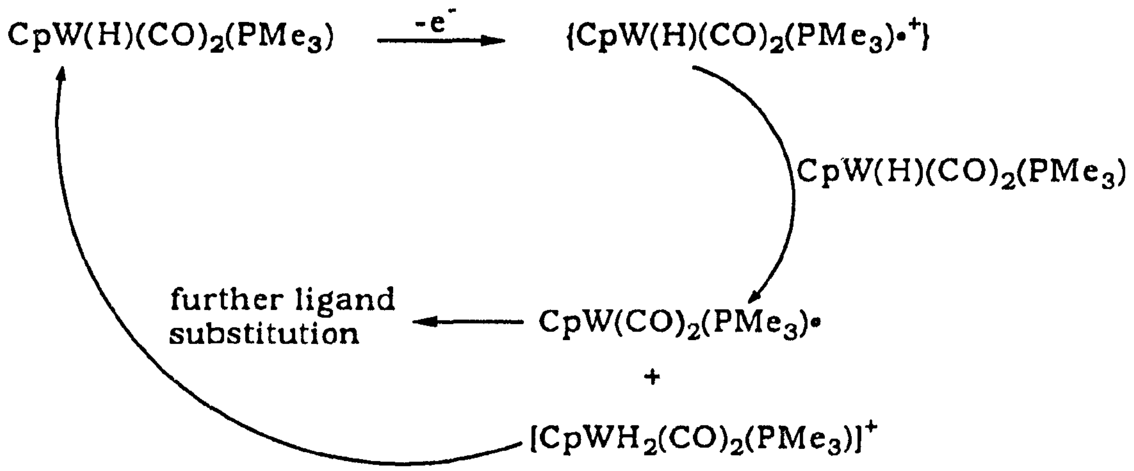
generally increases metal basicity.[17b]

The metal center in complexes containing the Cp* ligand are generally more basic than the corresponding Cp complexes because of the inductive effect of the methyl groups on Cp*.[29] Thus, the Mn-H bond in $Cp^*Mo(H)(CO)_3$ is 3.2 pK_a^{MeCN} units less acidic than that of $CpMo(H)(CO)_3$, and $Cp^*Fe(H)(CO)_3$ is less acidic than $CpFe(H)(CO)_3$ by 6.9 pK_a^{MeCN} units.[17a] Also, the average pK_a' value of $[Cp^*RuH_2(dppm)]BF_4$ (9.0) is 1.5 units larger than that of $[CpRu(\eta^2\text{-}H_2)(dppm)]BF_4$ (7.5).[26a] The Cp-Cp* replacement does not, however, increase the pK_a^s values in all of the above metal complexes by the same amount.

Radical Cation Hydrides

Ryan and coworkers[13a,b] have recently generated radical cation metal hydrides by chemical and electrochemical methods in MeCN solvent (Scheme II). All of the $M\text{-}H^{\bullet+}$ 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_2O).[13a,b]

Since the pK_a^{MeCN} values for the neutral metal hydrides (Table I)[17a] and oxidation potentials for the metal anions[9] are known, the


CpW(H)(CO)$_2$(PMe$_3$)
-e$^-$
{CpW(H)(CO)$_2$(PMe$_3$)•$^+$}
CpW(H)(CO)$_2$(PMe$_3$)
further ligand substitution
CpW(CO)$_2$(PMe$_3$)•
+
[CpWH$_2$(CO)$_2$(PMe$_3$)]$^+$

Scheme II

thermodynamic acidities ($pK_a^{MeCN}(M\text{-}H\cdot^+)$) of the radical cation hydrides are calculated from the following thermodynamic cycle:[13a]

$$\begin{array}{llll} M\text{-}H & \rightleftharpoons & M^- + H^+ & pK_a(M\text{-}H) \\ M^- & \rightleftharpoons & M\cdot + e^- & E_{ox}°(M^-) \\ \underline{M\text{-}H^+ + e^-} & \underline{\rightleftharpoons} & \underline{M\text{-}H} & \underline{E_{ox}°(M\text{-}H)} \\ M\text{-}H\cdot^+ & \rightleftharpoons & M\cdot + H^+ & pK_a(M\text{-}H\cdot^+) \end{array}$$

$$pK_a(M\text{-}H\cdot^+) = pK_a(M\text{-}H) + (F/2.303\ RT)[E_{ox}°(M^-) - E_{ox}°(M\text{-}H)] \quad (11)$$

The accuracy of the $pK_a^{MeCN}(M\text{-}H\cdot^+)$ 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.[9,13a,b] Therefore, the $pK_a^{MeCN}(M\text{-}H\cdot^+)$ 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.[30]

The radical cation hydride acidities (pK_a^{MeCN}) range from -9.5 for $[CpCr(H)(CO)_3\cdot]^+$ to 5.1 for $[CpW(H)(CO)_3\cdot]^+$ (Table IV) and they are about 20.6 ± 1.5 units less than the respective $pK_a^{MeCN}(M\text{-}H)$[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]

$[M\text{-}H\cdot]^+$	$pK_a^{MeCN}(M\text{-}H\cdot^+)$
$[CpCr(H)(CO)_3\cdot]^+$	-9.5
$[CpMo(H)(CO)_3\cdot]^+$	-6.0
$[Cp^*Mo(H)(CO)_3\cdot]^+$	-2.5
$[CpW(H)(CO)_3\cdot]^+$	-3.0
$[CpW(H)(CO)_3\cdot]^+$	5.1
$[CpRu(H)(CO)(PPh_3)\cdot]^+$	~4-5

Monodentate Anionic Ligands

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

$$\mathrm{IrCl(CO)(PPh_3)_2 < IrBr(CO)(PPh_3)_2 < IrI(CO)(PPh_3)_2\ (2.85)} \qquad (12)$$

This is consistent with the trend in electronegativities (in parentheses) of the halides: Cl$^-$ (3.16) > Br$^-$ (2.96) > 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 I$^-$ ligand is a better trans directing group than the Cl$^-$ ligand, its affinity for H$^+$ should also be greater. However, the order of Me$^-$ and 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 pK_a^{MeCN} values indicates that metal basicity increases as one goes down a column of the periodic table: CpCr(H)(CO)$_3$ (13.3) < CpMo(H)(CO)$_3$ (13.9) < CpW(H)(CO)$_3$ (16.1).[32] In group 8, there is a much larger difference in the pK_a^{MeCN} values between the first and second row elements: $FeH_2(CO)_4$ (11.4) < $RuH_2(CO)_4$ (18.7) < $OsH_2(CO)_4$ (20.8).[17a] Also, the Re in $Re(H)(CO)_5$ (pK_a^{MeCN} = 21.1) is more basic than the Mn in $Mn(H)(CO)_5$ (pK_a^{MeCN} = 15.1),[17b] and Cp_2Ru (H_o = -5.7) is more basic than Cp_2Fe (H_o = -7.7).[34] Pearson and Kresge[11] have shown a greater basicity for Ir than Rh in $MY(CO)(L)_2$ complexes (M = Ir, Rh; Y = Cl, Br, I; L = PPh_3, $AsPh_3$) in Table II (see also eq 5). The greater basicity of the heavier elements may be due to greater M-H bond strengths.[2b,9]

A few studies suggest that there are exceptions in the above trends as unpublished pK_a^{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).[2b] 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, PF_3.[35] However, that $Co(H)(dmgH)_2(P\text{-}n\text{-}Bu_3)$[36a] ($pK_a^s$ = 10.5, s = 50% aqueous MeOH/hexanes) has a higher pK_a^s value than $Rh(H)(dmgH)_2(PPh_3)$[36b,c] (pK_a^s = 9.5, s = 50% aqueous MeOH) is probably due to a combination of the stronger σ-donor ability of $P\text{-}n\text{-}Bu_3$ and the different solvent conditions in which pK_a^s 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.[17a] These trends do not appear to be well understood.

POLYMETALLIC HYDRIDE COMPLEXES

The few data available (Table V) indicate that the thermodymanic 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*-$MeOC_6H_4$ substituent (R) on the phosphorus in $(\mu\text{-}H)_2Fe_3(CO)_9(\mu_3\text{-}PR)$ with the better donating *t*-Bu group raises the pK_a^{MeCN} value from 9.0 to 11.4.[17b] The isoelectronic cyclohexylthio-capped monohydride cluster, $(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}SCy)$ is considerably less acidic ($pK_a^{MeCN} = 16.9$).[17b] Replacing a CO group with the stronger σ-donating and weaker π-accepting $P(OMe)_3$ group results in an increase in the pK_a^{MeCN} of $H_4Ru_4(CO)_{10}[P(OMe)_3](L)$ (L = CO, $P(OMe)_3$) by 3.0 units.[17b] The relative increase in the pK_a^{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 comples. Caution is advised when interpreting the pK_a^{MeOH} values of $H_4Ru(CO)_{10}(L)_2$ (L = CO, $P(OMe)_3$),[10b] that were determined by a stopped-flow kinetic method, because Kristjándóttir[17b] 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]

$$H_4Ru(CO)_{11}[P(OMe)_3] + MeO^- \rightleftharpoons H_4Ru_4(CO)_{10}(CO_2Me)[P(OMe)_3]^- \qquad (13)$$

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 $H_2Os(CO)_4$ (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 ($pK_{a1}^{MeCN} = 11.0$).[10a] The pK_{a1}^{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 ($1.2 \times 10^{-3}\ M^{-1}s^{-1}$) is 7 orders of magnitude slower than that of $FeH_2(CO)_4$ ($5.4 \times 10^4\ M^{-1}s^{-1}$).[10a]

Removal of a second proton from the Rh_{13} cluster, above, is thermodynamically more difficult ($pK_{a1}^{MeCN} = 16.5$) than the first.

This is also observed in the pK_a values of $H_3Re_3(CO)_{12}$ (Table V) which are 3 for pK_{a1}, 10 for pK_{a2}, and 25 for pK_{a3}.[16a]

Table V. pK_a values of polymetallic hydride complexes in various solvents

	pK_a, solvent =			
complex	MeOH	MeCN	other	ref
$H_3Re_3(CO)_{12}$			3^a	16a
$[H_2Re_3(CO)_{12}]^-$			10^a	16a
$[HRe_3(CO)_{12}]^-$			25^a	16a
$(\mu\text{-}H)_2Fe_3(CO)_9\text{-}[\mu_3\text{-}P(p\text{-}MeOC_6H_4)]$		9.0		17b
$(\mu\text{-}H)_2Fe_3(CO)_9[\mu_3\text{-}P(t\text{-}Bu)]$		11.4		17b
$(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}SCy)$		16.9		17b
$H_4FeRu_3(CO)_{12}$	11.2			10b
$H_2FeRu_3(CO)_{13}$	11.8			10b
$H_4Ru_4(CO)_{12}$	~11.7			10b,17b
$H_4Ru_4(CO)_{11}[P(OMe)]$		12.4		10b,17b
$H_4Ru_4(CO)_{10}[P(OMe)_3]_2$		15.4		10b,17b
$H_2Ru_4(CO)_{13}$	11.1			10b
$H_2Os_2(CO)_8$		20.4		32
$H_2Os_3(CO)_{12}$	14.7			10b
$H_4Os_4(CO)_{12}$	12.3			10b
$[H_3Rh_{13}(CO)_{24}](PPN)_2$		11.0		10a
$[H_2Rh_{13}(CO)_{24}](PPN)_3$		16.5		10a

[a] Solvent not specified.

SECTION II. CALORIMETRIC DETERMINATION OF THE HEATS OF PROTONATION OF THE METAL IN (METHYL-SUBSTITUTED CYCLOPENTADIENYL)IRIDIUM COMPLEXES, Cp'Ir(1,5-COD)

ABSTRACT

Titration calorimetry has been used to determine the enthalpies of protonation (ΔH_{HM}) of the iridium in the Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, x = 0, 1, 3-5) complexes according to the reactions, Cp'Ir(1,5-COD) + CF_3SO_3H (0.1 M) → [Cp'Ir(1,5-COD)]$^+CF_3SO_3^-$, at 25.0 °C in 1,2-dichloroethane. The ΔH_{HM} values become more exothermic from -22.8 ± 0.2 kcal mol^{-1} for Cp' = C_5H_5 to -28.5 ± 0.2 kcal mol^{-1} for C_5Me_5. A plot of ΔH_{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_5Me_5 ligand probably does not affect the ΔH_{HM} values. Each Me group contributes -1.1 kcal mol^{-1} to ΔH_{HM}. Correlations between ΔH_{HM} and the COD olefin ^1H 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 ΔG° is -0.89 kcal mol^{-1} and on ΔS° is -0.7 eu. Thus, ΔS° contributes little to the differences in equilibrium constants for protonation of the Cp'Ir(1,5-COD) complexes. A comparison of the common C_5H_5 and C_5Me_5 ligands shows that the replacement of C_5H_5 by C_5Me_5 increases the equilibrium constant for the protonation of Cp'Ir(1,5-COD) by 1900, makes ΔG° more favorable by -4.5 kcal mol^{-1}, causes ΔH_{HM} to be more exothermic by -5.7 kcal mol^{-1}, and reduces ΔS° 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.[1d,f] 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_{HM}) with triflic acid (CF_3SO_3H) in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1). Previously, Bush and Angelici reported

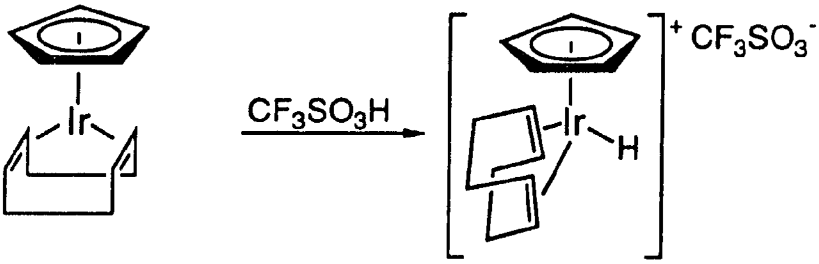
$$ML_x + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} H\text{-}ML_x^+ \, CF_3SO_3^- \quad , \Delta H_{HM} \qquad (1)$$

enthalpies of protonation (ΔH_{HP}) 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_5H_5) and its methyl-substituted analogs ($C_5Me_xH_{5-x}$, x= 1-5). Elschenbroich and Salzer[3] summarized some special properties of the pentamethylcyclopentadienyl ligand (C_5Me_5) as compared with C_5H_5. Properties that may affect the basicity of C_5Me_5 complexes relative to their C_5H_5 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 acidities[4] of uncoordinated C_5Me_5H and C_5H_6 in dimethyl sulfoxide solution show C_5Me_5H (pK_{HA} = 26.1) to be considerably less acidic than C_5H_6 (pK_{HA} = 18.0). Differences in the donor abilities of coordinated C_5H_5 and C_5Me_5 ligands have been explored by a variety of techniques.[1f,5,6] Gassman and co-workers[5a] showed by ESCA studies that the substitution of C_5H_5 by C_5Me_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 C_5H_5 ligands by two C_5Me_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 C_5H_5 vs C_5Me_5 by ^{59}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 C_5H_5 vs C_5Me_5 on the basicity of a metal center is provided by Moore and co-workers.[5e] They determined pK_a's of Cp'Mo$(CO)_3$H and Cp'Fe$(CO)_2$H (Cp' = C_5H_5, C_5Me_5) by deprotonation with organic bases for which the pK_a values of the conjugate acids are known in acetonitrile solution. For the Cp'Mo$(CO)_3$H complexes, the C_5Me_5 derivative was less acidic by 3.2 pK_a units than the C_5H_5 analog. In the iron series $(C_5Me_5)Fe(CO)_2H$ was 6.9 pK_a units less acidic than $(C_5H_5)Fe(CO)_2H$.

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' = C_5H_5, C_5MeH_4, 1,2,3-$C_5Me_3H_2$, C_5Me_4H, C_5Me_5) by measuring heats of protonation (ΔH_{HM}) of the reactions shown in eq 2.



1, Cp' = C_5H_5
2, Cp' = C_5MeH_4
3, Cp' = 1,2,3-$C_5Me_3H_2$
4, Cp' = C_5Me_4H
5, Cp' = C_5Me_5

1H$^+$, Cp' = C_5H_5
2H$^+$, Cp' = C_5MeH_4
3H$^+$, Cp' = 1,2,3-$C_5Me_3H_2$
4H$^+$, Cp' = C_5Me_4H
5H$^+$, Cp' = C_5Me_5

(2)

Also, competitive equilibrium studies for proton transfer between methyl-substituted Cp'Ir(1,5-COD) complexes have yielded values of K_{eq}, ΔG° and ΔS° for the reaction in eq 3. Comparisons of these thermodynamic quantities for the C_5H_5 and C_5Me_5 complexes permit a detailed discussion of their ligand properties as they affect the basicity of the metal.

$$\mathrm{Cp'Ir(H)(COD)^+ + Cp''Ir(COD)} \underset{25.0\ ^\circ\mathrm{C}}{\overset{K_{eq}}{\rightleftharpoons}} \mathrm{Cp'Ir(COD) + Cp''Ir(H)(COD)^+} \qquad (3)$$

a) Cp' = C_5H_5 (**1H$^+$**), Cp" = C_5MeH_4 (**2**)
b) Cp' = $C_5Me_3H_2$ (**3H$^+$**), Cp" = C_5Me_4H (**4**)
c) Cp' = C_5Me_5 (**5H$^+$**), Cp" = C_5Me_4H (**4**)
d) Cp' = C_5H_5 (**1H$^+$**), Cp" = C_5Me_5 (**5**)

In addition, protonation reactions of (indenyl)Ir(1,5-COD) (**6**), ($HBPz_3^*$)Ir(1,5-COD) (**7**) (Pz* = 3,5-dimethyl-1-pyrazolyl), and ($Me_3SiC_5H_4$)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.[7] 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.[8] 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.[9] Hexanes and petroleum ether "A" (b.p. 28 °C) were refluxed over CaH_2 and then distilled.[10] 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 P_4O_{10} under nitrogen. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under high vacuum for 9 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2.

The ^1H, 2-D COSY ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Nicolet-NT 300 MHz spectrometer (except as stated otherwise) using TMS ($\delta = 0.00$ ppm) and $CDCl_3$ ($\delta = 77.0$ ppm), respectively, as the internal references. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The preparations of $(C_5Me_5)Ir(1,5\text{-}COD)^{11}$ (**5**) and (indenyl)Ir(1,5-COD)[12] (**6**) have been described previously. Even though the synthesis of $(C_5H_5)Ir(1,5\text{-}COD)$ (**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 Cp'Ir(1,5-COD) compounds, $(HBPz^*_3)Ir(1,5\text{-}COD)$ (**7**) (Pz^* is 3,5-dimethyl-1-pyrazolyl) and $(Me_3SiC_5H_4)Ir(1,5\text{-}COD)$ (**8**).

Preparation of $(C_5H_5)Ir(1,5\text{-}COD)$ (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 $[ClIr(1,5\text{-}COD)]_2$[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 x10 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. ^1H NMR:[13b] δ 3.78 (br s, 4 H, =CH, COD), 2.03 (m, 4 H, exo-CH_2, COD), 1.78 (pseudo-q, 4 H, endo-CH_2, COD), 5.18 (s, 5 H, Cp). $^{13}C\{H\}$ NMR: δ 45.51 (=CH, COD), 33.85 (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.

(C_5MeH_4)Ir(1,5-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 $C_{14}H_{19}Ir$: C, 44.31; H, 5.05. Found: C, 44.04; H, 5.09. ^1H NMR:[17] δ 3.56 (br s, 4 H, =CH, COD), 2.05 (m, 4 H, exo-CH_2, COD), 1.80 (pseudo-q, 4 H, endo-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-$C_5Me_3H_2$)Ir(1,5-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 ^1H 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.[18b] The formation of 2,3,4-trimethylcyclopent-2-enone (**11**)[18a] by intramolecular aldol condensation of **10** was performed using the same conditions employed in the preparation of 3-methylcyclopent-2-enone.[18c] Finally, reduction of **11** with $LiAlH_4$ in Et_2O by the procedure described for the reduction of cyclopent-2-enone[18d] (excess $LiAlH_4$ was quenched by careful, dropwise addition of saturated, aqueous Na_2SO_4) followed by treatment with I_2 (see, for example, ref 18e) gave **9**. It was isolated by vacuum transfer at room temperature, 10^{-2} mm Hg, with a liq. N_2-cooled receiver in 9% overall yield. The organometallic product **3** was sublimed at 60-80 °C, 10^{-2} mm Hg. Yield: 60%. Anal. Calcd for $C_{16}H_{23}Ir$: C, 47.15; H, 5.68. Found: C, 47.19; H, 5.80. ^1H NMR: δ 3.16 (br s, 4 H, =CH, COD), 2.03 (m, 4 H, exo-CH_2, COD), 1.80 (pseudo-q, 4 H, endo-CH_2, COD), 4.87 (s, 2 H, H4, H5, Cp), 1.91 (s, 3 H, 2-MeCp), 1.84 (s, 6 H, 1,3-Me_2Cp). $^{13}C\{H\}$ NMR: δ 50.44 (=CH, COD), 34.07 (CH_2, COD), 96.76 (C2, Cp ring), 9.18 (2-MeCp), 95.14 (C1, C3, Cp ring), 10.84 (1,3-Me_2Cp), 78.18 (C4, C5, Cp ring).

$(C_5Me_4H)Ir(1,5\text{-}COD)$ (4)

The tetramethylcyclopentadiene was prepared from 2,3,4,5-tetramethylcyclopent-2-enone (Aldrich), as previously described.[19] It was metalated with 1 equiv of *n*-BuLi in THF. Sublimation of **4** at 60-80 °C (10^{-2} mm Hg) gave a 45% yield. Anal. Calcd for $C_{17}H_{25}Ir$:

C, 48.43; H, 5.98. Found: C, 48.20; H, 5.99. ^{1}H NMR: δ 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_2Cp), 1.73 (s, 6 H, Me_2Cp).

$(C_5Me_5)Ir(1,5\text{-}COD)$ (5)

^{1}H NMR:[11] δ 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_5Cp). $^{13}C\{H\}$ NMR: d 53.09 (=CH, COD), 34.16 (CH_2, COD), 92.10 (Cp ring), 9.20 (Me_5Cp).

$(HBPz^*_3)Ir(1,5\text{-}COD)$ (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_2O/hexanes (1:5). It was recrystallized from CH_2Cl_2/hexanes (1:10) at -40 °C. Yield: 60%. ^{1}H NMR:[20] δ 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*).

$(Me_3SiC_5H_4)Ir(1,5\text{-}COD)$ (8)

Trimethylsilylcyclopentadiene was prepared using a literature procedure[21] and was metalated with *n*-BuLi in THF.[22] Yield of 8: 58%. ^{1}H NMR: δ 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_3Si).

Protonation Reactions

Compounds **1-5** were protonated by dissolving approximately 50 mg of each compound in Et_2O (0 °C) and adding 1 equiv of CF_3SO_3H; a white precipitate formed immediately. Filtering the white precipitate and washing once with Et_2O (2 mL) and once with petroleum ether (2 mL) gave **$1H^+$** - **$5H^+$** as the $CF_3SO_3^-$ salts. Only complex **$1H^+$**PF_6^- was reported previously.[23] The white powders can be handled in the air for short periods except for **$4H^+$**$CF_3SO_3^-$ 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 **$1H^+$**$CF_3SO_3^-$. The data for each of these complexes are as follows:

$[(C_5H_5)Ir(H)(1,5\text{-COD})](CF_3SO_3)$ ($1H^+CF_3SO_3^-$)

Yield: 78%. Anal. Calcd for $C_{14}H_{18}F_3IrO_3S$: 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, $H_{Y'}$, COD), 6.02 (s, 5 H, Cp), -11.79 (s, 1 H, Ir-H). $^{13}C\{H\}$ NMR: δ 71.27 (=CH, COD), 69.17 (=CH, COD), 32.85 (CH_2, COD), 31.61 (CH_2, COD), 88.35 (Cp).

[(C_5MeH_4)Ir(H)(1,5-COD)](CF_3SO_3) ($2H^+CF_3SO_3^-$)

Yield: 86%. ^1H NMR:[17] δ 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, H2, H5, Cp), 5.73 (s, 2 H, H3, H4, Cp), 2.21 (s, 3 H, MeCp), -11.89 (s, 1 H, Ir-H). ^{13}C NMR (proton coupled):[24] δ 73.32 (d, J_{CH} = 159 Hz, =CH, COD), 69.66 (d, J_{CH} = 166 Hz, =CH, COD), 32.60 (t, J_{CH} = 132 Hz, CH_2, COD), 31.80 (t, J_{CH} = 134 Hz, CH_2, COD), 109.46 (s, C1, Cp ring), 12.47 (q, J_{CH} = 129 Hz, MeCp), 87.71 (dm, $^1J_{CH}$ = 186 Hz, C2, C5, Cp ring) 86.44 (dd, $^1J_{CH}$ = 186 Hz, $^2J_{CH}$ = 6.5 Hz, C3, C4, Cp ring).

[(1,2,3-$C_5Me_3H_2$)Ir(H)(1,5-COD)](CF_3SO_3) ($3H^+CF_3SO_3^-$)

Yield: 58%. ^1H NMR: δ 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, H4, H5, Cp), 2.17 (s, 6 H, 1,3-Me_2Cp), 2.07 (s, 3 H, 2-MeCp), -12.04 (s, 1 H, Ir-H).

[(C_5Me_4H)Ir(H)(1,5-COD)](CF_3SO_3) ($4H^+CF_3SO_3^-$)

Yield: 86%. ^1H NMR: δ 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).

[(C_5Me_5)Ir(H)(1,5-COD)](CF_3SO_3) ($5H^+CF_3SO_3^-$)

Yield: 66%. ^1H NMR: δ 4.04 (br m, 4 H, H_B, H_A, COD), 2.54 (m, 2 H, H_Y, COD), 2.36 (m, 4 H, $H_{Y'}$, H_X, COD), 2.17 (pseudo-q, 2 H, $H_{X'}$, COD), 2.02 (s, 15 H, Me_5Cp), -12.09 (s, 1 H, Ir-H). $^{13}C\{H\}$ NMR: δ 78.34 (=CH, COD), 71.28 (=CH, COD), 32.14 (CH_2, COD), 31.49 (CH_2, COD), 100.87 (Cp ring), 9.48 (Me_5Cp).

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

Reaction of 6 with CF_3SO_3H

An excess of triflic acid (~2 equiv) was added to a solution of **6** (4.7 mg) in 0.5 mL of $CDCl_3$ or CD_2Cl_2 yielding a bright red solution. The ^1H NMR spectrum revealed a transient Ir-H resonance (-13.3 ppm in $CDCl_3$) which disappeared after 15 min. The final product, [(η^6-indene)Ir(1,5-COD)](CF_3SO_3), was characterized spectroscopically; however, no attempt was made to isolate it. Assignment of the η^6-indene resonances are based on those made for [(η^6-indene)Rh(C_2H_4)$_2$]BF_4[25a] (see eq 5 for numbering scheme). ^1H NMR (CD_2Cl_2): δ 6.73 (d, J_{1-2} = 5.2 Hz, 1 H, H1), 7.03 (br s, 1 H, H2), 3.21 (d, $J_{3-3'}$ = 24.3 Hz, 1 H, H3), 2.64 (d, 1 H, H3'), 7.32 (d, J_{4-5} = 6 Hz, 1 H, H4), 6.24 (t, J_{5-4} = J_{5-6} = 6 Hz, 1 H, H5), 6.50 (t, J_{5-6} = J_{6-7} = 6 Hz, 1 H, H6), 7.23 (d, 1 H, H7), η^6-indene; 4.18 (m, 2 H, =CH, COD), 3.95 (m, 2 H, =CH, COD), 2.21-1.99 (br m, 8 H, CH_2, COD).

Reaction of 7 with CF_3SO_3H

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 $\{[(\eta^2\text{-HBPz}^*_2)(\text{Pz}^*\text{H})]\text{Ir}(1,5\text{-COD})\}(CF_3SO_3)$. ^1H NMR:[20a] δ 12.92 (s, 1 H, Pz*H), 6.19 (s, 1 H, Pz*, H4), 5.96 (s, 2 H, η^2-Pz*, H4), 2.54 (s, 3 H, 3-Pz*Me), 2.47 (s, 3 H, 5-Pz*Me), 2.41 (s, 6 H, η^2-3-Pz*Me), 2.36 (s, 6 H, η^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_3SO_3H

The protonation was done in Et_2O as described for compounds 1-5. The product was identified by its ^1H NMR spectrum as $1H^+CF_3SO_3^-$ (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:[26] 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_3SO_3H 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[2] was complicated by traces of H_2O in the reaction vessel. This was remedied by turning the buret on for 1 minute prior to data collection, in effect, neutralizing the adventitious H_2O 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 ΔH_{HM} values, at least two different standardized acid solutions were used for titrations of each compound. The ΔH_{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_3SO_3H 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 $3H^+CF_3SO_3^-$, 11.3 mg (0.0268 mmol) of 4 (eq 3b) and 10.4 mg (0.0426 mmol) of the internal standard Ph_3CH 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 ^1H NMR spectrum was taken at 298 K with a Bruker WM 200 NMR spectrometer using the methyl proton of Ph_3CH (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 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}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.

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

The equilibrium for eq 3b ($3H^+CF_3SO_3^-$, 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_3CH 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 ($1H^+CF_3SO_3^-$, 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 **5**$H^+CF_3SO_3^-$ (29.1 mg, 0.0497 mmol) and **4** (15.6 mg, 0.0370 mmol) with the Ph_3CH (11.7 mg, 0.0479 mmol) standard.

RESULTS

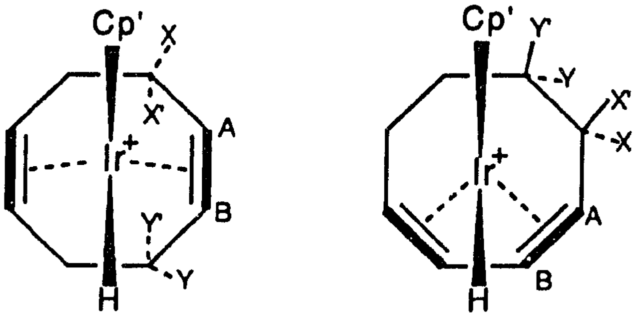
Characterization of Reactants and Products in Equation 2

Several preparations of **1** have been reported[13] previously including the synthesis from NaC_5H_5 and $[ClIr(1,5\text{-}COD)]_2$.[13a] However, no experimental details for the latter preparation are given. We describe the synthesis of **1** from KC_5H_5 and $[ClIr(1,5\text{-}COD)]_2$ in 66% yield which is higher than yields (< 50%) previously reported.[13b,c] Analogous Cp'Ir(1,5-COD) complexes, **2-4**, **7**, **8**, are also prepared in 45-84% yields by reaction of $[ClIr(1,5\text{-}COD)]_2$ 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.[27] (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 ^{13}C NMR spectra (see Experimental). The assignments of the 1,5-COD ligand resonances are based on assignments made for $[Rh(1,5\text{-}COD)(CH_2(Pz)_2)]ClO_4$ (Pz = pyrazolyl).[28a] 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 $[Cp'Ir(H)(1,5\text{-}COD)]^+$ 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_3SO_3H in diethyl ether results in precipitation of the white protonated products $1H^+CF_3SO_3^-$ - $5H^+CF_3SO_3^-$. Resonances are observed in the ^1H 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_3SO_3H to the neutral complexes, quantitative formation of **1H+** - **5H+** is observed by ^1H NMR. When the $CDCl_3$ solutions are air-free, no changes in the ^1H 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 ^1H NMR when 1 equiv of 1,3-diphenylguanidine 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 ^1H NMR data for $1H^+CF_3SO_3^-$ are nearly identical to those previously reported; however, further consideration of the ^1H, ^{13}C NMR and a 2-D COSY ^1H NMR experiment indicates that the formulation is more likely $[(C_5H_5)Ir(H)(1,5\text{-COD})]CF_3SO_3$, without an isomerized diene. Attempts to grow crystals of $1H^+CF_3SO_3^-$ 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 σ_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 ^1H NMR spectrum and four signals for C_A, C_B, C_X, and C_Y in the ^{13}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^+"



1A 1B

Figure1. (A) 1,5-COD coordination to $Cp'IrH^+$ or (B) 1,3-COD coordination. Protons X and Y are exo; protons X' and Y' are endo

when protonation was done with CF_3COOD.[30] 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;[31] consequently, incorporation of deuterium should occur (for example, the protonation of $(C_5H_5)Rh(1,5\text{-}COD)$ gives $[(C_5H_5)Rh(1,3,4\text{-}\eta^3\text{-}C_8H_{13})]PF_6$ [23]). Furthermore, protonation of Cp'Ir(1,3-diene)[32] (Cp' = C_5H_5, C_5Me_5; 1,3-diene = butadiene, 2,3-dimethylbutadiene, 1,3-cyclohexadiene) at room temperature gives products with fluxional NMR spectra consistent with the formation of η^3-allyl intermediates which are stabilized by an agostic C-H bond. Only upon cooling are the classical hydride structures seen in the NMR spectra.[32a] In view of this reactivity it is unlikely that a species such as $[(C_5H_5)Ir(H)(1,3\text{-}COD)]^+$ would have a stable Ir-H bond at room temperature.

An examination of the differences in chemical shifts between ^1H and ^{13}C NMR resonances at positions A and B (see Figure 1), given as $|\Delta^1H_{AB}|$ and $|\Delta^{13}C_{AB}|$, 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[33] give $|\Delta^1H_{AB}|$ values from 1.43 to 2.02, and three of these complexes give $|\Delta^{13}C_{AB}|$ values which range from 28.6 to 35.5. Kruczynski and Takats[34] have also noted a significant difference between the ^{13}C 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[28b,c,35] gives $|\Delta^1H_{AB}|$ values in the range 0.2-1.7 (average = 0.77) and $|\Delta^{13}C_{AB}|$ values in the range 0.6-

28.2 (average = 4.5). The $|\Delta^1H_{AB}|$, $|\Delta^{13}C_{AB}|$ values for **1H**$^+$ are 0.91 and 2.1, respectively. In fact, for compounds **2H**$^+$ - **5H**$^+$ the $|\Delta^1H_{AB}|$ 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, $(C_5H_5)Ru(H)(1,5\text{-COD})$,[35e] which is isoelectronic with **1H**$^+$, is known to have 1,5-COD coordination and has a $|\Delta^1H_{AB}|$ value of 0.6 and a $|\Delta^{13}C_{AB}|$ value of 1.4. The crystal structure of $(C_5Me_5)Ru(H)(1,5\text{-COD})$ has been reported recently;[35g] the $|\Delta^1H_{AB}|$ and $|\Delta^{13}C_{AB}|$ values are 0.3 and 8, respectively. The Δ 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 Δ values clearly fall within the asymmetric 1,5-COD complex ranges but not in the higher ranges for 1,3-COD complexes.

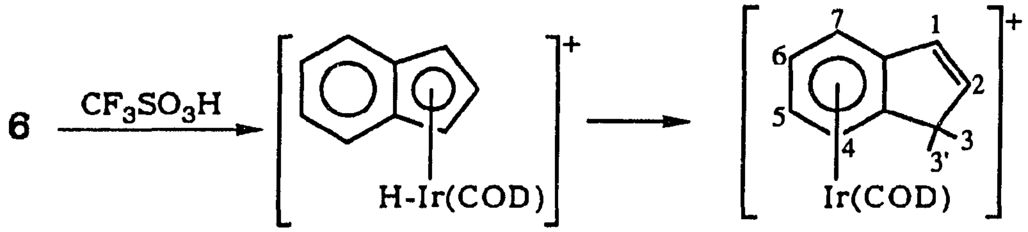
Also the 2-D COSY ^1H NMR spectrum[36] of **1H**$^+$ shows ^1H-^1H coupling more indicative of a 1,5-COD structure. One cross peak connects the 5.43 ppm (H_B) resonance to the left side of the broad multiplet at 2.5 ppm, and another cross peak connects the 4.52 ppm (H_A) resonance to the right side of the 2.5 ppm multiplet. This indicates that the multiplet at 2.5 ppm consists of two different types of protons coincidentally overlapped. There is also a weak cross peak connecting 5.43 and 2.27 ppm. The pattern is typical for coordinated 1,5-COD;[28a] in particular, it has been shown[28a] 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 **5H$^+$** to those of **3H$^+$** and **4H$^+$** 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.[37] Normal chemical shifts are observed for the COD olefin and methylene groups in the ^1H NMR spectra of **1H$^+$** - **5H$^+$** and in the ^{13}C NMR spectra of **2H$^+$** and **5H$^+$**. In addition, the proton coupled ^{13}C NMR spectrum of **2H$^+$** was investigated as low values for J_{CH} are diagnostic of agostic CH interactions.[38] However, normal coupling constants for the COD sp^2 carbons (J_{CH} = 159 Hz and 166 Hz) and the sp^3 carbons (J_{CH} = 132 Hz and 134 Hz) were found.[39]

The protonation reactions of **6**-**8** proceed differently than those of compounds **1**-**5**. Protonation of (indenyl)Ir(1,5-COD) (**6**) in $CDCl_3$ gives a transient Ir-H resonance at -13.3 ppm probably due to [(η^5-indenyl)Ir(H)(1,5-COD)]CF_3SO_3 (see eq 5) but this resonance disappears within 15 minutes. The resulting product has ^1H resonances which are indicative of an η^6-indene complex[25] (see Experimental). A very similar reaction is reported by Clark and co-workers[25a] for the protonation of (η^5-indenyl)Rh$(C_2H_4)_2$ with $HBF_4{\cdot}Et_2O$. Our data suggest that the proton is transferred from the metal to the indenyl ligand resulting in an η^5 to η^6 haptotropic rearrangement forming $[(\eta^6\text{-indene})Ir(1,5\text{-}COD)]CF_3SO_3$ (eq 5).



(5)

Protonation of $(HBPz^*_3)Ir(1,5\text{-}COD)$ (7) does not give a detectable Ir-H resonance in the ^1H 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 $\{[(\eta^2\text{-}HBPz^*_2)(Pz^*H)]Ir(1,5\text{-}COD)\}CF_3SO_3$. Ball and co-workers[20a] have obtained a similar rhodium complex by protonation of $(\eta^3\text{-}HBPz^*_3)Rh(CO)_2$ with $HBF_4{\cdot}Et_2O$. Surprisingly, they also observed that protonation of $(\eta^3\text{-}HBPz^*_3)Ir(CO)_2$ occurs at the Ir.[20a]

Reaction of $(Me_3SiC_5H_4)Ir(1,5\text{-}COD)$ (8) with CF_3SO_3H in Et_2O gives a white precipitate but the product is identified to be $1H^+CF_3SO_3^-$ (40% yield) by ^1H 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_3SO_3H 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 ΔH_{HM} values were the same within experimental error whether or not the product solution was slightly colored. Analysis of the resultant titrate solutions by ^1H 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 (ε = 10.36)[41] 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;[2] it was concluded that they contribute less than 2% to the total ΔH_{HP} value. Presumably these reactions also contribute negligibly to ΔH_{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 **1**H^+ and **2** (eq 3a), and **5**H^+ and **4** (eq 3c) were studied in $CDCl_3$, while the **3**H^+/**4** equilibrium (eq 3b) was studied in both $CDCl_3$ and d_4-DCE. An error of 10% is estimated for each K_{eq}; therefore, the K_{eq} values in all four studies, including that in d_4-DCE, are approximately the same within experimental error. Values of ΔG° were calculated ($\Delta G^{\circ} = -RT \ln K_{eq}$)[42] from the K_{eq} values. Because of the similarity of the K_{eq} values for the **3**H^+/**4** equilibrium (eq 3b) in $CDCl_3$ and d_4-DCE, we combined ($\delta\Delta H_{HM} = \Delta G^{\circ} + T\Delta S^{\circ}$) relative ΔH_{HM} values ($\delta\Delta H_{HM}$ = -1.1 kcal mol^{-1}) in DCE and ΔG° values in $CDCl_3$ to obtain the ΔS° of each reaction. An error of ± 0.06 kcal mol^{-1} in ΔG° 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 ΔS° is as large as ΔS° itself, values for the four reactions (Table II) are consistently negative. Thermodynamic constants for the equilibrium between **1**$H^+CF_3SO_3^-$ and **5** (eq 3d) are calculated from the average K_{eq} values in Table II, and ΔH_{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 ΔH_{HM}, ΔG^{θ}, and ΔS^{θ}; the data are summarized in Table II.

Table I. Heats of protonation (ΔH_{HM}) of Cp'Ir(1,5-COD) complexes[a]

Cp'Ir(1,5-COD)	$-\Delta H_{HM}$, kcal mol^{-1}
(C_5H_5)Ir(COD), **1**	22.8 (±0.2)[b]
(C_5MeH_4)Ir(COD), **2**	24.1 (±0.1)
(1,2,3-$C_5Me_3H_2$)Ir(COD), **3**	26.4 (±0.2)
(C_5Me_4H)Ir(COD), **4**	27.5 (±0.2)
(C_5Me_5)Ir(COD), **5**	28.5 (±0.2)

[a] For protonation with CF_3SO_3H (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.

reactants	K_{eq}[a]	ΔG° kcal mol^{-1} [a]	ΔS° eu[b]
$1H^+/2$[c]	4.4	-0.88	-0.74
$3H^+/4$[c]	5.0	-0.95	-0.50
$3H^+/4$[d]	4.8	-0.93	-0.57
$4H^+/5$[c]	3.9	-0.81	-0.97
$1H^+/5$[e]	1900	-4.5	$\sim$-4

[a] Estimated error in K_{eq} is 10% and ± 0.06 for ΔG°.

[b] Calculated using $\delta\Delta H_{HM} = -1.1$ kcal mol^{-1} for eq 3. Estimated error is ± 0.7 eu.

[c] In $CDCl_3$.

[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. ΔG° was calculated ($\Delta G^\circ = -RT \ln K_{eq}$) from K_{eq}, and ΔS° 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 ΔH_{HM}. The ΔH_{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 ΔH_{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.

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

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 $(C_5Me_5)Ru(H)(1,5\text{-}COD)$[35g]) to make room for the hydride ligand. It is conceivable that steric repulsion between the COD and a highly methylated Cp' would cause ΔH_{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.

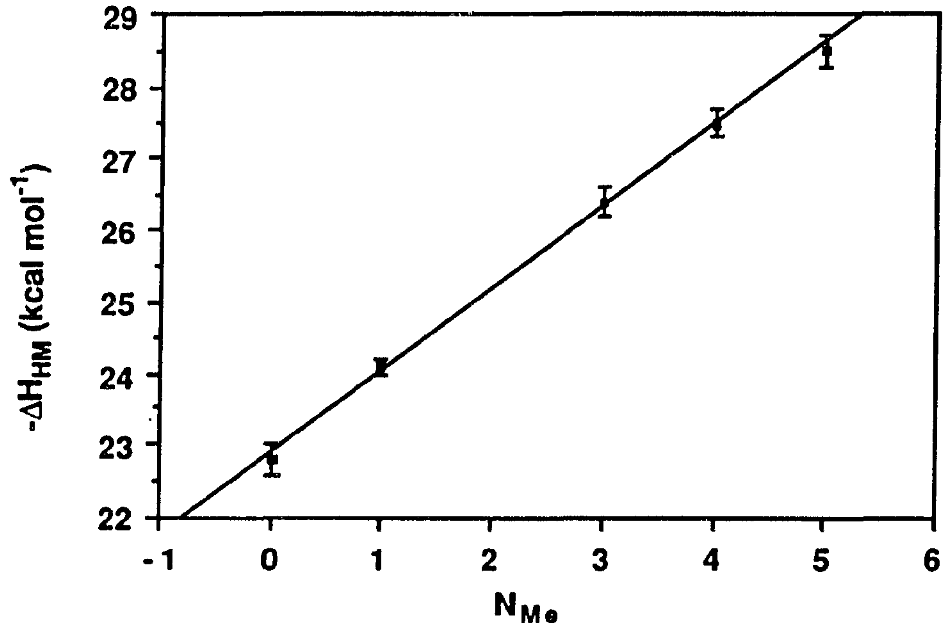


Figure 2. Plot of ΔH_{HM} (kcal mol^{-1}) for the protonation (eq 2) of Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, x = 0, 1, 3-5) vs the number of methyl groups on Cp' (N_{Me})

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 C_5Me_5 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 $(C_5Me_5)Ir(1,5\text{-}COD)$.

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

$$-\Delta H_{HM} = 43.2 - 5.4x \quad (\text{kcal mol}^{-1}) \qquad (7)$$

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 $d\pi\text{-}p\pi^*$ 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-$Me_3C_5H_2$ 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 ΔH_{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 ΔG°) 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 ~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 ΔG° of -0.89 ± 0.06 kcal mol^{-1} per methyl group. There is only a relatively small difference between ΔG° (-0.89 ± 0.06 kcal mol^{-1}) and $\delta\Delta H_{HM}$ (-1.1 ± 0.2 kcal mol^{-1}), especially considering the estimated errors. It is likely, however, that there is a small decrease in ΔS° (-0.7 ± 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_6H_6 in $(\eta^6-C_6H_6)Mo(CO)_3$ with methyl-substituted arenes 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 C_5H_5 and C_5Me_5 on ΔH_{HM}, ΔG°, and ΔS° 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° for this reaction is -4.5 kcal mol^{-1}. From these ΔH_{HM} and ΔG° values, ΔS° is estimated to be ~-4 eu. The small value of ΔS° 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° difference (-4.5 kcal mol^{-1}) between $(C_5H_5)Ir(COD)$ (1) and $(C_5Me_5)Ir(COD)$ (**5**), one can choose other pairs of complexes containing C_5H_5 and C_5Me_5 ligands. Moore and co-workers^{5e} determined K_{eq} values for the protonation of Cp'Mo(CO)$_3^-$ and Cp'Fe(CO)$_2^-$, where Cp' is C_5H_5 or C_5Me_5, in acetonitrile solution. After converting their K_{eq} values to ΔG°'s, one finds that the ΔG° for protonation of the C_5Me_5 molybdenum complex is -4.4 kcal mol^{-1} more favorable than for the corresponding C_5H_5 complex. Thus, replacing C_5H_5 by C_5Me_5 in either Cp'Ir(COD) or Cp'Mo(CO)$_3^-$ causes essentially the same increase in metal basicity (ΔG° = ~-4.5 kcal mol^{-1}). On the other hand, ΔG° for the protonation of $(C_5Me_5)Fe(CO)_2^-$ is -9.4 kcal mol^{-1} more favorable than for $(C_5H_5)Fe(CO)_2^-$ Thus, in the iron system, the replacement of C_5H_5 by C_5Me_5 produces a much larger increase in metal basicity than in the Ir and Mo complexes. So it is evident that the substitution of C_5Me_5 for C_5H_5 does not cause the same increase in metal basicity in all metal complex systems.

SUMMARY

These studies of methyl-substituted Cp'Ir(1,5-COD) complexes show that protonation with CF_3SO_3H definitely occurs at the metal center to form products formulated as [Cp'Ir(H)(1,5-COD)]CF_3SO_3. The basicity of the iridium center as determined by the heats of protonation (ΔH_{HM}) of the complexes in 1,2-dichloroethane increases linearly with the number of methyl groups in Cp' (N_{Me}) from C_5H_5 to C_5Me_5. For each methyl group ΔH_{HM} changes by -1.1 kcal mol^{-1} ($\delta\Delta H_{HM}$). The ΔH_{HM} values correlate with the chemical shift of the olefin ^1H NMR resonance in the 1,5-COD ligand of the neutral complexes and the Ir-H ^1H 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 ΔG° -0.89 ± 0.06 kcal mol^{-1} per methyl group and ΔS° by -0.7 ± 0.7 eu per methyl. Thus, the differences in basicities (K_{eq} or ΔG°) of the various methyl-substituted Cp'Ir(1,5-COD) complexes is largely determined by ΔH_{HM} values of the complexes, and ΔS° makes a relatively small contribution. Comparing the common C_5H_5 and C_5Me_5 ligands, one finds that replacing C_5H_5 in (C_5H_5)Ir(1,5-COD) by C_5Me_5 increases the equilibrium constant, K_{eq}, for the protonation of the complex by 1900; ΔG° becomes more favorable by -4.5 kcal mol^{-1}; ΔH_{HM} becomes more favorable by -5.7 kcal mol^{-1}, while ΔS° becomes slightly less favorable by ~-4 eu.

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geometry to $1H^+CF_3SO_3^-$ 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 (δ 6.0 ppm) after 3 days.

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SECTION III. HEATS OF PROTONATION OF TRANSITION METAL COMPLEXES: THE EFFECT OF PHOSPHINE BASICITY ON METAL BASICITY IN CpIr(CO)(PR_3) AND Fe($CO)_3(PR_3)_2$ COMPLEXES

ABSTRACT

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

INTRODUCTION

There is considerable interest in 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,1,9-11] are available concerning the relationship between phosphine basicity and metal basicity. Recently, Bush and Angelici[7] reported heats of protonation (ΔH_{HP} in eq 1) in 1,2-dichloroethane solvent as a measure of phosphine basicity.

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

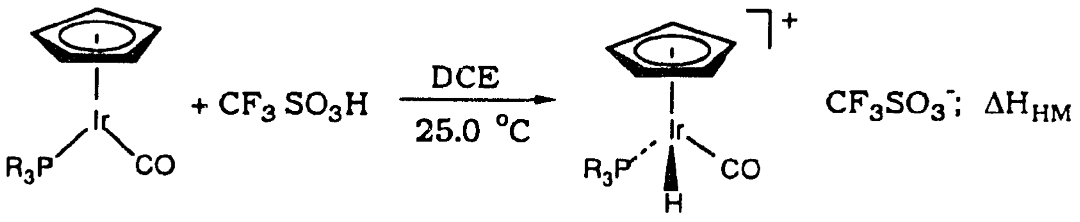
In the present study, quantitative correlations between the basicities of these phosphines and their iridium and iron complexes are reported.

Heats of protonation (ΔH_{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_3SO_3H) in 1,2-dichloroethane (DCE) solution (eq 2), the same conditions that were used to

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

determine the heats of protonation (ΔH_{HP}) of phosphines (eq 1). Previously, it was established that the basicity (ΔH_{HM}) of the iridium in Cp'Ir(1,5-COD) complexes (Cp' = $C_5Me_xH_{5-x}$, x = 0, 1, 3-5) increases linearly as the number of methyl groups in the cyclopentadienyl ring increases.[3]

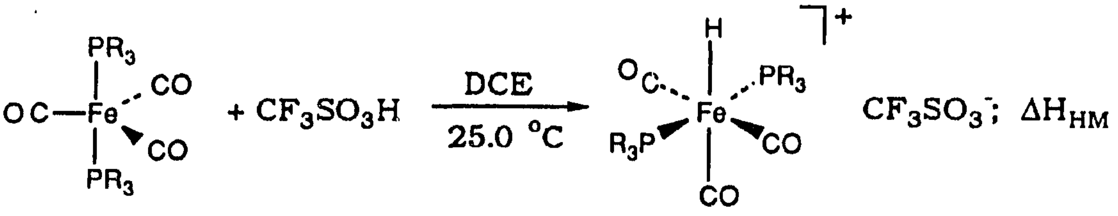
In this paper, studies of the basicities (ΔH_{HM}) of two series of complexes, CpIr(CO)(PR_3) (eq 3) and $Fe(CO)_3(PR_3)_2$ (eq 4), in which the basicity of the phosphine ligand is systematically varied are reported.



(3)

1 - 5 $\qquad$ $1H^+CF_3SO_3^-$ - $5H^+CF_3SO_3^-$

PR_3; $P(p\text{-}ClC_6H_4)_3$ (1, $1H^+$), PPh_3 (2, $2H^+$), $PMePh_2$ (3, $3H^+$)
PMe_2Ph (4, $4H^+$), PMe_3 (5, $5H^+$)



(4)

6 - 10 **$6H^+CF_3SO_3^-$ - $10H^+CF_3SO_3^-$**

PR_3; PPh_3(**6**, **$6H^+$**), $P(p\text{-}MeOC_6H_4)_3$ (**7**, **$7H^+$**), $PMePh_2$ (**8**, **$8H^+$**)
PMe_2Ph (**9**, **$9H^+$**), PMe_3 (**10**, **$10H^+$**)

In addition, we include protonation studies of (indenyl)Ir(CO)(PPh_3) (**11**), CpIr(CS)(PPh_3) (**12**), Cp*Ir$(CO)_2$ (**13**), and (1,2,3-$C_5Me_3H_2$)-Ir(CO)(PPh_3) (**14**).

EXPERIMENTAL

General Methods

All preparative reactions, chromatography, and manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The solvents were purified under nitrogen as described below using the methods in Perrin et al.[12] Hexanes and CH_2Cl_2 were refluxed over CaH_2 and then distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Benzene was distilled from $LiAlH_4$ and toluene from sodium metal. Deuteriochloroform (Aldrich) was stored over molecular sieves in air or distilled from P_2O_5 under nitrogen. Anhydrous ethanol was obtained by distillation of absolute ethanol from $Mg(OEt)_2$ under nitrogen. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under high vacuum (10^{-5} mm Hg) for 9 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2.

The ^1H NMR spectra were recorded in $CDCl_3$ on a Nicolet-NT 300 MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. A Varian VXR-300 MHz instrument was used to obtain the $^{13}C\{H\}$ NMR spectra in $CDCl_3$ solvent (internal reference, $CDCl_3$, δ = 77.0 ppm). Infrared spectra of the neutral complexes **1**-**14** were recorded on a Digilab FTS-7 FT-IR spectrometer. Spectra of the protonated products were obtained either on the Digilab (**1H$^+$**, **3H$^+$**, **4H$^+$**, **7H$^+$**, **11H$^+$**, **13H$^+$**) or on a Nicolet 710 FT-IR spectrometer for the remaining compounds. Sodium chloride cells with 0.1 mm spacers were used to record all FT-IR spectra. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The phosphine compounds $P(p\text{-}ClC_6H_4)_3$ and $P(p\text{-}MeOC_6H_4)_3$ were purchased from Strem while PPh_3, $PMePh_2$, PMe_2Ph, and PMe_3 (1.0 M in toluene) were purchased from Aldrich. Vaska's complex, $IrCl(CO)(PPh_3)_2$, used in the preparation of **2**, **11**, and **14** was synthesized according to an updated procedure.[13] The iridium complexes **2**,[14] **12**,[15] **13**[16] were prepared as previously reported. The compounds $[CpIrI_2]_n$ and $CpIr(I)_2(PMe_3)$ used for the preparations of **1** and **5**, respectively, were prepared as reported by Heinekey et al.[17] The starting material for **6**-**10**, $Fe(CO)_3(bda)$ (bda = benzylideneacetone), was prepared according to Brookhart and co-workers.[18a] Preparations of compounds **6**,[19-21] **8**,[19b,20,21] **9**,[21] and **10**[19a,22] have been previously reported by other methods.

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

$CpIr(CO)[P(p\text{-}ClC_6H_4)_3]$ (1)

The starting material, $CpIr(I)_2[P(p\text{-}ClC_6H_4)_3]\cdot CH_2Cl_2$, was prepared using the same procedure described for the synthesis of $CpIr(I)_2(PMe_3)$.[17] It co-precipitated with one equiv of CH_2Cl_2 as a deep red powder in 92% yield [^1H NMR: δ 5.44 (d, J_{PH} = 1.3 Hz, 5H, Cp), 7.42 (m, 6H, Ph), 7.51 (m, 6H, Ph)]. A mixture of $CpIr(I)_2[P(p\text{-}ClC_6H_4)_3]\cdot CH_2Cl_2$ (908 mg, 0.944 mmol), Na_2CO_3 (830 mg, 7.83 mmol) and anhydrous EtOH (30 mL) was heated to reflux under a slow stream of carbon monoxide (1 atm) for 24 h. The color of the mixture gradually turned from red to clear yellow. When monitoring the reaction by ^{1}H NMR spectroscopy we observed a yellow intermediate [^{1}H NMR: δ 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_2Cl_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_2O/hexanes (1:5) gave a yellow band containing **1**. After evaporation of the solvents, the resulting solid was recrystallized from CH_2Cl_2/hexanes at -40 °C to give 390 mg of **1** as a yellow-orange powder in 63% yield. ^{1}H NMR: δ 5.13 (s, 5H, Cp), 7.36 (m, 6H, Ph), 7.48 (m, 6H, Ph). IR(CH_2Cl_2): υ(CO) 1929 cm^{-1}.

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

This compound was prepared in 56% yield from KCp[3] and IrCl(CO)(PPh$_3$)$_2$[13] according to the previously reported procedure.[14] ^{1}H NMR: δ 5.14 (d, J_{PH} = 1.0 Hz, 5H, Cp), 7.34-7.61 (m, 15H, Ph). IR(CH_2Cl_2): υ(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_2O/hexanes (1:10) gave a yellow band which was collected. The solvent was slowly evaporated under vacuum until a precipitate began to form. Cooling the solution to -20 °C gave yellow crystals of **3** (108 mg, 82% yield). ^{1}H NMR: δ 2.30 (d, J_{PH} = 9.9 Hz, 3H, Me), 5.13 (s, 5H, Cp), 7.4-7.6 (m, 10H, Ph). IR(CH_2Cl_2): υ(CO) 1922 cm^{-1}.

CpIr(CO)(PMe_2Ph) (4)

To a solution of **2** (403 mg, 0.735 mmol) in benzene (20 mL) was added PMe_2Ph (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_2O/hexanes (1:5). An initial pale yellow band containing unreacted PMe_2Ph 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_2O/hexanes and filtered through a 2 x 3 cm column of alumina. Recrystallization from Et_2O/hexanes at -20 °C gave yellow crystals of 4 (178 mg, 56%

yield). Anal. Calcd. for $C_{14}H_{16}IrOP$: C, 39.71; H, 3.81. Found: C, 39.61; H, 3.88. ^1H NMR: δ 2.02 (d, J_{PH} = 10.2 Hz, 6H, Me), 5.24 (s, 5H, Cp), 7.40-7.80 (m, 6H, Ph). IR(CH_2Cl_2): ν(CO) 1917 cm^{-1}.

CpIr(CO)(PMe_3) (5)

A mixture of CpIr(I)$_2$(PMe_3)[17] (435 mg, 0.741 mmol) and Na_2CO_3 (600 mg, 5.66 mmol) in anhydrous EtOH (30 mL) was heated to reflux under a slow stream of carbon monoxide for 16 h. During this time the red suspension turned to a milky orange-yellow suspension. The mixture was then allowed to cool slowly to room temperature while maintaining the CO atmosphere. After removing the solvent under vacuum, the residue was extracted with 30 mL of hexanes. The hexanes solution was added to a neutral alumina column (15 x 1.5 cm) and a yellow band was eluted with Et_2O/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 $C_9H_{14}IrOP$: C, 29.91; H, 3.90. Found: C, 30.19; H, 3.95. ^1H NMR: δ 1.77 (d, J_{PH} = 10.5 Hz, 9H, Me), 5.30 (s, 5H, Cp). IR(CH_2Cl_2): ν(CO) 1914 cm^{-1}. IR(hexanes): ν(CO) 1937 cm^{-1}.

(Indenyl)Ir(CO)(PPh_3) (11)

This compound was prepared in 63% yield from K(indenide)[3] and IrCl(CO)(PPh_3)$_2$ according to the procedure reported for the synthesis of **2**.[14] Anal. Calcd. for $C_{28}H_{22}IrOP$: C, 56.27; H, 3.71.

Found: C, 55.92; H, 3.69. ^{1}H NMR: δ 5.18 (br s, 2H, H1, H3), 6.25 (m, 1H, H2), 6.81 (m, 4H, H4-H7), η^5-indenyl;[23] 7.0-7.4 (m, 15H, Ph). IR(CH_2Cl_2): υ(CO) 1934 cm^{-1}.

CpIr(CS)(PPh_3) (12)

This complex was prepared from KCp[3] and IrCl(CS)(PPh_3)$_2$[24] according to the previously reported procedure.[15] Yield: 45%. ^{1}H NMR: δ 5.06 (s, 5H, Cp), 7.39-7.70 (m, 15H, Ph). IR(nujol mull): υ(CS) 1291 cm^{-1}.

Cp*Ir(CO)$_2$ (13)

This complex was synthesized from [Cp*$IrCl_2$]$_2$[16b] and $Fe_3(CO)_{12}$[25] as previously reported.[16a] Yield: 64%. ^{1}H NMR: δ 2.19 (s, 15H, Cp*). IR(CH_2Cl_2): υ(CO) 2010 (s), 1938 (s) cm^{-1}.

(1,2,3-$C_5Me_3H_2$)Ir(CO)(PPh_3) (14)

Compound **14** was prepared using K(1,2,3-$C_5Me_3H_2$)[3] in the same manner as previously described for the synthesis of **2**.[14] Yield of **14**: 45%. Anal. Calcd. for $C_{27}H_{26}IrOP$: C, 54.99; H, 4.44. Found: C, 54.60; H, 4.61. ^{1}H NMR: δ 1.85 (d, J_{PH} = 1.9 Hz, 6H, 1,3-Me$_2$Cp), 2.06 (d, J_{PH} = 1.1 Hz, 3H, 2-MeCp), 4.77 (s, 2H, Cp), 7.3-7.6 (m, 15H, Ph). IR(CH_2Cl_2): υ(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_2Cl_2, layering this solution with Et_2O (10 x volume of CH_2Cl_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_2Cl_2 and added to a neutral alumina column (20 × 1.5 cm). Elution with CH_2Cl_2 gave a very pale yellow band. Evaporation of the eluent to dryness and recrystallization from CH_2Cl_2/hexanes (1:10) at -20 °C gave the desired product.

$Fe(CO)_3(PPh_3)_2$ (6)

Method A. Reaction time: 20 h. Yield: 82%. ^1H NMR: δ 7.40-7.60 (m, Ph). IR(CH_2Cl_2): υ(CO) 1965(w), 1881(s) cm^{-1}.

$Fe(CO)_3[P(p\text{-}MeOC_6H_4)_3]_2$ (7)

Method A. Reaction time: 15 h. Yield: 78%. ^1H NMR: δ 3.82 (s, 18H, Me), 6.91-7.51 (m, 24H, Ph). IR(CH_2Cl_2): υ(CO) 1964(w), 1875(s) cm^{-1}.

$Fe(CO)_3(PMePh_2)_2$ (8)

Method B. Reaction time: 15 h. Yield: 87%. ^1H NMR: δ 2.18 (d, J_{PH} = 6.8 Hz, 6H, Me), 7.39-7.67 (m, 20H, Ph). IR(CH_2Cl_2): υ(CO) 1965(w), 1876(s) cm^{-1}.

$Fe(CO)_3(PMe_2Ph)_2$ (9)

Method B. Reaction time: 24 h. Yield: 72%. ^1H NMR: δ 1.88 (s, 12H, Me), 7.42-7.78 (m, 10H, Ph). IR(CH_2Cl_2): υ(CO) 1965(w), 1870(s) cm^{-1}.

$Fe(CO)_3(PMe_3)_2$ (10)

Method B. Reaction time: 96 h. Yield: 74%. ^1H NMR: δ 1.59 (d, J_{PH} = 8.3 Hz, Me). IR(CH_2Cl_2): υ(CO) 1963(w), 1864(s) cm^{-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_2Cl_2 under N_2. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe. Immediately, the color of the solution was bleached. The IR spectra showed new υ(CO) bands at higher frequency (~140 cm^{-1}, see below) and the complete disappearance of the bands corresponding to the neutral starting material (see above). Solutions of the protonated complexes are stable as long as they are kept under nitrogen or argon. By adding 1 equiv of 1,3-diphenylguanidine base 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_3SO_3H to solutions of the neutral complex (~10 mg) in $CDCl_3$ (~0.5 mL). The yields as determined by ^1H NMR spectroscopy are also quantitative.

Compounds **$11H^+CF_3SO_3^-$** and **$14H^+CF_3SO_3^-$** were isolated as white solid precipitates by protonation of **11** (20.7 mg, 0.0346 mmol) and **14** (39.0 mg, 0.0661 mmol), respectively, with CF_3SO_3H (1 equiv) in Et_2O (5 mL) solution. After filtration, **$11H^+CF_3SO_3^-$** (18.1 mg, 0.0242 mmol) was obtained in 70% yield, and **$14H^+CF_3SO_3^-$** (36.8 mg, 0.0497 mmol) 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:

$\{CpIr(H)(CO)[P(p\text{-}ClC_6H_4)_3]\}CF_3SO_3$ ($1H^+CF_3SO_3^-$)

^1H NMR: δ 5.94 (s, 5H, Cp), 7.35 (d, J_{HH} = 9.0 Hz, 6H, meta-Ph protons), 7.57 (dd, J_{PH} = 12.3 Hz, 6H, ortho-Ph protons), -14.45 (d, J_{PH} = 24.41 Hz, 1H, Ir-H). IR(CH_2Cl_2): υ(CO) 2063 cm^{-1}.

$[CpIr(H)(CO)(PPh_3)]CF_3SO_3$ ($2H^+CF_3SO_3^-$)

^1H NMR: δ 5.88 (s, 5H, Cp), 7.56-7.40 (m, 15H, Ph), -14.44 (d, J_{PH} = 24.10 Hz, 1H, Ir-H). IR(CH_2Cl_2): υ(CO) 2063 cm^{-1}.

$[CpIr(H)(CO)(PMePh_2)]CF_3SO_3$ ($3H^+CF_3SO_3^-$)

^1H NMR: δ 5.90 (s, 5H, Cp), 2.70 (d, J_{PH} = 12.3 Hz, 3H, Me), 7.5 (m, 10H, Ph), -14.66 (d, J_{PH} = 23.21 Hz, 1H, Ir-H). IR(CH_2Cl_2): υ(CO) 2061 cm^{-1}.

$[CpIr(H)(CO)(PMe_2Ph)]CF_3SO_3$ ($4H^+CF_3SO_3^-$)

^1H NMR: δ 5.89 (s, 5H, Cp), 2.36 (d, J_{PH} = 11.6 Hz, 3H, Me), 2.39 (d, J_{PH} = 11.4 Hz, 3H, Me), 7.27-7.62 (m, 5H, Ph), -15.03 (d, J_{PH} = 25.11 Hz, 1H, Ir-H). IR(CH_2Cl_2): υ(CO) 2057 cm^{-1}.

$[CpIr(H)(CO)(PMe_3)]CF_3SO_3$ ($5H^+CF_3SO_3^-$)

^1H NMR: δ 6.01 (s, 5H, Cp), 2.12 (d, J_{PH} = 12.1 Hz, 9H, Me), -15.32 (d, J_{PH} = 25.33 Hz, 1H, Ir-H). IR(CH_2Cl_2): υ(CO) 2052 cm^{-1}.

$[(Indenyl)Ir(H)(CO)(PPh_3)]CF_3SO_3$ ($11H^+CF_3SO_3^-$)

^1H NMR: δ 6.63 (br s, 2H, H1, H3), 7.19 (t, $J_{1,3\text{-}2}$ = 7.6 Hz, 1H, H2), 7.84 (d, $J_{5,6\text{-}4,7}$ = 8.4 Hz, 2H, H4, H7), 6.32 (d, 2H, H5, H6), η^5-indenyl;[23] 7.00 (m, 6H, ortho-Ph protons), 7.51 (m, 9H, meta-, para-Ph protons), -17.14 (d, J_{PH} = 21.6 Hz, 2H, Ir-H). IR(CH_2Cl_2): υ(CO) 2058 cm^{-1}.

[CpIr(H)(CS)(PPh_3)]CF_3SO_3 (12H$^+CF_3SO_3^-$)

^{1}H NMR: δ 5.85 (s, 5H, Cp), 7.44-7.56 (m, 15H, Ph), -13.72 (d, J_{PH} = 24.32 Hz, 1H, Ir-H). IR(CH_2Cl_2): υ(CS) 1372 cm^{-1}.

[(C_5Me_5)Ir(H)$(CO)_2$]CF_3SO_3 (13H$^+CF_3SO_3^-$)

^{1}H NMR: δ 2.43 (s, 15H, Me), -13.80 (br s, 1H, Ir-H). IR(CH_2Cl_2): υ(CO) 2119 (s), 2080 (s) cm^{-1}.

[(1,2,3-$C_5Me_3H_2$)Ir(H)(CO)(PPh_3)]CF_3SO_3 (14H$^+CF_3SO_3^-$)

^{1}H NMR: δ 1.93 (s, 3H, 2-Me), 2.13 (s, 3H, 1,3-Me_2), 2.22 (s, 3H, 1,3-Me_2), 5.59 (s, 2H, Cp), 7.56-7.38 (m, 15H, Ph), -14.43 (d, J_{PH} = 25.5 Hz, 1H, Ir-H). IR(CH_2Cl_2): 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 $CDCl_3$ through a short column of Celite (2 x 0.5 cm), under N_2, resulted in better quality ^{1}H NMR spectra of the protonated products **6**H$^+CF_3SO_3^-$ - **10**H$^+CF_3SO_3^-$. Yields of the protonated products as determined by IR and ^{1}H NMR spectroscopy are quantitative. Only the protonation of **6** in H_2SO_4 solution was reported previously.[27] Attempts to isolate the protonated complexes as solids were unsuccessful. However, solutions are stable if kept under N_2 or Ar. The spectroscopic data for **$6H^+CF_3SO_3^-$** - **$10H^+CF_3SO_3^-$** are given below:

$[Fe(H)(CO)_3(PPh_3)_2]CF_3SO_3$ ($6H^+CF_3SO_3^-$)

^1H NMR: δ 7.45-7.61 (m, 30H, Ph), -7.90 (t, J_{PH} = 30.7 Hz, 1H, Fe-H). IR(CH_2Cl_2): υ(CO) 2088(w), 2039 (m, sh), 2026 (s) cm^{-1}.

$\{Fe(H)(CO)_3[P(p\text{-}MeOC_6H_4)_3]_2\}CF_3SO_3$ ($7H^+CF_3SO_3^-$)

^1H NMR: δ 3.88 (s, 18H, Me), 7.06-7.33 (m, 24H, Ph), -7.89 (t, J_{PH} = 29.9 Hz, 1H, Fe-H). IR(CH_2Cl_2): υ(CO) 2080(vw), 2032 (m, sh), 2020(s) cm^{-1}.

$[Fe(H)(CO)_3(PMePh_2)_2]CF_3SO_3$ ($8H^+CF_3SO_3^-$)

^1H NMR: δ 2.82 (s, 6H, Me), 7.6 (m, 20H, Ph), -8.27 (t, J_{PH} = 34.2 Hz, 1H, Fe-H). IR(CH_2Cl_2): υ(CO) 2092(w), 2027(s) cm^{-1}.

$[Fe(H)(CO)_3(PMe_2Ph)_2]CF_3SO_3$ ($9H^+CF_3SO_3^-$)

^1H NMR: δ 2.07 (br, s, 12H, Me), 7.5 (m, 10H, Ph), -8.92 (t, J_{PH} = 36.7 Hz, 1H, Fe-H). IR(CH_2Cl_2): υ(CO) 2090(w), 2023(s) cm^{-1}.

$[Fe(H)(CO)_3(PMe_3)_2]CF_3SO_3$ ($10H^+CF_3SO_3^-$)

^1H NMR: δ 1.76 (d, J_{PH} = 8.5 Hz, 18H, Me), -9.49 (t, J_{PH} = 36.6 Hz, 1H, Fe-H). IR(CH_2Cl_2): υ(CO) 2090(w), 2023(s) cm^{-1}.

Calorimetric Titrations

The calorimetric titration procedure was similar to that previously described.[3,7] Typically a run consisted of three sections: initial heat capacity calibration, titration (at 25.0 °C), and final heat capacity calibration. Each section was preceded by a baseline acquisition period. The titration period involved the addition of ~1.2 mL of a standardized 0.1 M (± 0.2 mM) CF_3SO_3H 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 (ΔH_{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 $CpM(CO)(PR_3)$ complexes where M = Co, Rh,[4a,9b] only the preparations of Ir complexes **2**[14] and **4**[28] have been reported previously. However, **5** was recently identified spectroscopically in a solid CO matrix as a product from the photolysis of $CpIr(C_2H_4)(PMe_3)$.[29] Compounds **1**-**5**, **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 N_2 and solutions were prepared using dry deaerated solvents. Compound **5**, however, is best stored for long periods under vacuum in a sealed glass ampoule.

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

$$KCp' + IrCl(CO)(PPh_3)_2 \xrightarrow[\text{reflux}]{\text{benzene}} Cp'Ir(CO)(PPh_3)$$

$$\begin{array}{l} Cp' = \text{indenyl, } \mathbf{11}\text{, } 40\% \\ Cp' = 1,2,3\text{-}C_5Me_3H_2\text{, } \mathbf{14}\text{, } 45\% \end{array} \quad (5)$$

Attempts to prepare **3** and **4** from KCp and $IrCl(CO)(PR_3)_2$ (PR_3 = $PMePh_2$, PMe_2Ph)[31] resulted in only low yields of the desired products. But starting from **2**, the PPh_3 ligand was easily replaced with $PMePh_2$ or PMe_2Ph (eq 6). The synthesis of complex **4** required less vigorous reaction conditions and a shorter reaction

$$\mathrm{CpIr(CO)(PPh_3)} \xrightarrow[\text{or xs PMe}_2\text{Ph, benzene } \upharpoonleft\!\downharpoonright]{\text{xs PMePh}_2\text{, toluene } \upharpoonleft\!\downharpoonright} \begin{array}{l} \mathrm{CpIr(CO)PR_3} \\ \mathrm{PR_3 = PMePh_2,\ \mathbf{3},\ 60\%} \\ \mathrm{PR_3 = PMe_2Ph,\ \mathbf{4},\ 82\%} \end{array} \qquad (6)$$

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 PPh_3 ligand was completely replaced.

Unfortunately, the reaction conditions used to prepare **3** and **4** (eq 6) were not successful for the synthesis of the PMe_3 derivative **5** as only decomposition of the starting material **2** was observed. However, reduction of $CpIr(I)_2(PMe_3)$[17] in slightly basic alcoholic solution[32] under an atmosphere of carbon monoxide gave **5** (eq 7) in variable yields (27-54%) which tended to be lower for prolonged

$$\mathrm{CpIr(I)_2(PR_3)} + \mathrm{CO\ (1\ atm)} \xrightarrow[\mathrm{Na_2CO_3}]{\text{EtOH, reflux}} \mathrm{CpIr(CO)(PR_3)} \qquad (7)$$

$$\begin{array}{l} \mathrm{PR_3 = P(p\text{-}ClC_6H_4)_3,\ \mathbf{1},\ 60\%} \\ \mathrm{PR_3 = PMe_3,\ \mathbf{5},\ 27\text{-}54\%} \end{array}$$

reaction times. The $P(p\text{-}ClC_6H_4)_3$ derivative **1** was prepared similarly. The syntheses of **1** and **5** are best followed by ^1H NMR spectroscopy. An intermediate, which is observed in each reaction (see Experimental), is tentatively assumed to be CpIr(H)(OEt)(PR_3).[33] Carbon monoxide induced reductive elimination of EtOH then produces the CpIr(CO)(PR_3) product.

Protonation Reactions of the Iridium Complexes

The protonated complexes **2H$^+$X$^-$** (X^- = BPh_4^-, BF_4^-),[14a,17] **12H$^+$Cl$^-$**,[15] and **13H$^+$BF$_4^-$**[26] have been isolated and characterized previously. It was established that protonation occurred at the iridium metal center. We observe that the addition of one equiv of CF_3SO_3H to solutions of the neutral metal complexes (**1**-**5**, **11**-**14**) in CH_2Cl_2 results in quantitative formation of **1H$^+$**$CF_3SO_3^-$ - **5H$^+$**$CF_3SO_3^-$ and **11H$^+$**$CF_3SO_3^-$ - **14H$^+$**$CF_3SO_3^-$ as indicated by IR spectroscopy. The υ(CO) band moves by ~140 cm^{-1} (or 81 cm^{-1} for the υ(CS) band of **12**) to higher frequency (see Experimental). Quantitative formation of **1H$^+$** - **5H$^+$** and **11H$^+$** - **14H$^+$** in $CDCl_3$ solution is also observed by ^1H NMR spectroscopy. Hydride resonances for **1H$^+$** - **5H$^+$** occur as doublets between -14.45 ppm (**1H$^+$**) and -15.32 ppm (**5H$^+$**) with $^2J_{PH}$ = 24-25 Hz due to coupling with the phosphine phosphorus. The Ir-H resonances for **11H$^+$** - **14H$^+$** are found in a wider range, -13.72 for **12H$^+$** to -17.14 ppm for **11H$^+$**. Complexes **11H$^+$**$CF_3SO_3^-$ and **14H$^+$**$CF_3SO_3^-$ were isolated as white solids in yields of 70% and 75%, respectively, from reactions of **11** and **14** with CF_3SO_3H in Et_2O solutions.

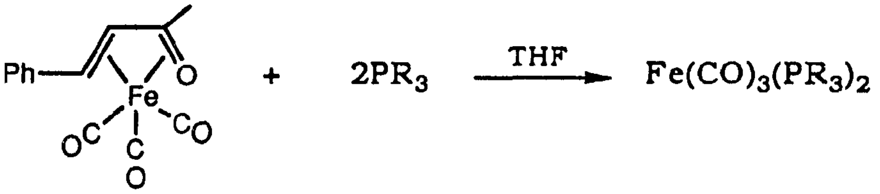
The structures of the protonated products are shown in eq 3. In **4H$^+$**$CF_3SO_3^-$ the Me groups in the PMe_2Ph ligand are diastereotopic;[17] thus, they are observed as two sets of doublets centered at 2.32 ppm ($^2J_{PH}$ = 11.6 Hz) and 2.39 ppm ($^2J_{PH}$ = 11.4 Hz) in the ^{1}H NMR spectrum. Also, the 1,3-Me groups in the 1,2,3-C_5Me_3H ligand of **14H$^+$CF$_3$SO$_3^-$** are diasteriotopic 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 ^{1}H NMR resonances.

The protonated complexes are stable in solution as long as they are kept under an atmosphere of N_2 or Ar. However, solutions of **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-diphenylguanidine base and recovered by chromatography.

Syntheses of Iron Complexes, $Fe(CO)_3(bda)$

The use of $Fe(CO)_3(bda)$ (bda = benzylideneacetone) as a source of the $Fe(CO)_3$ moiety in the preparation of $Fe(CO)_3(\eta^4\text{-diene})$ complexes has been described.[18,34] Except for brief reports of the synthesis of $Fe(CO)_3(PPh_3)_2$ (**6**),[19c-e] $Fe(CO)_3(bda)$ has not been widely used as a precursor to other $Fe(CO)_3(PR_3)_2$ complexes. We used $Fe(CO)_3(bda)$ to prepare all of the $Fe(CO)_3(PR_3)_2$ compounds, **6**-

10 (eq 8). The generality of this reaction and the ability to store $Fe(CO)_3(bda)$ (under N_2) makes this an excellent synthetic method for these complexes.



(8)

Complexes **6**,[19-21] **8**,[19b,20,21] **9**,[21] and **10**[19a,22] were characterized by comparison of their ^1H NMR and IR spectra with those 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 $Fe(CO)_3(PR_3)_2$ 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 N_2 at 0 °C. Complex **10** is only moderately air-stable. However, solutions of **6-10** were handled under nitrogen or argon using Schlenk techniques.

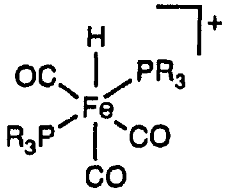
Protonation of $Fe(CO)_3(PR_3)_2$ Complexes

It has been previously shown by ^1H NMR and IR spectroscopy that **6** protonates at the metal center in conc. H_2SO_4 solution.[27] With one equiv of CF_3SO_3H we observe quantitative protonation of **6** to give $\mathbf{6}H^+CF_3SO_3^-$ (eq 4). Three $\upsilon(CO)$ infrared bands (2088(w), 2039(m, sh), 2026(s) cm^{-1}) in CH_2Cl_2 solution are observed for $\mathbf{6}H^+CF_3SO_3^-$ shifted by > 100 cm^{-1} from the unprotonated **6** values

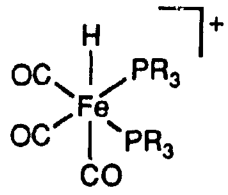
(1965(w), 1881(s) cm^{-1}). A trace of unprotonated **6** is also detected in the spectrum. This is probably due to deprotonation of **6**$H^+CF_3SO_3^-$ by adventitious water or even Cl^- in the NaCl IR cells since titration calorimetry, vide infra, establishes that protonation of **6** with CF_3SO_3H is quantitative. The ^1H NMR spectrum of **6**$H^+CF_3SO_3^-$ in $CDCl_3$ shows a high field triplet hydride resonance at -7.90 ppm ($^2J_{PH}$ = 30.7 Hz) which is coupled to two equiv phosphine ligands.

Compounds **7-10** are also quantitatively protonated at the metal center as determined by IR and ^1H NMR spectroscopy with one equiv of CF_3SO_3H. The two υ(CO) bands of weak and strong intensity in **7**$H^+CF_3SO_3^-$ - **10**$H^+CF_3SO_3^-$ are >100 cm^{-1} higher than those of their neutral precursors. The ^1H NMR spectra of **7**H^+-**10**H^+ show characteristic high field triplets (-7.89 ppm, J_{PH} = 29.9 Hz, for **7**H^+ to -9.49, J_{PH} = 36.6 Hz, for **10**H^+) for the hydride ligand. The proton resonances of the PR_3 ligands are shifted downfield from those in the unprotonated complexes. The protonated complexes **6**$H^+CF_3SO_3^-$ - **10**$H^+CF_3SO_3^-$ are stable in solution as long as they are kept under nitrogen or argon. Also, the solution (CH_2Cl_2) IR spectra of **6**$H^+CF_3SO_3^-$, **8**$H^+CF_3SO_3^-$, and **10**$H^+CF_3SO_3^-$ show no absorptions characteristic of coordinated $CF_3SO_3^-$.[36]

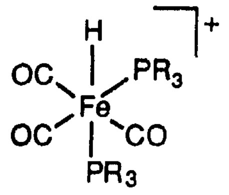
There are three possible isomers for **6**H^+-**10**H^+, structures **A**, **B**, and **C**.[37] The triplet Fe-H resonances and the equivalence of the PR_3 ligands in the ^1H NMR spectra of **6**H^+-**10**H^+ eliminate



A



B



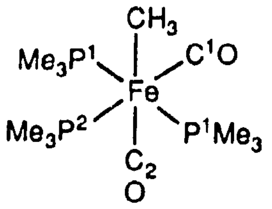
C

structure **C** and rule out the possibility of having a mixture of isomers as it is unlikely that **A** and **B** would give the same ^1H NMR spectrum.

The number and relative intensities of the υ(CO) bands in the IR spectra of **6H⁺**-**10H⁺** are consistent with the *mer* geometry **A**. Such complexes with C_{2v} symmetry are expected to give three IR bands of weak, strong, and strong relative intensities corresponding to two A_1, and a B_1, vibrational modes, respectively.[38] For **6H⁺**-**10H⁺**, the weak band at high frequency corresponds to one A_1 mode and the strong band at lower frequency corresponds to the remaining A_1 and B_1 modes that are only partially resolved for **6H⁺** and **7H⁺** and unresolved for **8H⁺**-**10H⁺** in CH_2Cl_2 solution.[38b] The following related complexes have also been assigned the *mer* geometry **A** based on their IR spectra in the υ(CO) region: $[Fe(CH_3)(CO)_3(PMe_3)_2]^+$,[39] $[Ru(H)(CO)_3(PPh_3)_2]PF_6$,[40a] $[Os(H)(CO)_3(PPh_3)_2]PF_6$,[40b] $Mn(H)(CO)_3(PPh_3)_2$,[41] $Mn(H)(CO)_3(PMePh_2)_2$,[42] $Re(H)(CO)_3(PPh_3)_2$,[37] $Re(H)(CO)_3(PEt_3)_2$.[37] The structures of $Mn(H)(CO)_3(PPh_3)_2$[41] and $Mn(H)(CO)_3(PMePh_2)_2$[42] which are isoelectronic with **6H⁺** and **8H⁺**, respectively, have been established by X-ray crystallography. The *fac*-geometry **B** for **6H⁺**-**10H⁺** is unlikely since this structure having C_s symmetry is predicted to give three ν(CO) bands of equal intensity (2A' + A").[38]

In principle, "virtual coupling"[43] of the *trans* phosphines in structure **A** should cause the Me resonances in **8H⁺**-**10H⁺** to appear as triplets in the ^{1}H NMR spectrum. However, they occur as singlets in **8H⁺** and **9H⁺** and as a doublet (J_{PH} = 8.5 Hz) in **10H⁺**. The Me resonances for *mer*-$Mn(H)(CO)_3[P(OPh)_2Me]_2$[44] and *mer*-$Mn(H)(CO)_3(PMePh_2)_2$[42] also occur as doublets in spite of their having *trans*-PR_3 groups. Thus, in these cases the ^{1}H NMR spectra do not distinguish between the *mer* (**A**) and *fac* (**B**) structures.

The ^{13}C NMR for the CO ligands, however, are more conclusive in supporting the *mer* (**A**) structure for **6H⁺**-**10H⁺**. For **8H⁺**, two 1:2:1 triplets[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 *trans* CO groups leaving the remaining triplet to the CO *trans* to the hydride in **A**. A comparison of the $^2J_{PC}$ values in **8H⁺** with those in $[Fe(CH_3)(CO)_2(PMe_3)_3]^+$, **D**[46], also supports structure **A** for these complexes. In **D**, the $^2J_{PC}$ values



D

for the *cis* CO and PMe_3 ligands ($^2J_{P1C1}$ = 27.3 Hz, $^2J_{P2C2}$ = $^2J_{P1C2}$ = 18.4 Hz) are much smaller than those for *trans* CO and PMe_3 ligands ($^2J_{P2C1}$ = 41.3 Hz). The J_{PC} values in **8**H^+ (23.65 and 13.35 Hz) indicate that there are only *cis* CO and PR_3 groups as required by structure **A**; there are no coupling constants in the range of 41 Hz which should be observed if there were *trans* CO and PR_3 ligands as in structure **B**. Supporting the *mer* structure **A** for these cations is the ^{13}C NMR spectrum of **6**$H^+CF_3SO_3^-$ which also gives small $^2J_{PC}$ values of 23.3 Hz (204.88 ppm, t, 2CO) and 15.3 Hz (204.0 ppm, t, CO). Thus, the IR and ^{13}C NMR data strongly support structure **A** for the products of the protonation reactions (eq 4).

Calorimetric Studies

Heats of protonation (ΔH_{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 $Fe(CO)_3(PR_3)_2$ **6**-**10** with 0.1 M CF_3SO_3H(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.[47] The only exception to this behavior was that of $Fe(CO)_3(PMePh_2)_2$ **8** for which the plots were slightly curved; the curvature was probably due to a small amount of decomposition of the reactant. However, the ΔH_{HM} value (-17.6 kcal mol^{-1}) obtained from these plots, which has a larger error (±0.4 kcal mol^{-1}) than the other Fe complexes, is reasonable because it is between those of the less basic $Fe(CO)_3(PPh_3)_2$ (**6**) (-14.1 kcal mol^{-1}) and the more basic $Fe(CO)_3(PMe_2Ph)_2$ (**9**) (-21.2 kcal mol^{-1}).

Infrared spectra were taken of the titrated solutions. Those of the iridium complexes **1-5**, **11**, **13** gave υ(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 ΔH_{HM} value. For reasons which are not understood, we were unable to obtain a reproducible ΔH_{HM} value for **14** even though this complex and its protonated product **14H$^+$**$CF_3SO_3^-$ appeared to be stable under the conditions of the titrations.

Table I. Heats of protonation (ΔH_{HM}) of Cp'Ir(L)(L') and $Fe(CO)_3(PR_3)_2$ complexes

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

[a] For protonation with CF_3SO_3H in DCE solvent at 25.0 °C.

[b] Ref 7.

[c] Numbers in parentheses are average deviations.

[d] Ref 3.

DISCUSSION

In this section, we examine trends in the basicities of the CpIr(CO)(PR_3) and Fe(CO)$_3$(PR_3)$_2$ complexes as a function of the PR_3 ligand. Phosphine basicity is measured by ΔH_{HP} (eq 1);[7] however, since ΔH_{HP} is linearly related to the pK_a of the phosphine, correlations involving ΔH_{HP} may also be expressed as correlations with pK_a.

Basicities of the CpIr(CO)(PR_3) Complexes 1-5

The basicity of the metal (ΔH_{HM}) in these complexes increases as the free phosphine basicity (ΔH_{HP}) increases (Table I). The basicities of the phosphines extend over a wide range from the weakly basic P(*p*-ClC$_6$H$_4$)$_3$ (ΔH_{HP} = -17.9 kcal mol^{-1}; pK_a = 1.03) to the very basic PMe$_3$ (ΔH_{HP} = -31.6 kcal mol^{-1}; pK_a = 8.65).[7] However, the ΔH_{HM} values only range from -29.2 kcal mol^{-1} for CpIr(CO)[P(*p*-ClC$_6$H$_4$)$_3$] (1) to -33.2 kcal mol^{-1} for CpIr(CO)(PMe$_3$) (5). A linear correlation (eq 9a) with a correlation coefficient (r) of 0.996 is obtained when ΔH_{HM} is plotted vs phosphine ΔH_{HP} (Figure 1).

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

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

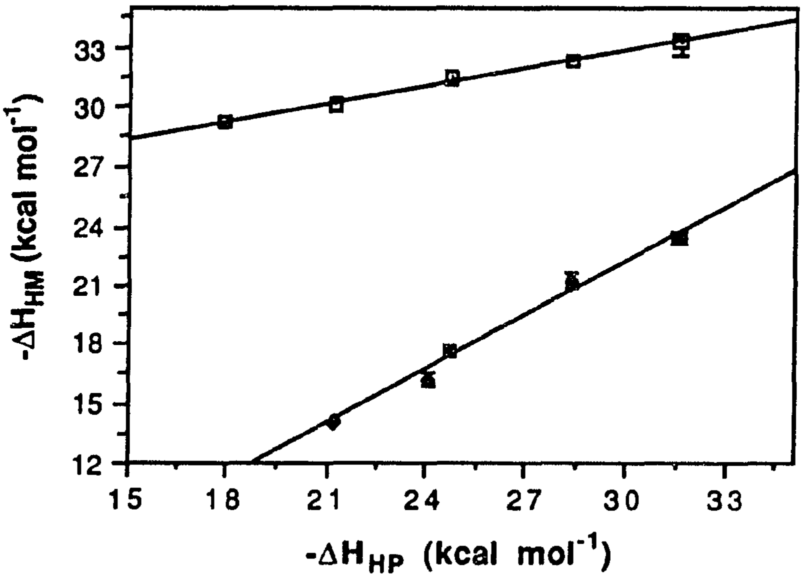


Figure 1. Correlations of metal basicity (ΔH_{HM}) with phosphine basicity (ΔH_{HP}) as determined by calorimetric titration with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. Upper line is for the $CpIr(CO)(PR_3)$ complexes. Lower line is for the $Fe(CO)_3(PR_3)_2$ complexes

The correlation between the ΔH_{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 ΔH_{HP}) and a metal fragment (CpIr(CO)) contribution (23.9).[48] The 0.298 coefficient for ΔH_{HP} (eq 9a) indicates that a change in phosphine basicity of 1.0 kcal mol^{-1} increases the basicity of the iridium complex by only 0.298 kcal mol^{-1}. Thus, only a fraction (0.298) of the phosphine basicity change is evident in the basicity change of the iridium.

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

The ΔH_{HM} values are inversely proportional (eq 10, r = -0.969) to the ν(CO) values (Figure 2) of the CpIr(CO)(PR_3) compounds **1-5** in CH_2Cl_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.[38b,c] It is apparent, however, that relatively small changes in $\upsilon(CO)$ (15 cm^{-1})

$$-\Delta H_{HM} = 0.274[2034-\upsilon(CO)]; \quad \text{in kcal mol}^{-1} \qquad (10)$$

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 $\upsilon(CO)$ values be measured in one solvent since changing solvents from CH_2Cl_2 (for **2**, $\upsilon(CO) = 1923$ cm^{-1}) to hexanes (for **2**, $\upsilon(CO) = 1946$ cm^{-1}) affects the $\upsilon(CO)$ value by ~20 cm^{-1}.[49]

A correlation ($r = 0.978$) (eq 11) of ΔH_{HM} with the Ir-H chemical shift (δ) in the complexes **2H+**-**5H+** is also obtained.

$$-\Delta H_{HM} = -4.31(\delta) - 32.4; \quad \text{in kcal mol}^{-1} \qquad (11)$$

However, it is of limited use since data for **1H+**, **11H+**, and **13H+** deviate significantly from it.

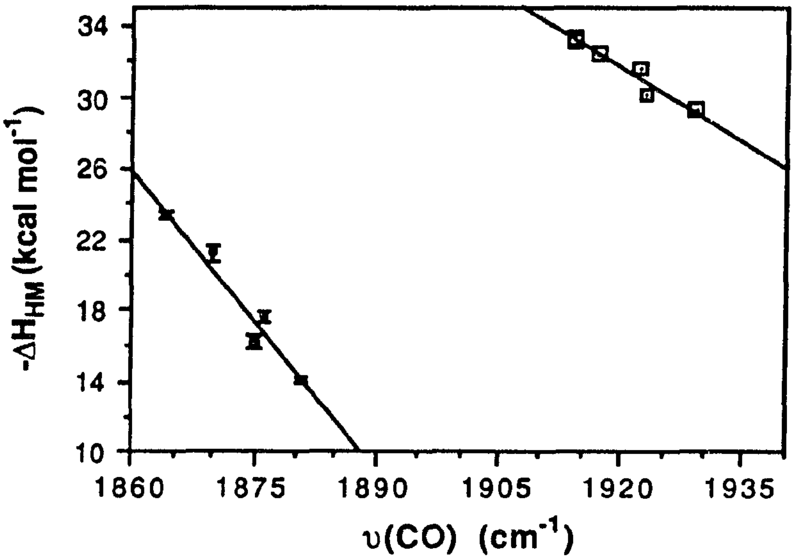


Figure 2. Correlation of metal basicity (ΔH_{HM}) with υ(CO) stretching frequency of CpIr(CO)(PR$_3$) complexes (upper line) and Fe(CO)$_3$(PR$_3$)$_2$ complexes (lower line)

Basicities of the $Fe(CO)_3(PR_3)_2$ Complexes 6-10

The ΔH_{HM} values for these complexes range from -14.1 kcal mol^{-1} for **6** to -23.3 kcal mol^{-1} for **10**. As for the CpIr(CO)(PR_3) series, there is a linear correlation (eq 12a, r = 0.993) of ΔH_{HM} with ΔH_{HP} (Figure 1). The corresponding pK_a correlation (r = 0.981) is given in eq 12b. Equation 12a shows that as the basicity of the

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

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

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 ΔH_{HM} and ΔH_{HP} suggests the metal basicity is determined by the σ-donor ability of the phosphine. However, as noted in the iridium discussion, it is not possible to exclude unequivocally some contribution of phosphorus π-bonding; Mossbauer studies[50] of $Fe(CO)_3(PR_3)_2$ complexes have been interpreted to support such π-bonding.

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

$$-\Delta H_{HM} = 0.562[1907 - \upsilon(CO)] ; \quad \text{in kcal mol}^{-1} \qquad (13)$$

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

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

Comparisons of the Basicities of the CpIr(CO)(PR$_3$) and Fe(CO)$_3$(PR$_3$)$_2$ Complexes

The iridium complexes **1-5** are much more basic than the corresponding Fe(CO)$_3$(PR$_3$)$_2$ complexes **6-10** (Figure 1). Using the PPh$_3$ complexes for comparison, CpIr(CO)(PPh$_3$) (**2**) (ΔH_{HM} = -30.1 kcal mol^{-1}) is 16.0 kcal mol^{-1} more basic than Fe(CO)$_3$(PPh$_3$)$_2$ (**6**) (ΔH_{HM} = -14.1 kcal mol^{-1}). Assuming ΔS° = 0 eu, the estimated equilibrium constant (ΔG° = ΔH_{HM} = -RTlnK) for the reaction (eq 15), is 5.4 x 10^{11}, which illustrates

$$\text{CpIr(CO)(PPh}_3) + \text{HFe(CO)}_3(\text{PPh}_3)_2^+ \overset{K}{\rightleftharpoons} \text{CpIr(H)(CO)(PPh}_3)^+ + \text{Fe(CO)}_3(\text{PPh}_3)_2 \qquad (15)$$

this very large difference in basicities. The free phosphines, e.g., PPh$_3$ (ΔH_{HP} = -21.2 kcal mol^{-1}) have basicities which are intermediate between those of their CpIr(CO)(PR$_3$) and

$Fe(CO)_3(PR_3)_2$ complexes. The very basic nature of the iridium in these types of complexes is emphasized by the observation that the related $[CpIr(H)(PPh_3)_2]^+$ cannot be deprotonated even with *n*-BuLi.[51]

In the correlations of ΔH_{HM} with ΔH_{HP} (Figure 1), the contributions of the metal fragments are -23.9 kcal mol^{-1} for CpIr(CO) (eq 9a) and +5.36 kcal mol^{-1} for $Fe(CO)_3$ (eq 12a).[48] Thus, the major factor which makes the $CpIr(CO)(PR_3)$ complexes more basic than the $Fe(CO)_3(PR_3)_2$ 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 ΔH_{HM} is indicated by the coefficients of the ΔH_{HP} terms in eq 9a (0.298) for $CpIr(CO)(PR_3)$ and in eq 12a (0.916) for $Fe(CO)_3(PR_3)_2$. If a change in phosphine basicity were to produce the same change in metal basicity in both series of complexes, one would expect the ΔH_{HP} coefficient to be twice as large for the iron complexes than for the iridium because two phosphines are being substituted in the iron series. However, in the $Fe(CO)_3(PR_3)_2$ series each PR_3 contributes 0.458 kcal mol^{-1} (0.916/2) for 1.0 kcal mol^{-1} change in ΔH_{HP}, while in the $CpIr(CO)(PR_3)$ complexes each PR_3 contributes only 0.298 kcal mol^{-1}. Thus, it appears that the $CpIr(CO)(PR_3)$ system is better able to dissipate additional PR_3 electron density than the $Fe(CO)_3(PR_3)_2$ complexes. One might have expected that the CO ligands in $Fe(CO)_3(PR_3)_2$ would have been more effective at removing electron density from the metal than the Cp and CO ligands in $CpIr(CO)(PR_3)$. Thus, it is not clear why changes in phosphine basicity affect these series of complexes differently. However, the structures and bonding in the reactants and products (eqs 3 and 4) are very different, and it would not be surprising if their ΔH_{HM} values behaved differently. In fact, it might be considered surprising that the phosphine contributions (0.298 and 0.458) are so similar given their structural differences and the much higher overall basicity of the iridium series as compared with that of the iron.

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

It is instructive to compare our results to related quantitative data reported in the literature. Pearson and Kresge[10] measured equilibrium constants (K_{H+}) for the oxidative-addition (eq 16) of CF_3SO_3H to $IrCl(CO)(PR_3)_2$ in MeOH solvent at 25.0 °C.

$$IrCl(CO)(PPh_3)_2 + CF_3SO_3H \rightleftharpoons trans\text{-}Ir(H)Cl(CO)(PR_3)_2(O_3SCF_3) \qquad (16)$$

(That $CF_3SO_3^-$ 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}) < $PMePh_2$

(302 M^{-1}) < PMe_2Ph (631 M^{-1}). While the trend is the same as the ΔH_{HM} values in the $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes, the K_{H^+} values change relatively little with different phosphines. This could be due to the fact that both protonation and $CF_3SO_3^-$ (or MeOH) coordination are involved, and the Ir-H and IrO_3SCF_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 ΔH_{HP} values of -21.2 kcal mol^{-1} for PPh_3[7] and -24.9 kcal mol^{-1} for $PEtPh_2$,[52] one obtains equation 17 which is analogous to 9a and 12a for the $CpIr(CO)(PR_3)$. Although this equation is based on only two points, the ΔH_{HP} coefficient

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

(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 isoelectronic except for the substitution of a CO ligand by PR_3. In order to establish the range and meaning of the ΔH_{HP} coefficient, other studies of the effects of phosphine basicity on metal basicity are required.

Basicities of Iridium Complexes 11-13

Comparison of the basicities of **2** (ΔH_{HM} = -30.1 ± 0.2 kcal mol^{-1}) and CpIr(1,5-COD) (ΔH_{HM} = -22.8 ± 0.3 kcal mol^{-1})[3] indicates $(CO)(PPh_3)$ ligand combination makes the metal 7.3 kcal mol^{-1} more basic than does the 1,5-COD ligand (eq 18).

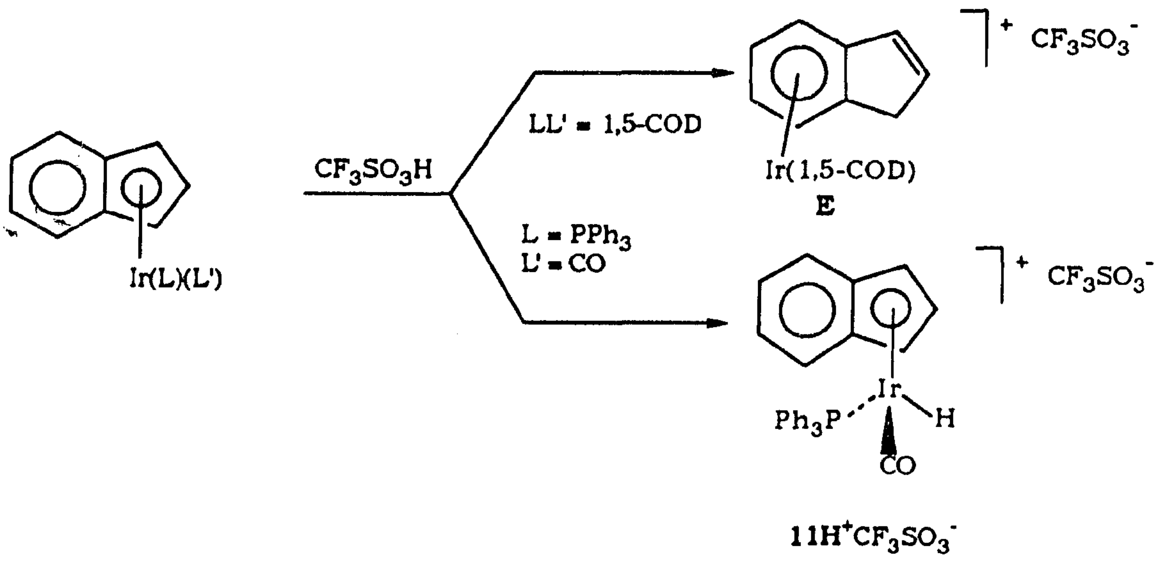
$$\underbrace{\underset{-30.1}{\mathrm{CpIr(CO)(PPh_3)}} > \underset{-22.8}{\mathrm{CpIr(1,5\text{-}COD)}}}_{7.3\ \mathrm{kcal\ mol^{-1}}} \quad \underbrace{\underset{-28.5}{\mathrm{Cp^{*}Ir(1,5\text{-}COD)}} > \underset{-21.4}{\mathrm{Cp^{*}Ir(CO)_2}}}_{7.1\ \mathrm{kcal\ mol^{-1}}} \qquad (18)$$

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 $(CO)(PPh_3)$ 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 PPh_3 produces a very large increase in the basicity of the metal. This effect is also observed in the pK_a values for the following pairs of compounds determined in acetonitrile:[2b,d] $Co(H)(CO)_4$ (8.3) vs $Co(H)(CO)_3(PPh_3)$ (15.4), $Mn(H)(CO)_5$ (15.1) vs $Mn(H)(CO)_4(PPh_3)$ (20.4), $CpW(H)(CO)_3$ (16.1) vs

CpW(H)(CO)$_2$(PMe$_3$) (26.6). It is evident, however, from these data that substitution of CO by PR$_3$ does not cause the same magnitude of increase in metal basicity in all metal complexes.

A variety of studies[53] indicate that CS is a more electron-withdrawing ligand than CO, as a result of its greater π-accepting ability. This is also evident in the ΔH_{HM} values of CpIr(CS)(PPh$_3$) (**12**) (-26.51 kcal mol^{-1}) and CpIr(CO)(PPh$_3$) (**2**) (-30.1 kcal mol^{-1}), which show that the metal in the CS compound **12** is 3.6 kcal mol^{-1} less basic than that in **2**.

Recently,[3] we showed that (indenyl)Ir(1,5-COD) is initially protonated with CF$_3$SO$_3$H at the iridium but the proton migrates within 15 min to the indenyl ligand to form [(η^6-indene)Ir(1,5-COD)]CF$_3$SO$_3$ (**E**) (Scheme 1).



Scheme 1

However, knowing that the (CO)(PPh_3) ligand combination in **2** increases the iridium basicity by 7.3 kcal mol^{-1} relative to the 1,5-COD ligand in the analogous CpIr(1,5-COD) complex (vide supra) we predicted that the iridium in **11** would be sufficiently basic that proton transfer from it to the indenyl ligand probably would not occur (Scheme 1). Indeed, the protonated complex **11**$H^+CF_3SO_3^-$ 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 ΔH_{HM} value for (indenyl)Ir(CO)(PPh_3) (**11**) (-29.8 ± 0.3 kcal mol^{-1}) which is the same within experimental error as that for the Cp analog CpIr(CO)(PPh_3) (**2**) (-30.1 ± 0.2 kcal mol^{-1}), suggesting that the indenyl and Cp ligands have the same donor properties. Since the crystal structure of [(indenyl)Ir(H)(PPh_3)$_2$]SbF_6 shows the indenyl ligand to be substantially slipped toward η^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 ΔH_{HM} and phosphine basicity (ΔH_{HP} or pK_a) for the CpIr(CO)(PR_3) and $Fe(CO)_3(PR_3)_2$ series of complexes, respectively. However, for each 1.0 kcal mol^{-1} change in phosphine basicity (ΔH_{HP}), there is a greater change in $Fe(CO)_3(PR_3)_2$ basicity (0.916 kcal mol^{-1}) than in CpIr(CO)(PR_3) basicity (0.298 kcal mol^{-1}). In general, the CpIr(CO)(PR_3) complexes are much more basic than those in the $Fe(CO)_3(PR_3)_2$ series. The ΔH_{HM} values also correlate linearly with the respective ν(CO) frequencies of the CpIr(CO)(PR_3) and $Fe(CO)_3(PR_3)_2$ complexes. These correlations permit the estimation of basicities (ΔH_{HM}) of other complexes in these series which contain different phosphines whose ΔH_{HP} (or pK_a) values or ν(CO) stretching frequencies are known.

Comparisons of ΔH_{HM} values for several CpIr(L)(L') complexes demonstrate that the (CO)(PPh_3) ligand combination makes the Ir 7.3 kcal mol^{-1} more basic than the bidentate 1,5-COD ligand does; however, the 1,5-COD makes the metal more basic than $(CO)_2$ by 7.1 kcal mol^{-1}. For the CpIr(CX)(PPh_3) complexes (X = O, S), the CS ligand reduces the basicity of the iridium by 3.6 kcal mol^{-1} as compared with the CO-containing complex. The donor properties of the Cp and indenyl ligands are very similar since the ΔH_{HM} values of the complexes CpIr(CO)(PPh$_3$) and (indenyl)Ir(CO)(PPh$_3$) are the same. These studies provide a quantitative basis for understanding how systematic changes in ligands affect the proton basicity of transition metal complexes.

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SECTION IV. BIDENTATE PHOSPHINE BASICITIES AS DETERMINED BY ENTHALPIES OF PROTONATION

ABSTRACT

Enthalpies for both the first (ΔH_{HP1}) and the second (ΔH_{HP2}) protonations of the phosphorus donors in bidentate phosphines have been determined by titration calorimetry using CF_3SO_3H in 1,2-dichloroethane solvent. The ΔH_{HP1} values for the series $Ph_2P(CH_2)_nPPh_2$, 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 ΔH_{HP2} values also become more exothermic from -14.9 ± 0.2 to -24.9 ± 0.1 kcal mol^{-1} with increasing alkyl chain length. The ΔH_{HP1} and ΔH_{HP2} values for other bidentates, $Ph_2P(bridge)EPh_2$ (E = P, bridge = *cis*-CH=CH, *trans*-CH=CH, 1,2-C_6H_4; E = As, bridge = CH_2CH_2) and $Me_2PCH_2PMe_2$, have also been determined. Correlations of ΔH_{HP1} and ΔH_{HP2} 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.[1] 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 (ΔH_{HP}, eq 1) of several aryl, mixed alkyl/aryl and alkyl phosphines with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) solution.

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

These ΔH_{HP} 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 CF_3SO_3H in DCE are reported. For the dibasic phosphines, which are listed with their abbreviations in Table I, ΔH_{HP1} represents the heat liberated during the addition of the first equivalent of acid, while ΔH_{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

$$P^\frown P + CF_3SO_3H \xrightarrow[25.0\ ^{\circ}C]{DCE} HP^\frown P^+CF_3SO_3^- \tag{2}$$

$$HP^\frown P^+CF_3SO_3^- + CF_3SO_3H \xrightarrow[25.0\ ^{\circ}C]{DCE} HP^\frown PH^{2+}(CF_3SO_3^-)_2 \tag{3}$$

ΔH_{HP1} and ΔH_{HP2}, respectively, as will be discussed. The results of these studies give a quantitative measure (ΔH_{HP1} and ΔH_{HP2}) of the σ-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[6] a study of the effect of

$$ML_x + CF_3SO_3H \xrightarrow[25.0\ ^{\circ}C]{DCE} H\text{-}ML_x^+\ CF_3SO_3^- \ ;\ \Delta H_{HM} \tag{4}$$

methyl groups in the cyclopentadienyl ligand in Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, 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.[7]

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*-trifluoromethylphenyl)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 CH_2Cl_2 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 C_6H_6, 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.[5,6] 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 ΔH_{HP1}, the titration period involved the addition of ~1.2 mL of a standardized 0.1 M (± 0.2 mM) CF_3SO_3H solution in DCE at a constant rate during 3 minutes time to 50 mL of a ~2.6 mM solution of the phosphine (~10% excess) in DCE at 25.0 °C. To obtain ΔH_{HP2}, slightly more than one equiv of CF_3SO_3H (0.1 M, ~0.105 mmol) was added to a 50 mL solution of the bidentate phosphine (~0.100 mmol). The second equiv of acid was then added (0.095 mmol) at a constant rate during ~2 min time to titrate at 25.0 °C the remaining unprotonated phosphine. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (-0.2 kcal mol^{-1}).[6]

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 ΔH_{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 ΔH_{HP} values for the monodentate PR_3 compounds presented previously (-17.9 kcal mol^{-1} for (p-$ClC_6H_4)_3P$ to -36.6 for (t-$Bu)_3P$).[5] However, the ΔH_{HP2} values for the smaller chelates, for example, dppm (-14.9 kcal mol^{-1}), are much less exothermic than any ΔH_{HP} values have yet reported.[5,6] Nevertheless, all titration curves were linear indicating stoichiometric reaction of the acid with the neutral and monoprotonated species.

The low dielectric constant (ε = 10.36)[8] 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;[5] it was concluded that they contribute a total of ~0.3 kcal mol^{-1} to the ΔH_{HP} value. Presumably these reactions also contribute negligibly to the ΔH_{HP1} and even the weakly exothermic ΔH_{HP2} values in this study.

The ΔH_{HP} value (eq 1) of the monodentate, weakly-basic (p-$CF_3C_6H_4)_3P$ was determined to be -13.6 kcal mol^{-1}.

Table I. ΔH_{HP1}, ΔH_{HP2} and pK_{a1}, pK_{a2} values for bidentate phosphines

Phosphine	$-\Delta H_{HP1}$,[a] kcal mol^{-1}	pK_{a1}[b]	$-\Delta H_{HP2}$,[c] kcal mol^{-1}	pK_{a2}[b]
$Ph_2PCH_2PPh_2$ (dppm)	22.0 (±0.1)	3.81	14.9 (±0.2)	-2.73
$Ph_2P(CH_2)_2PPh_2$ (dppe)	22.8 (±0.2)	3.86	20.2 (±0.1)	0.99
$Ph_2P(CH_2)_3PPh_2$ (dppp)	23.4 (±0.1)	4.50	22.4 (±0.3)	2.53
$Ph_2P(CH_2)_4PPh_2$ (dppb)	24.6 (±0.1)	4.72[f]	23.8 (±0.2)	4.28[f]
$Ph_2P(CH_2)_5PPh_2$ (dppent)	24.8 (±0.2)	4.84[f]	24.5 (±0.1)	4.67[f]
$Ph_2P(CH_2)_6PPh_2$ (dpph)	25.2 (±0.1)	5.05[f]	24.9 (±0.1)	4.89[f]
cis-$Ph_2P(CH{=}CH)PPh_2$ (*cis*-dppv)	19.9 (±0.3)	2.27	10.0 (±0.2)	-6.20[g]
trans-$Ph_2P(CH{=}CH)PPh_2$ (*trans*-dppv)	21.7 (±0.2)	2.74	12.7 (±0.1)	-4.30[g]
$Ph_2P(1,2\text{-}C_6H_4)PPh_2$ (dppbz)	21.3 (±0.1)	2.91[f]	10.7 (±0.3)	-5.70[g]
$Ph_2P(CH_2)_2AsPh_2$ (arphos)	23.2 (±0.4)	3.96[f]	8.2 (±0.1)	-7.46[g]
$Me_2PCH_2PMe_2$ (dmpm)	31.0 (±0.3)	8.24[f]	25.8 (±0.2)	4.93[g]
$Et_2P(CH_2)_2PEt_2$ (depe)	31.3[f]	8.41[b]	26.0[g]	5.04[b]

$(p\text{-}CF_3C_6H_4)_3P$	13.6 (±0.2)[d]	-1.32[f]
PPh_3	21.2 (±0.1)[d,e]	2.73[e]
PPh_2Me	24.7 (±0.0)[d,e]	4.59[e]
PMe_3	31.6 (±0.2)[d,e]	8.65[e]

[a] For protonation with 1 equiv of CF_3SO_3H in DCE solvent at 25.0 °C.

[b] Ref 10.

[c] For addition of a second equiv of CF_3SO_3H in DCE solvent at 25.0 °C.

[d] ΔH_{HP}, eq 1.

[e] Selected from ref 5.

[f] Calculated from eq 7.

[g] Calculated from eq 8.

DISCUSSION

ΔH_{HP1} and ΔH_{HP2} Values for the Series $Ph_2P(CH_2)_nPPh_2$

The -ΔH_{HP1} values for the $Ph_2P(CH_2)_nPPh_2$ 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[9] further indicate the electron-withdrawing character of the PPh_2 group (Hammett constant, σ_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 ΔH_{HP1}. At this point, ΔH_{HP1} is about -25.0 kcal mol^{-1} which is within experimental error the same as ΔH_{HP} (-24.7 kcal mol^{-1}) of PPh_2Me (Table I).

The -ΔH_{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 ΔH_{HP1} (-22.0 kcal mol^{-1}) and ΔH_{HP2} (-14.9 kcal mol^{-1}) for dppm shows that PPh_2H^+ is a much stronger electron withdrawing group than PPh_2. However, the effect of the PPh_2H^+ is rapidly attenuated to the point that at large n values both ΔH_{HP1} and ΔH_{HP2} reach the same limiting value of approximately -24.8 kcal mol^{-1}, which is essentially the same as the value for PPh_2Me (-24.7 kcal mol^{-1}).

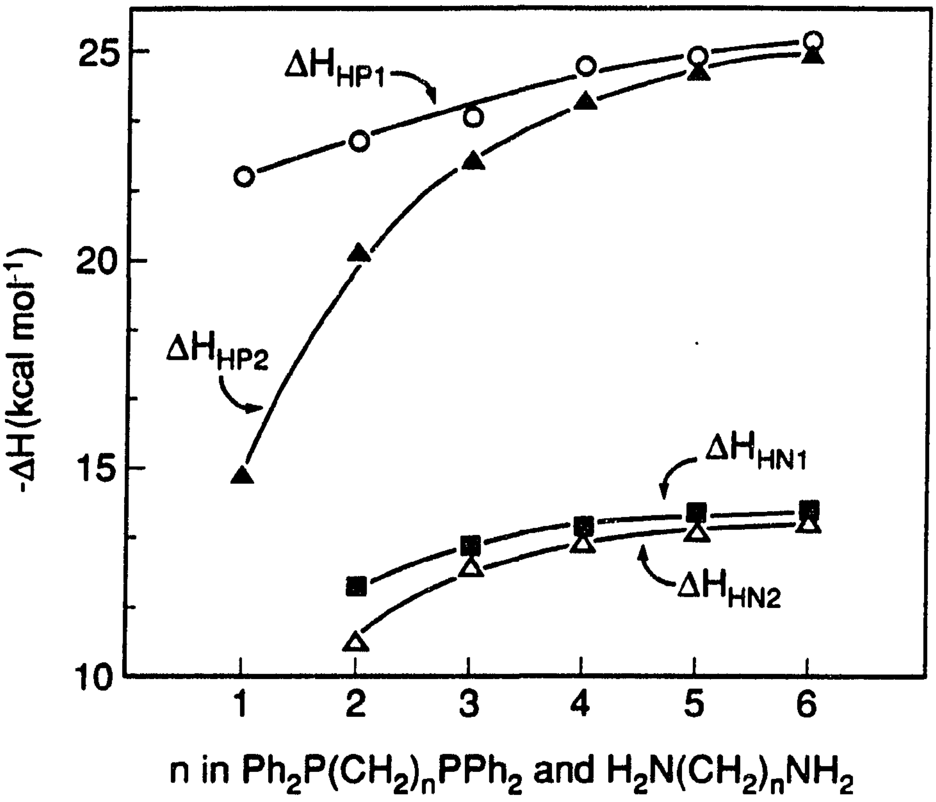

Figure 1. Plot of ΔH_{HP} vs n of $Ph_2P(CH_2)_nPPh_2$ (upper two curves) and ΔH_{HN} vs n of $H_2N(CH_2)_nNH_2$ (lower two curves). ΔH_{HN} values are taken from ref 11a

Thus, for the n = 5 and 6 ligands, dppent 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, PPh_2 or PPh_2H^+.

A consequence of this is that during titration with the first equiv of acid, both mono- and diprotonated $P^{\frown}P$ are probably formed (eqs 2 and 3). Thus, ΔH_{HP1} does not simply correspond to the enthalpy of eq 2. To determine to what extent ΔH_{HP1} corresponds to eq 2 for the bidentate phosphines, the amounts of $P^{\frown}P$, $HP^{\frown}P^+$, and $HP^{\frown}PH^{2+}$ present in solution after the addition of one equiv of CF_3SO_3H were estimated. Assuming the relative pK_{a1} and pK_{a2} values (Table I)[10] for dppm, dppe, and dppp measured in CH_3NO_2 to be the same in DCE, the concentrations of $P^{\frown}P$, $HP^{\frown}P^+$, and $HP^{\frown}PH^{2+}$ in the titration solutions after 1 equiv of CF_3SO_3H has been added are calculated with use of eq 5.

$$K = \frac{K_{a1}}{K_{a2}} = \frac{[P^{\frown}P][HP^{\frown}PH^{2+}]}{[HP^{\frown}P^{+}]^{2}} \qquad (5)$$

For the addition of 1 equiv of CF_3SO_3H to 50 mL (the 1.2 mL volume change is negligible) of 2.6 mM $P^{\frown}P$ (1.2×10^{-4} mol), the percentage of the ligand in the monoprotonated form ($HP^{\frown}P^+$) is >99% for dppm, 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_3NO_2 (< 0.0 pK_a units), the ΔH_{HP1} values correspond to protonations of $P^\frown P$ to form primarily $HP^\frown P^+$ (eq 2), and ΔH_{HP2} values correspond primarily to protonations of $HP^\frown P^+$ to form $HP^\frown PH^{2+}$ (eq 3). The ΔH_{HP1}, ΔH_{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 ΔH_{HP1} (-31.0 kcal mol^{-1}) and ΔH_{HP2} (-25.8 kcal mol^{-1}) values of dmpm correspond to the formation of $HP^\frown P^+$ and $HP^\frown PH^{2+}$, respectively.

For the titrations of dppb, dppent and dpph, significant amounts of $P^\frown P$ and $HP^\frown PH^{2+}$ 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 ΔH_{HP1} values which correspond to the formation of a mixture of $P^\frown P$, $HP^\frown P^+$, and $HP^\frown PH^{2+}$. However, since the P-donors in these ligands are separated so far, ΔH_{HP1} and ΔH_{HP2} are very similar anyway.

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

$$-\Delta H_{HP} = 16.3 + 1.82\, pK_a; \quad \text{in kcal mol}^{-1} \qquad (6)$$

above and in Table I, pK_{a1} and pK_{a2} values for several bidentate phosphines have also been determined[10] from glass electrode potentials (ΔHNP's) at half neutralization with $HClO_4$ in CH_3NO_2; these ΔHNP's were then converted to pK_a values in water. As for the monodentate phosphines, there is a correlation between ΔH_{HP1} and pK_{a1} of bidentate phosphines. When plotted (Figure 2) on the same graph as the ΔH_{HP} and pK_a values for monodentate phosphines, ΔH_{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 (ΔH_{HP1}) phosphines gives a new equation (eq 7) (correlation coefficient r = 0.982) which is only slightly different from that in eq 6.

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

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

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

eq 7 is largest for dppm and dppe in which the charges in the diprotonated species, $HP^\frown PH^{2+}$, 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 PPh_2H^+ 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 ΔH_{HP1} and ΔH_{HP2} values have been measured.

It is interesting to compare ΔH_{HP1} and ΔH_{HP2} data for the bidentate phosphines with ΔH_{HN1} and ΔH_{HN2} values for the protonation of the diamines, $H_2N(CH_2)_nNH_2$ ($n = 2\text{-}6$), with HNO_3 in water[11] (eqs 9 and 10).

$$N^\frown N + H^+ \xrightarrow[25.0\ ^\circ C]{H_2O} HN^\frown N^+ \tag{9}$$

$$HN^\frown N^+ + H^+ \xrightarrow[25.0\ ^\circ C]{H_2O} HN^\frown NH^{2+} \tag{10}$$

As for the $Ph_2P(CH_2)_nPPh_2$ series, $-\Delta H_{HN1}$ increases with the number of CH_2 groups until it levels off at $\sim n = 4$ (Figure 1). The relative effect of alkyl chain length on phosphorus basicity vs nitrogen basicity can be obtained by plotting ΔH_{HP1} vs ΔH_{HN1} and ΔH_{HP2} vs ΔH_{HN2} (Figure 3) for ligands with the same number (n) of CH_2 groups. When plotted on the same graph, one line correlating the ΔH_{HP1}, ΔH_{HN1} and the ΔH_{HP2}, ΔH_{HN2} data can be drawn (Figure 3). A linear-least squares analysis gives eq 11 ($r = 0.979$). The slope

$$-\Delta H_{HPx} = 2.64 + 1.61\,(\Delta H_{HNy});\ \text{in kcal mol}^{-1} \tag{11}$$
$$\text{for } x = 1,\ y = 1$$
$$\text{for } x = 2,\ y = 2$$

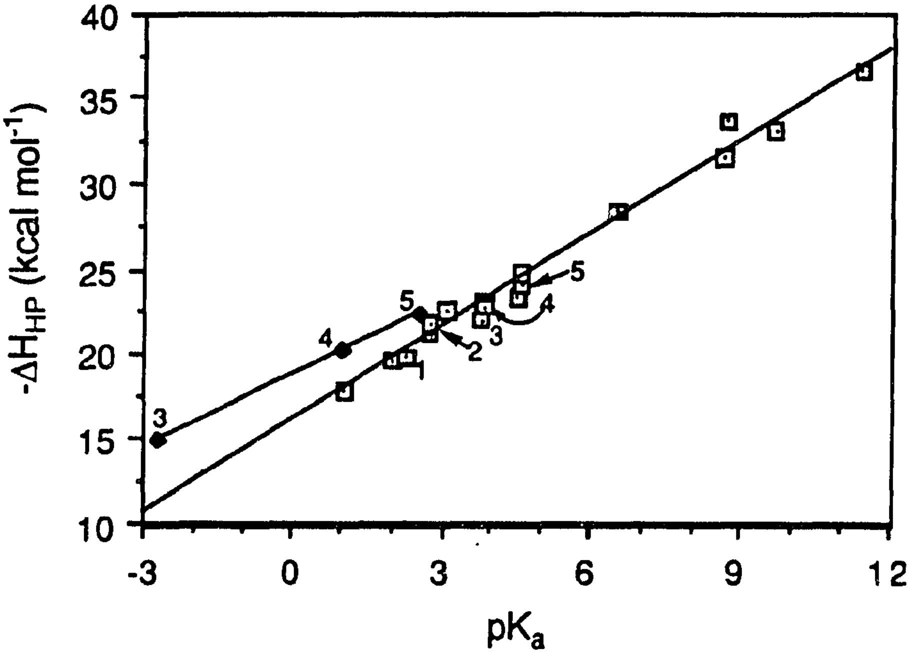

Figure 2. Plot of ΔH_{HP1} vs pK_{a1} (◘) and ΔH_{HP2} vs pK_{a2} (♦) for bidentate and monodentate phosphines. Numbers refer to the following compounds: 1) *cis*-dppv, 2) *trans*-dppv, 3) dppm, 4) dppe, 5) dppp. Points (◘) not labeled are monodentate (PR_3) ΔH_{HP} values from ref 5. The pK_{a1} and pK_{a2} values are taken from ref 10

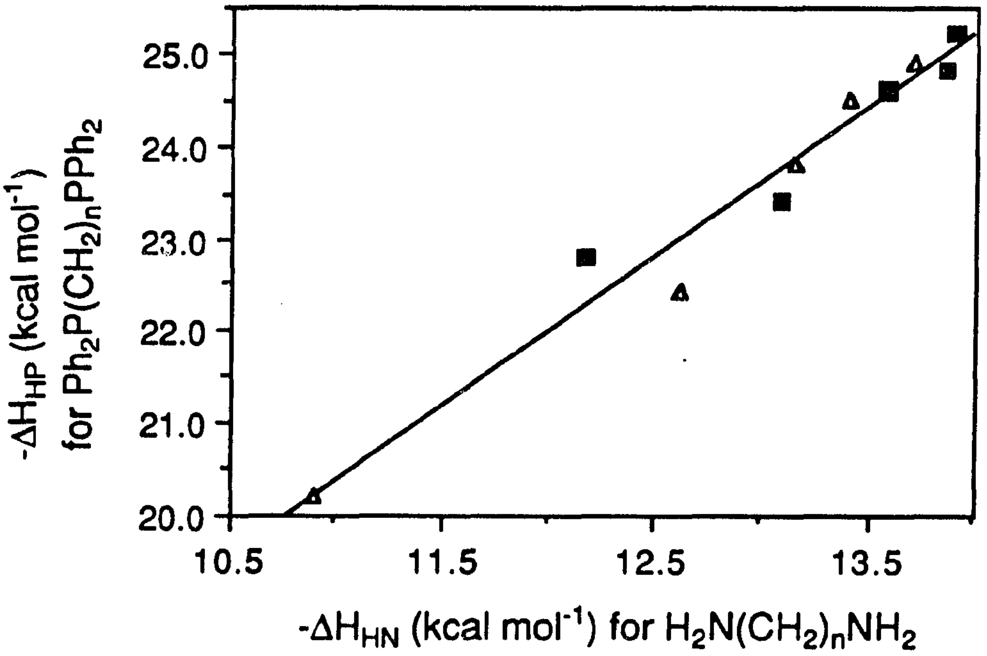

Figure 3. Plot of ΔH_{HP1} vs ΔH_{HN1} (■) and ΔH_{HP2} vs ΔH_{HN2} (▲) for $Ph_2P(CH_2)_nPPh_2$ and $H_2N(CH_2)_nNH_2$ (n = 2-5). The ΔH_{HN1} and ΔH_{HN2} values are taken from ref 11a

of 1.61 shows that the relative effect of the PPh_2 (or PPh_2H^+) groups on phosphorus basicity drops off more rapidly than the effect of NH_2 (or NH_3^+) on nitrogen basicity as the $(CH_2)_n$ 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.

ΔH_{HP1} and ΔH_{HP2} Values for Other Bidentate Phosphines

The less exothermic ΔH_{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 backbone[10] as compared with $-CH_2CH_2-$. The basicity of dppbz is more comparable to that of PPh_3 (-21.2 kcal mol^{-1})[5] than PPh_2Me (-24.7 kcal mol^{-1}),[5] which suggests that the PPh_2 group in dppbz has the same electronic effect as the ortho H in PPh_3. Thus, while the PPh_2 group is electron-withdrawing[9] in the $Ph_2P(CH_2)_nPPh_2$ series of ligands, this is not the case in dppbz. That PPh_2 and H have similar electronic effects in aromatic systems is supported by the σ_p value (-0.01)[12] for PPh_2 obtained from measurements of dissociation constants of substituted phosphinic and benzoic acids in aqueous THF. However, others[13] have suggested that the PPh_2 group is electron-withdrawing (σ_p = 0.19) in aromatic systems. Our results support the former conclusion.

The difference between ΔH_{HP1} and ΔH_{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 PPh_2H^+ group is more effectively transferred through the unsaturated 1,2-phenylene bridge in dppbz than through the -CH_2CH_2- link in dppe. It is also possible that the rigid 1,2-phenylene bridge which maintains the two PPh_2H^+ groups in the diprotonated dppbz species in close proximity, will also reduce ΔH_{HP2} 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 ΔH_{HP1} and ΔH_{HP2}.

As for dppbz, the *cis*- and *trans*-dppv ligands are also less basic than dppe (Table I). The ΔH_{HP1} measurements show *cis*-dppv to be 1.8 kcal mol^{-1} less basic than *trans*-dppv; the same trend is observed in their pK_{a1} values[10] (2.27 and 2.74, respectively). In addition, the heats of reaction (ΔH_{Hg})[14] of these compounds with Lewis acids HgX_2 (X = Cl, Br, I), eq 12, follow the same trend with *cis*-dppv (ΔH_{Hg} = -80 kcal mol^{-1}, X = Cl) being 7 kcal mol^{-1} less basic towards these Lewis acids than *trans*-dppv (ΔH_{Hg} = -87 kcal mol^{-1}, X = Cl). (*Cis*- and *trans*-dppv behave only as monodentate ligands towards $HgCl_2$.)[14] The greater ΔH_{HP1} basicity of the *trans*-dppv compound

$$P\overset{\frown}{\ }P + HgX_2 \longrightarrow P\overset{\frown}{\ }PHgX_2;\ \Delta H_{Hg} \tag{12}$$

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 $:PPh_2$ group. As $:PPh_2$ 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_{a2} 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_{a2} 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_2H^+ 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 PPh_3 as determined by both ΔH_{HP} and pK_a measurements (Table I) suggests that the *trans*-CH=CHPPh$_2$ and Ph groups have essentially the same effect on phosphorus basicity. This observation is supported[14] by ΔH_{Hg} values (eq 12) for Lewis adduct formation of $HgBr_2$ with *trans*-dppv (-79 ± 2 kcal mol^{-1}), PPh_3 (-77 ± 4 kcal mol^{-1}), and $PPh_2(CH{=}CH_2)$ (-78 ± 2 kcal mol^{-1}), which are the same within experimental error.

For the arphos ligand the ΔH_{HP1} value (-23.2 ± 0.4 kcal mol^{-1}) is comparable to ΔH_{HP1} of dppe (-22.8 ± 0.2 kcal mol^{-1}) which indicates that protonation occurs at the phosphorus atom, and $AsPh_2$ is within experimental error as electron-withdrawing as PPh_2. The much lower ΔH_{HP2} 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 $AsPh_3$ (pK_B = 10.60) compared with PPh_3 (pK_B = 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 CF_3SO_3H in $CDCl_3$ 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 BH_3.[16] The heat of adduct formation of $BH_3(g)$ with the phosphorus in $Ph_2PCH_2CH_2AsPh_2$ is -155.3 kcal mol^{-1}, while that for the subsequent addition of BH_3 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 ΔH_{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, ΔH_{HP1} (-31.3 kcal mol^{-1}) and ΔH_{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 ΔH_{HP1} values, their basicities decrease in the following order:

> depe ≥ dmpm >> dpph > dppent > dppb > dppp > dppe >
> dppm > *trans*-dppv > dppbz > *cis*-dppv

The same trend is also observed in the ΔH_{HP2} values. Since this series summarizes the energetics of phosphine bond formation with H^+, it presumably also represents the relative σ-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-$CF_3C_6H_4)_3P$,[15] which is presumed to be very weakly basic,[2a] has also been determined. The ΔH_{HP} value of -13.6 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-$XC_6H_4)_3P$ (X = CF_3, Cl, F, H, Me, OMe, 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

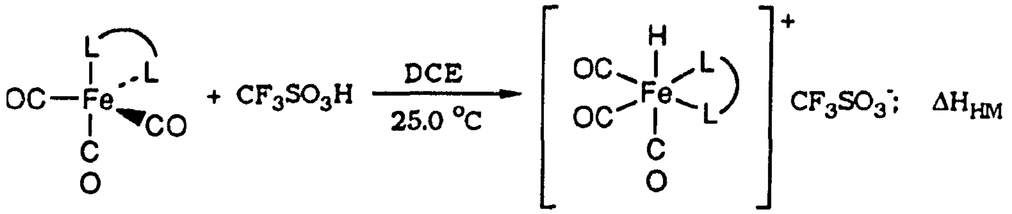
ABSTRACT

Titration calorimetry has been used to determine the heats of protonation (ΔH_{HM}) of $Fe(CO)_3(L^\frown L)$ complexes ($L^\frown L$ = dppm, dppe, dppp, dppb, dppbz, *cis*-dppv, arphos, dmpm, dcpe, and diars) with CF_3SO_3H (0.1 M) in 1,2-dichloroethane solution. Spectroscopic studies show that protonation occurs at the metal center to form *fac*-$[Fe(H)(CO)_3(L^\frown L)]CF_3SO_3$. For the series $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$, n = 1-4, ΔH_{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 $Fe(CO)_3(PPh_2Me)_2$ (ΔH_{HM} = -17.6 ± 0.3 kcal mol^{-1}). Likewise, $Fe(CO)_3$(dmpm) is much more basic (ΔH_{HM} = -30.2 ± 0.4 kcal mol^{-1}) than $Fe(CO)_3(PMe_3)_2$ (ΔH_{HM} = -23.3 ± 0.3 kcal mol^{-1}). The higher basicities of complexes with small chelate ligands is ascribed to distortions imposed on the $Fe(CO)_3(L^\frown L)$ 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 $Fe(CO)_3(L^\frown L)$ complexes, as measured by their heats of protonation (ΔH_{HM}) with CF_3SO_3H 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 (PR_3),[4a] diphosphines[4b] and a series of methyl-



(1)

where $L^\frown L$ is

$Ph_2P(CH_2)PPh_2$ (dppm)
$Ph_2P(CH_2)_2PPh_2$ (dppe)
$Ph_2P(CH_2)_3PPh_2$ (dppp)
$Ph_2P(CH_2)_4PPh_2$ (dppp)

$Ph_2P(1,2\text{-}C_6H_4)PPh_2$ (dppbz)
cis-$Ph_2P(CH{=}CH)PPh_2$ (*cis*-dppv)
$Ph_2P(CH_2)_2AsPh_2$ (arphos)
$Me_2As(1,2\text{-}C_6H_4)AsMe_2$ (diars)

$Me_2P(CH_2)PMe_2$ (dmpm)
$Cy_2P(CH_2)_2PCy_2$ (dcpe)

cyclopentadienyl complexes Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, x = 0, 1, 3-5), in which protonation occurs at the 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.[6] Hexanes and CH_2Cl_2 were refluxed over CaH_2 and then distilled.[7] Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Deuteriochloroform was stored over molecular sieves in air or distilled from P_2O_5 under nitrogen. The phosphine and arsine ligands were purchased from commercial sources.

The ^1H NMR spectra were recorded in $CDCl_3$ (except as stated otherwise) on a Nicolet-NT 300 MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. The $^{31}P\{H\}$ NMR spectra were recorded in 10 mm tubes on a Brucker WM 200 NMR spectrometer in $CDCl_3$ using 85% H_3PO_4 (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 $1H^+CF_3SO_3^-$ was performed by Galbraith Laboratories Inc., Knoxville, TN.

Synthesis of $Fe(CO)_3(L\frown L)$

Although complexes **1**,[8] **2**,[8a,9] **3**,[10] **5**,[11] **6**,[12] and **10**[9e,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 ^1H NMR spectroscopies.

Samples for ^1H and $^{31}P\{H\}$ NMR spectra were prepared by dissolving ~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 (~2 x 0.5 cm) directly into an NMR tube to remove paramagnetic impurities. An additional 0.5 mL of $CDCl_3$ for ^1H NMR samples and 2 mL for $^{31}P\{H\}$ 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 (υ(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_2Cl_2 and chromatographed on a column of neutral alumina (15 x 3 cm, ~150 mesh) with a 1:3 mixture of CH_2Cl_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_2Cl_2 and layering with 10 x that volume with hexanes and then cooling to -20 °C for ~24 h afforded orange crystals of 5 (0.63 g, 64%). ^{1}H NMR: δ 7.56-7.40 (m, C_6H_5, C_6H_4). IR(CH_2Cl_2) υ(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 $Fe(CO)_3(L^\frown L)$ 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, $^2J_{PH}$ = 10.8 Hz, CH_2), 7.55 (m, Ph), 7.37 (m, Ph). $^{31}P\{H\}$ NMR: δ 14.87. IR(CH_2Cl_2) υ(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:[9a] δ 2.44 (pseudo-t, J = 17.6 Hz, 4 H), 7.57-7.39 (m, Ph). $^{31}P\{H\}$ NMR:[9a] δ 96.08. IR(CH_2Cl_2) υ(CO), cm^{-1}: 1982 s, 1913 m, 1892 s.

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

Reaction time: 16 h. Yield: 52%. MS (70 eV):[10] 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, $^2J_{HH}$ = $^2J_{PH}$ = 5.2 Hz, 4 H, $P(CH_2)$), 7.31 (m, Ph), 7.45 (m, Ph). $^{31}P\{H\}$ NMR:[10] δ 46.35. IR(CH_2Cl_2) υ(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). ^{1}H NMR: δ 1.73 (br s, 4 H, CH_2), 2.40 (br s, 4 H, $P(CH_2)$), 7.49 (m, Ph), 7.35 (m, Ph). $^{31}P\{H\}$ NMR: δ 57.12. IR(CH_2Cl_2)υ(CO), cm^{-1}: 1981 s, 1908 m, 1879 s.

$Fe(CO)_3$(*cis*-dppv) (6)

Reaction time: 26 h. Yield: 67%. ^{1}H NMR:[12] δ 7.50-7.38 (m, Ph), =CH not identified. IR(CH_2Cl_2) υ(CO), cm^{-1}: 1988 s, 1918 m(sh), 1897 s.

$Fe(CO)_3$(arphos) (7)

Reaction time: 16 h. Yield: 55%. ^{1}H NMR: δ 2.19 (dt, $^2J_{PH}$ = 23.9 Hz, $^2J_{HH}$ = 7.0 Hz, 2 H, $P(CH_2)$), 2.47 (q, $^2J_{HH}$ = $^2J_{PH}$ = 7.0 Hz, 2 H, $As(CH_2)$), 7.56-7.34 (m, Ph). IR(CH_2Cl_2) υ(CO), cm^{-1}: 1982 s, 1910 m, 1890 s.

$Fe(CO)_3$(dmpm) (8)

Reaction time: 16 h. Yield: 53%. ^{1}H NMR (CD_2Cl_2, decomposes in $CDCl_3$): δ 1.63 (t, $^2J_{PH}$ = 5.1 Hz, 12 H, CH_3), 3.23 (t, J_{PH} = 11.0 Hz, 2 H, CH_2). IR(CH_2Cl_2) υ(CO), cm^{-1}: 1975 s, 1899 m(sh), 1884 s.

$Fe(CO)_3$(dcpe) (9)

Reaction time: 16 h. Yield: 20%. ^{1}H NMR: δ 1.24-1.93 (m, Cy and CH_2). IR(CH_2Cl_2) υ(CO), cm^{-1}: 1968 s, 1890 s(sh), 1871 s.

$Fe(CO)_3$(diars) (10)

Reaction time: 20 h. Yield: 38%. ^1H NMR(CD_2Cl_2, decomposes in $CDCl_3$):[13] δ 7.67 (m, 4 H, C_6H_4), 1.67 (s, 12 H, Me). IR(CH_2Cl_2) υ(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_2Cl_2 under N_2. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe. Immediately the color of the solution was bleached 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 $[Fe(H)(CO)_3(L^\frown L)]^+$ 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_2Cl_2 solvent the original color immediately reappeared as did the IR bands corresponding to the unprotonated starting material. Samples for ^1H NMR spectra of **$1H^+$-$10H^+$** were prepared by adding 1 equiv of CF_3SO_3H to solutions of the neutral complexes in $CDCl_3$ which were prepared as described above.

Isolation of $[Fe(H)(CO)_3(dppm)]CF_3SO_3$ ($1H^+CF_3SO_3^-$)

To a stirred solution of 1 (0.18 g, 0.34 mmol) in CH_2Cl_2 (4.0 mL), one equiv of CF_3SO_3H was added. The solution was then layered with Et_2O (15 mL) and cooled slowly to -78 °C. It was stored at that temperature for three days giving pale yellow air-sensitive crystals of $1H^+CF_3SO_3^-$ (0.18 g, 79%). Anal. Calcd for $C_{29}H_{23}F_3FeO_6P_2S$: C, 51.65; H, 3.44. Found: C, 51.44; H, 3.85. ^1H NMR: δ 4.31 (dt, $^2J_{H_bH_c}$ = 16.8 Hz, $^2J_{PH_c}$ = 13.2 Hz, 1 H, H_c), 5.57 (m, 9 lines, $^2J_{PH_b}$ = 10.5 Hz,[15] 1 H, H_b), 7.59 (m, Ph), 7.80 (m, Ph), -6.53 (td, $^2J_{PH}$ = 42.6 Hz, $^4J_{H_aH_b}$ = 3.9 Hz,.1 H, Fe-H, H_a). IR(CH_2Cl_2) υ(CO), cm^{-1}: 2090 s, 1939 s.

[Fe(H)(CO)$_3$(dppe)]CF$_3$SO$_3$ (2H$^+$CF$_3$SO$_3^-$)

^1H NMR: δ 2.68 (m, 2 H, CH_2), 3.46 (m, 2 H, CH_2), 8.0-7.5 (m, Ph), -8.97 (t, $^2J_{PH}$ = 43.9 Hz, 1 H, Fe-H). IR(CH_2Cl_2) υ(CO), cm^{-1}: 2094 s, 2042 s.

[Fe(H)(CO)$_3$(dppp)]CF$_3$SO$_3$ (3H$^+$CF$_3$SO$_3^-$)

^1H NMR: δ 1.83 (br m, 1 H, CH_2), 2.95 (br m, 5 H, CH_2), 7.45 (m, Ph), 7.65 (m, Ph), -7.49 (5, $^2J_{PH}$ = 40.4 Hz, 1 H, Fe-H). IR(CH_2Cl_2) υ(CO), cm^{-1}: 2087 s, 2034 s.

[Fe(H)(CO)$_3$(dppb)]CF$_3$SO$_3$ (4H$^+$CF$_3$SO$_3^-$)

^1H NMR: δ 1.80 (br s, 4 H, CH_2), 2.80 (br s, 4 H, CH_2), 7.9 (m, Ph), -7.55 (5, $^2J_{PH}$ = 45.4 Hz, 1 H, Fe-H). IR(CH_2Cl_2) υ(CO), cm^{-1}: 2091 s, 2033 s.

[Fe(H)(CO)$_3$(dppbz)]CF$_3$SO$_3$ (5H$^+$CF$_3$SO$_3^-$)

^1H NMR: δ 8.0-7.4 (m, Ph), -8.76 (t, $^2J_{PH}$ = 44.3 Hz, 1 H, Fe-H). IR(CH_2Cl_2) υ(CO), cm^{-1}: 2096 s, 2045 s.

[Fe(H)(CO)$_3$(*cis*-dppv)]CF$_3$SO$_3$ (6H$^+$CF$_3$SO$_3^-$)

^{1}H NMR: δ 7.69-7.39 (m, Ph), = CH not identified, -9.50 (t, $^2J_{PH}$ = 45.5 Hz, 1 H, Fe-H). IR(CH$_2$Cl$_2$) υ(CO), cm^{-1}: 2095 s, 2044 s.

[Fe(H)(CO)$_3$(arphos)]CF$_3$SO$_3$ (7H$^+$CF$_3$SO$_3^-$)

^{1}H NMR: δ 2.25 (m, 1 H, CH$_2$), 2.75 (br m, 1 H, CH$_2$), 3.5 (m, 2 H, CH$_2$), 7.4-8.0 (m, Ph), -9.28 (d, $^2J_{PH}$ = 44.4 Hz, 1 H, Fe-H). IR(CH$_2$Cl$_2$) υ(CO), cm^{-1}: 2089 s, 2038 s.

[Fe(H)(CO)$_3$(dmpm)]CF$_3$SO$_3$ (8H$^+$CF$_3$SO$_3^-$)

^{1}H NMR(CD$_2$Cl$_2$): δ 1.95 (t, J_{PH} = 6.5 Hz, 12 H, CH$_3$), 3.59 (m, 9 lines, $^2J_{PH_b}$ = 10.0 Hz,[15] 1 H, H$_b$), 3.82 (q, $^2J_{H_bH_c}$ = $^2J_{PH_c}$ = 14.5 Hz, H$_c$), -7.75 (td, $^2J_{PH}$ = 45.6 Hz, $^4J_{HH}$ = 4.3 Hz, 1 H, Fe-H, H$_a$). IR(CH$_2$Cl$_2$) υ(CO), cm^{-1}: 2087 s, 2031 s.

[Fe(H)(CO)$_3$(dcpe)]CF$_3$SO$_3$ (9H$^+$CF$_3$SO$_3^-$)

^{1}H NMR: δ 1.25-1.95 (br m,Cy and CH$_2$), -9.95 (t, $^2J_{PH}$ = 43.8 Hz, 1 H, Fe-H). IR(CH$_2$Cl$_2$) υ(CO), cm^{-1}: 2079 s, 2023 s.

[Fe(H)(CO)$_3$(diars)]CF$_3$SO$_3$ (10H$^+$CF$_3$SO$_3^-$)

^{1}H NMR (CD$_2$Cl$_2$): δ 2.00 (s, 6 H, CH$_3$), 2.07 (s, 6 H, CH$_3$), 8.0-7.8 (m, 4 H, Ph), -10.64 (s, 1 H, Fe-H). IR(CH$_2$Cl$_2$) υ(CO), cm^{-1}: 2089 s, 2034 s.

Calorimetry Studies

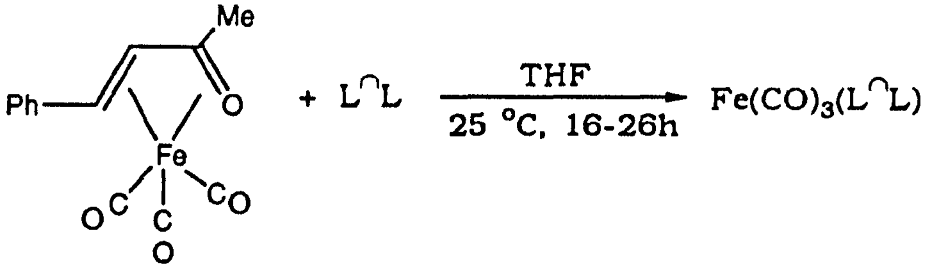
Determinations of the heats of protonation of the Fe(CO)$_3$(L$^\frown$L) compounds were performed using a Tronac Model 458 isoperibol calorimeter as previously described.[4,5] Typically a run consisted of three sections:[16] initial heat capacity calibration, titration (at 25.0 °C), and final heat capacity 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_3SO_3H solution in 1,2-dichloroethane (DCE) at a constant rate during 3 minutes time to 50 mL of a 2.6 mM solution of $Fe(CO)_3(L^\frown L)$ (10% excess) in DCE. The $Fe(CO)_3(L^\frown L)$ 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})[5] 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 $Fe(CO)_3(L^\frown L)$

Complexes **1-10**, in this study are prepared from $Fe(CO)_3(bda)$[14a] (bda = benzylideneacetone) in yields ranging from 20% for **9** to 81% for **1** (eq 4). This method is of general use for the synthesis of $Fe(CO)_3(L^\frown L)$ complexes.[17,18] Complexes **1-10** should be stored under N_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_2 or Ar.



(2)

The observation of three ν(CO) bands in the solution infrared spectra (CH_2Cl_2) of **1-10** is consistent with these complexes having approximately trigonal bipyramidal structures[19] with a ligand donor coordinated in axial and equatorial sites. The structures of **1**,[8b] **2**,[9c] **5**,[11] and **10**[13] determined by X-ray crystallography have been described as having distorted trigonal bipyramidal or square pyramidal geometries.

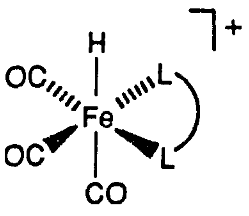
Singlet resonances in the $^{31}P\{H\}$ NMR spectra of **1-4** and **5**[11] at room temperature indicate that the PPh_2 groups in these molecules are equivalent. This is probably due to the fluxionality[10] of the $Fe(CO)_3(L^\frown L)$ molecules ($L^\frown L$ = bidentate phosphine). This has been studied in detail previously[10] and is probably accomplished by relatively slight twists and bends of the M-L groups.[8b,9c,10] The ^{31}P chemical shift of the $^{31}P\{H\}$ NMR resonances in $Fe(CO)_3(L^\frown L)$ depends on the size of the $L^\frown L$ chelate ring.[20]

Protonation reactions of $Fe(CO)_3(L^\frown L)$

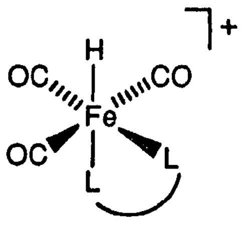
Bidentate complexes **1-10** were protonated with 1 equiv of CF_3SO_3H in CH_2Cl_2 solution as shown in eq 1. Only the protonation of **10** has been described previously and then only as a personal communication to the authors in reference 21. These reactions occur immediately as indicated by the bleaching of the solution color, the disappearance of the starting complex ν(CO) bands and the appearance of new ν(CO) bands at higher frequency than those of the corresponding neutral starting complexes. These shifts in the ν(CO) bands are characteristic of protonation at the metal.[22]

Solutions of $1H^+$-$10H^+$ are stable as long as they are kept under a nitrogen or argon atmosphere. Complex $1H^+CF_3SO_3^-$ 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 **$2H^+$-$10H^+$**; they were characterized by their IR and NMR spectra.

The two possible geometries for the protonated products are the *fac* (C) and *mer* (D) isomers.



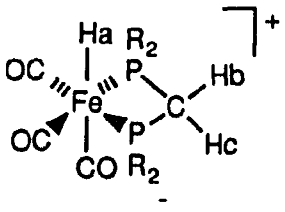
C



D

Infrared spectra of $1H^+$-$10H^+$ show two strong bands in the υ(CO) region suggesting that these complexes have the *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 *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 *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 υ(CO) absorption at high frequency for the symmetrical stretching vibrational mode. The absence of this weak band indicates these $[Fe(H)(CO)(L^\frown L)]^+$ complexes do not have structure **D**.

The ^1H NMR spectra of $\mathbf{1H^+}$-$\mathbf{10H^+}$ 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 $\mathbf{1H^+}$, $\mathbf{6H^+}$, $\mathbf{8H^+}$, and $\mathbf{9H^+}$, supports the assignment of *fac* (**C**) geometry for these complexes. For complexes $\mathbf{1H^+}$ and $\mathbf{8H^+}$ 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 $\mathbf{1H^+}$ reduced the Fe-H triplet of doublets resonance at -6.53 ppm to a triplet. Similarly for $\mathbf{8H^+}$, 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 ($^4J_{HH}$ = 3.9 Hz) or dmpm ($^4J_{HH}$ = 4.3 Hz) ligand (see structure **E**). The complexes $Re(H)(CO)_3(dppm)$[24b], and $(C_5Me_5)Ru(H)(dppm)$[3c] were also



E

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 (ΔH_{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 ΔH_{HM} values is probably within the experimental error.

Because DCE has a low dielectric constant (ε = 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 ΔH_{HP} value. Presumably these reactions also contribute negligibly to ΔH_{HM} values in the current study.

Also listed in Table I are the heats of protonation, ΔH_{HP1} and ΔH_{HP2}, for the free bidentate ligands[4b,30] determined under the same conditions (25.0 °C, in DCE solution) with 1 and 2 equiv of CF_3SO_3H. The ΔH_{HP1} and ΔH_{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 ΔH_{HP1} and ΔH_{HP2}. When this difference is small as for dppb, both

$$\mathrm{P}^{\frown}\mathrm{P} + \mathrm{CF_3SO_3H} \xrightarrow[25.0\ ^{\circ}\mathrm{C}]{\mathrm{DCE}} \mathrm{HP}^{\frown}\mathrm{P^{+}CF_3SO_3^{-}} \tag{3}$$

$$\mathrm{HP}^{\frown}\mathrm{P^{+}CF_3SO_3^{-}} + \mathrm{CF_3SO_3H} \xrightarrow[25.0\ ^{\circ}\mathrm{C}]{\mathrm{DCE}} \mathrm{HP}^{\frown}\mathrm{PH^{2+}(CF_3SO_3^{-})_2} \tag{4}$$

reaction 3 and 4 occur simultaneously, as discussed previously, and have essentially the same values of ΔH_{HP1} and ΔH_{HP2}.

Table I. Heats of protonation (ΔH_{HM}) of $Fe(CO)_3(L^\frown L)$ and $Fe(CO)_3(L)_2$ complexes and the uncoordinated phosphines[a]

$Fe(CO)_3(L^\frown L)$,[b] $Fe(CO)_3(L)_2$	$-\Delta H_{HM}$, kcal mol^{-1}	chelate ring size	$-\Delta H_{HP1}$,[c] kcal mol^{-1}	ΔH_{HP2},[d] kcal mol^{-1}
$Fe(CO)_3$(dppm) **1**	24.0 (±0.2)[e]	4	22.0 (±0.1)	14.9 (±0.2)
$Fe(CO)_3$(dppe) **2**	23.2 (±0.1)	5	22.8 (±0.2)	20.2 (±0.1)
$Fe(CO)_3$(dppm) **3**	21.1 (±0.2)	6	23.4 (±0.1)	22.4 (±0.3)
$Fe(CO)_3$(dppb) **4**	20.1 (±0.2)	7	24.6 (±0.1)	23.8 (±0.2)
$Fe(CO)_3$(dppbz) **5**	23.4 (±0.2)	5	21.3 (±0.1)	10.7 (±0.3)
$Fe(CO)_3$(*cis*-dppv) **6**	23.1 (±0.3)	5	19.9 (±0.3)	10.0 (±0.2)
$Fe(CO)_3$(arphos) **7**	22.6 (±0.1)	5	23.2 (±0.4)	8.3 (±0.1)
$Fe(CO)_3$(dmpm) **8**	30.2 (±0.4)	4	31.0 (±0.3)	25.8 (±0.2)
$Fe(CO)_3$(dcpe) **9**	28.4 (±0.2)	5		
$Fe(CO)_3$(diars) **10**	26.5 (±0.3)	5		
$Fe(CO)_3(PPh_2Me)_2$	17.6 (±0.3)[f]		24.7 (±0.0)[g]	
$Fe(CO)_3(PMe_3)_2$	23.3 (±0.3)[f]		31.6 (±0.2)[g]	

[a] For protonation with CF_3SO_3H (0.1M) in DCE solvent at 25.0 °C.

[b] Ligand abbreviations: $Ph_2P(CH_2)PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2P(1,2\text{-}C_6H_4)PPh_2$ (dppbz), *cis*-$Ph_2P(CH{=}CH)PPh_2$ (*cis*-dppv), $Ph_2P(CH_2)_2AsPh_2$ (arphos), $Me_2P(CH_2)PMe_2$ (dmpm), $(Cy)_2P(CH_2)_2P(Cy)_2$ (dcpe), $Me_2As(1,2\text{-}C_6H_4)AsMe_2$ (diars).

[c] Represents the addition of 1 equiv of CF_3SO_3H to 1 equiv of the free phosphine, see ref 4b.

[d] Represents the addition of a second equiv of CF_3SO_3H to 1 equiv of the free phosphine, see ref 4b.

[e] Numbers in parentheses are average deviations.

[f] Ref 31.

[g] ΔH_{HP}, ref 4a.

DISCUSSION

Dependence of ΔH_{HM} on Chelate Size in $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$

A series of protonation reactions (eq 1) of the $Fe(CO)_3$-$[Ph_2P(CH_2)_nPPh_2]$, **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 (ΔH_{HM} = -24.0 kcal mol^{-1}) for the smallest chelate (n = 1) and smallest for the largest chelate (n = 4, ΔH_{HM} = -20.1 kcal mol^{-1}); in terms of equilibrium constants K for protonation, assuming $\Delta S°$ 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 ΔH_{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 $Ph_2P(CH_2)_nPPh_2$ 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 $Ph_2P(CH_2)_nPPh_2$[4b,30] from -22.0 kcal mol^{-1} (ΔH_{HP1}, 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

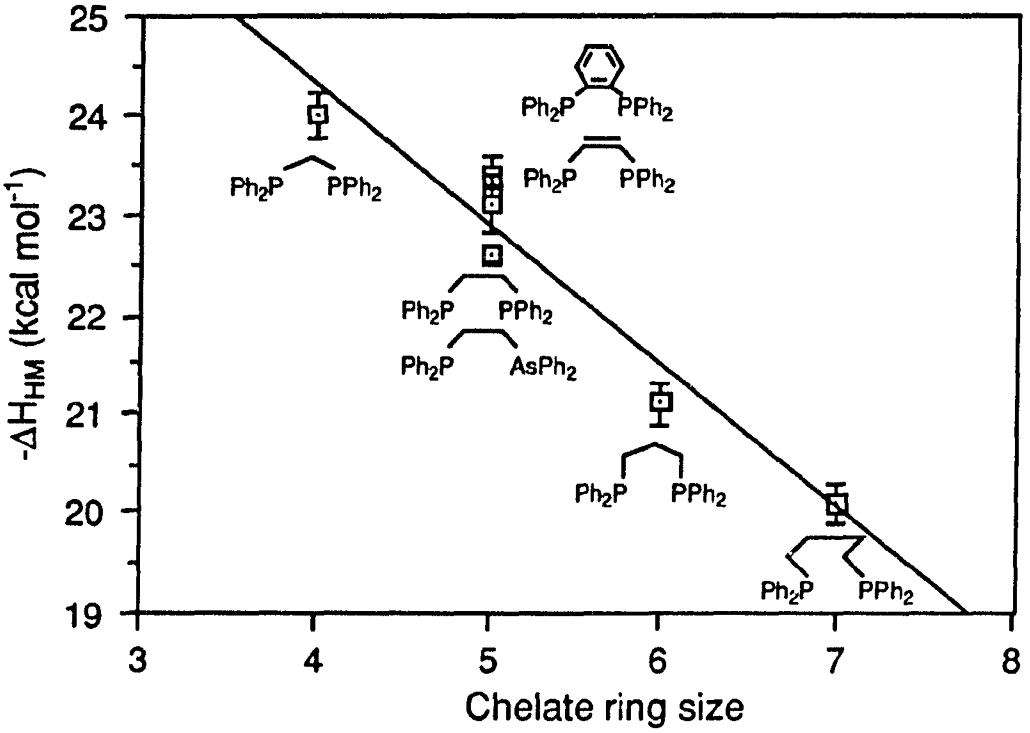
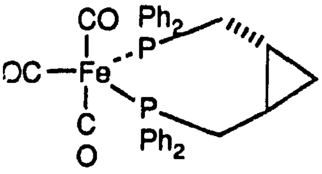
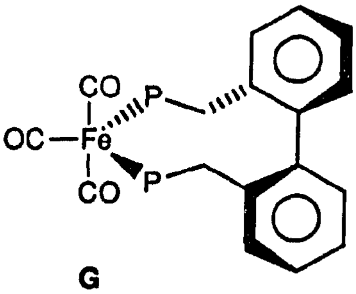


Figure 1. Effect of chelate ring size on the basicity (ΔH_{HM}) of the iron center in the $Fe(CO)_3(L^\frown L)$ complexes

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 $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes. The structure adopted and predicted by theoretical calculations[32] by all $Fe(CO)_3(PR_3)_2$ 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 $Fe(CO)_3(P^\frown P)$ complexes change substantially depending on the chelate ring size. Thus, the P-Fe-P angle in **1**[8b] (chelate ring size = 4) is only 73.5° as compared with 84.1° in the dppe complex (**2**)[9c] (chelate ring size = 5). For $Fe(CO)_3$[trans-1,2-bis((diphenylphosphino)methyl)cyclopropane] (F),[17] 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)[17] 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 °.



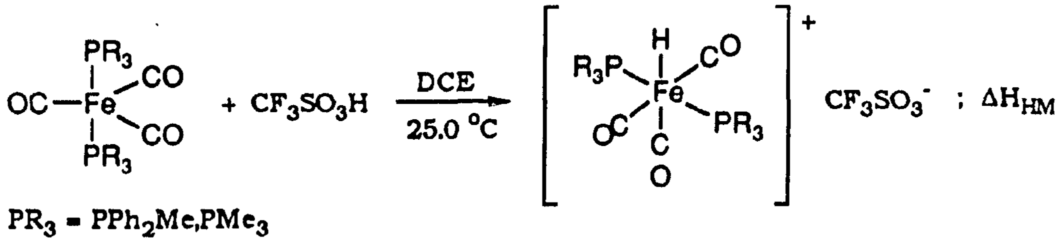
F



G

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 $Fe(CO)_3(PPh_2Me)_2$ will be less basic than any of the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes. This is indeed true as ΔH_{HM} for this complex (Table I) is only -17.6 kcal mol^{-1}. This value for $Fe(CO)_3(PPh_2Me)_3$ compares with -20.1 kcal mol^{-1} for **4**, which has the largest chelating ligand. (It should be noted that both the PPh_2Me and dppb ligands have the about same basicity, $\Delta H_{HP} = -24.7$ 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 $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ and $Fe(CO)_3[PPh_2Me]_2$ reactants. However, it is possible that there are differences in energy in the protonated products especially since the $\{Fe(H)(CO)_3[Ph_2P(CH_2)_nPPh_2]\}^+$ (eq 1) complexes have a *fac* geometry and $[Fe(CO)_3(PPh_2Me)_2]^+$ has a *mer* structure (eq 5).[31]



(5)

The *mer* structure is presumably more stable than the *fac* since $[Fe(CO)_3(PPh_2Me)_2]^+$ with the unconstraining monodentate ligands adopts this geometry. The *fac* geometry of the chelate complexes $\{Fe(H)(CO)_3[Ph_2P(CH_2)_nPPh_2]\}^+$ would then be of higher energy. Thus, if the relative basicities (ΔH_{HM}) of the $Fe(CO)_3(PPh_2Me)_2$ and $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes were determined by the energies of the protonated products, $Fe(CO)_3(PPh_2Me)_2$ 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 $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes more basic than $Fe(CO)_3(PPh_2Me)_2$.

These large chelate effects on metal complex basicity are illustrated by the equilibrium in eq 6. The difference between ΔH_{HM} values for $Fe(CO)_3(PPh_2Me)_2$ and 1 gives a ΔH value of -6.4 kcal mol^{-1}

$$[Fe(H)(CO)_3(PPh_2Me)_2]^+ + Fe(CO)_3(dppm) \rightleftharpoons Fe(CO)_3(PPh_2Me)_2 + [Fe(H)(CO)_3(dppm)]^+ \quad (6)$$

for this reaction. Assuming ΔS = 0 e.u., the equilibrium constant for eq 6 is 4.9 x 10^4. A very similar enhancement (-6.9 kcal mol^{-1}) in metal basicity is seen in the comparison of ΔH_{HM} values (Table I) for the chelate complex $Fe(CO)_3(dmpm)$ (**8**) (-30.2 kcal mol^{-1}) and the monodentate analog $Fe(CO)_3(PMe_3)_2$ (-23.3 kcal mol^{-1}).

Effects on ΔH_{HM} of Other Bidentate Ligands in $Fe(CO)_3(L^\frown L)$

The basicities of the free bidentate ligands[4b,30] in complexes **5-7** are somewhat weaker donor ligands than dppe, as measured by their ΔH_{HP} values(Table I). This results from the relatively electron-withdrawing bridging groups, 1,2-C_6H_4 in dppbz and *cis*-CH=CH in *cis*-dppv, and the poorer donor ability of the $AsPh_2$ group in arphos. Despite the weaker donating abilities of these ligands, complexes **5-7** have ΔH_{HM} 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 ΔH_{HP} values, it is the chelate ring size which is the most important factor controlling the ΔH_{HM} 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 **2**[9c] and **5**[11] 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 ΔH_{HM} values of the $Fe(CO)_3(L^\frown L)$ 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,

$$[\mathrm{Fe(H)(CO)_3(dppm)}]^+ + \mathrm{Fe(CO)_3(dmpm)} \rightleftharpoons \mathrm{Fe(CO)_3(dppm)} + [\mathrm{Fe(H)(CO)_3(dmpm)}]^+ \quad (7)$$

compound **8** is 3.5 x 10^4 times more basic than 1 (assuming $\Delta S° = 0$ e.u.). Similarly, the cyclohexyl groups in dcpe make $Fe(CO)_3(dcpe)$ (**9**) 5.2 kcal mol^{-1} more basic than $Fe(CO)_3(dppe)$ (**2**). Jia and Morris[3c] recently reported a similar trend as pK_a values of $[CpRuH_2(R_2P(CH_2)_2PR_2)]BF_4$ complexes (R = *p*-$CF_3C_6H_4$, Ph, *p*-$MeOC_6H_4$, Me) increase with increasing σ-donor ability of the chelate. The weaker basicity (-26.5 kcal mol^{-1}) of $Fe(CO)_3(diars)$ (**10**) as compared with $Fe(CO)_3(dcpe)$ (-28.4 kcal mol^{-1}) is presumably due to the weaker donor ability of arsines as compared to that of arsines.[33]

CONCLUSION

The most important result of these studies is the observation that chelating ligands increase the basicity (ΔH_{HM}) of the metal in the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes by 3.5-6.4 kcal mol^{-1} as compared to the analogous monodentate complex $Fe(CO)_3(PPh_2Me)_2$. That these are substantial changes in basicity is illustrated by the factor of 4.9×10^4 difference in basicities of $Fe(CO)_3(dppm)$ and $Fe(CO)_3(PPh_2Me)_2$. A chelate-imposed distortion of the complexes from the most stable diaxial geometry of $Fe(CO)_3(PPh_2Me)_2$ 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 C_5H_5 ligand in $(C_5H_5)Ir(1,5\text{-}COD)$ with C_5Me_5 increases the iridium basicity by -5.7 kcal mol^{-1}. Systematic substitution of the methyl groups in Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, 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 (ΔH_{HP}) in $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes results in a linear increase in the basicity of the iridium or iron metal center (ΔH_{HM}). This quantitative trend has not been previously demonstrated. Also, linear correlations between ΔH_{HM} and the respective CO stretching frequencies of the iridium and iron complexes are obtained.

In the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ (n=1-4) complexes the basicity (ΔH_{HM}) of the iron center increases as chelate size decreases. This trend is opposite the trend in free bidentate phosphine basicities, as determined by ΔH_{HP}, which increase with chelate size. However, the chelate complexes are more basic than their respective non-chelate derivatives $Fe(CO)_3(PR_3)_2$. The effects of chelate size on metal basicity are ascribed to the distortion the chelate imposes on the $Fe(CO)_3(L^{\frown}L)$ complex.

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