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Basicities, nucleophilicities, and bond dissociation enthalpies of organometallic complexes

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Basicities, nucleophilicities, and bond dissociation enthalpies of organometallic complexes

By

Dongmei Wang

A Dissertation Submitted to the
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To my parents, Jun, and son

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GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains three papers in the format required for journal publication, describing the research I performed at Iowa State University. Preceding these papers is a literature review of metal-hydrogen bond dissociation enthalpies of organometallic complexes. In the literature review as well as the papers, the literature citations, tables, figures, and schemes pertain only to the chapters in which they appear. After the final paper is a general summary.

Abbreviations

Cp, η^5-C_5H_5 ligand
Cp*, η^5-C_5Me_5 ligand
Cp', substituted cyclopentadienyl ligand
Cy, cyclohexyl group
COD, cyclooctadiene ligand
dppm, $Ph_2PCH_2PPh_2$
dppe, $Ph_2P(CH_2)_2PPh_2$
dppp, $Ph_2P(CH_2)_3PPh_2$
dmpm, $Me_2PCH_2PMe_2$
dmpe, $Me_2P(CH_2)_2PMe_2$
arphos, $Ph_2P(CH_2)_2AsPh_2$
triphos, $Ph_2P(CH_2CH_2PPh_2)_2$
tripod, $MeC(CH_2PPh_2)_3$

METAL-HYDROGEN BOND DISSOCIATION ENTHALPIES OF ORGANOMETALLIC COMPLEXES

Introduction

The field of organometallic thermochemistry has gained recognition as one of great relevance to catalysis.[1] A knowledge of metal-hydrogen bond enthalpies is essential for an understanding of catalytic reaction mechanisms, which often involve the cleavage and formation of M-H bonds, and their chemistry continues to be vigorously explored.[2]

The aim of this review is to summarize the presently available information relating to transition metal hydrogen bond dissociation enthalpies (BDE). Other metal-ligand bond energies, such as metal-alkyl,[3] metal-olefin,[3] metal-carbonyl,[4] metal-cyclopentadienyl,[5] metal-boron,[6] and metal-metal[7] bond energies, are not included in this review.

The present survey covers the literature through the end of 1993, with some references from 1994.

Bond Dissociation Enthalpy Values

Diatomic Hydrides

The simplest systems with metal-hydrogen bonds are the diatomic MH molecules. These are transient species, formed in the gas phase and studied spectroscopically. Earlier studies show that average E-H bond energies, such as those tabulated by Pauling,[8] are large when E is an electronegative element and small when E is of low electronegativity. However, the situation for transition-metal-hydrides is not that simple.

The available BDE data for M-H and M^+-H, limited mainly to the first and second rows, are presented in Table 1. Most values are the results of guided ion beam experiments performed by Armentrout and co-workers.[9,10] The results were derived mainly from the determination of thresholds for reactions 1 and 2, respectively, where RH is a hydrocarbon for which ΔH_f^0 (R^+, g) is well established. The maximum M^+-H bond dissociation enthalpy (BDE)

$$M^+ + RH \longrightarrow MH + R^+, \quad \text{BDE (M-H)} \tag{1}$$

$$M^+ + H_2 \longrightarrow MH^+ + H, \quad \text{BDE (M}^+\text{-H)} \tag{2}$$

of first and second row transition metals is about 58 kcal/mol. One useful way of thinking about this maximum is that it may represent any metal-hydride BDE once an orbital on the metal has been prepared for efficient bonding. Generalized valence bond plus configuration interaction calculations have also been used to estimate the BDEs of the monopositive diatomic metal hydride ions of the second-row transition-metal series.[11] There are substantial variations from one metal to the next, which do not follow simple trends. Some of the variations are easy to understand. They arise from the requirement of a promotion energy from the ground state of the atom to the reactive valence state. More recently, Siegbahn has reported a study of diatomic M-H bond dissociation enthalpies of second row transition metals (Figure 1).[14] The M-H BDE values fall in the range of 40-70 kcal/mol.

Table 1. The Bond Dissociation Enthalpy of Diatomic Hydrides M-H (kcal/mol)

		M-H			M^+-H		
	M	a	b	c	d	e	f
Sc	d^1s^2	48±2			55±2	55.2	56±2
Ti	d^2s^2	47±3			55±2	54.0	54±3
V	d^3s^2	41±4		41±4	47±2	43.6	48±2
Cr	d^5s^1	41±3			28±2	24.3	33±2
Mn	d^5s^2	30±4			47±3	39.6	48±3
Fe	d^6s^2	46±3	43±6	46±3	47±4	47.0	50±2
Co	d^7s^2	46±2	54±10	47±3	46±2	43.6	47±2
Ni	d^8s^2	58±3	65±6	59±4	39±2	35.7	40±2
Cu	$d^{10}s^1$	61±4		60±5	22±2	20.9	22±3
Y	d^1s^2				58±3	57.8	59±3
Zr	d^2s^2				54±3	54.6	55±3
Nb	d^4s^1				53±3	48.7	54±3
Mo	d^5s^1	50±4	46±3	53±5	41±3	31.2	42±3
Tc	d^5s^2					46.3	
Ru	d^7s^1	56±5	56±5			31.7	41±3
Rh	d^8s^1	59±5	59±5			34.8	36±3
Pd	$d^{10}s^0$	56±6	56±6		53±3	40.6	47±3
Ag	$d^{10}s^1$	51±2			15±3	2.1	16±3
Hf	d^2s^2						
Ta	d^3s^2						
W	d^4s^2						
Re	d^5s^2						

Table 1. Cont'd

Os	d^6s^2	
Ir	d^7s^2	
Pt	d^9s^1	84±9
Au	$d^{10}s^1$	70±2

[a] Reference 12. [b] Reference 13. [c,f] Reference 10. [d] Reference 9. [e] Reference 11.

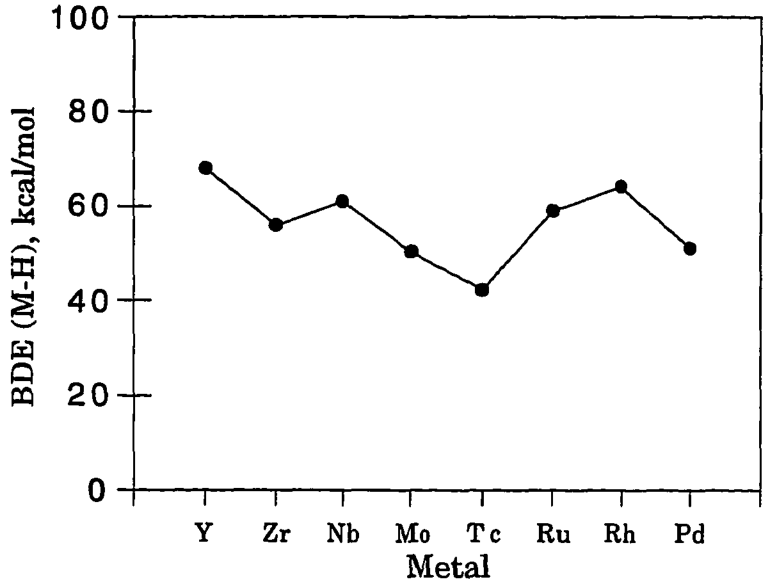

Figure 1. The bond dissociation enthalpies of diatomic M-H as a function of metal[14]

Group 3

The available bond enthalpy data for group 3 organometallic complexes containing metal-hydrogen bonds are still very few (Table 2). A large number of thermochemical studies on thorium and uranium complexes have been reported by the group of T. Marks.[16, 17] The technique used was either titration or batch reaction calorimetry, and the experimental procedure involved the measurement of enthalpies of alcoholysis of the complexes in toluene. The BDE values were calculated from the reaction enthalpies by assuming that the solvation enthalpies cancel and data rely on known M-O bond strength. Drago[18] claimed that solution bond dissociation energies are relatively free of solvation energies. Molecular orbital calculations based on density-functional

Table 2. Group 3 M-H Bond Dissociation Enthalpy

molecule	BDE, kcal/mol	Method/Ref.[a]
Cp_2ScH	50.0	TC/15
Cp_2YH	67.0	TC/15
Cp_2LaH	63.2	TC/15
$Cp^*_2Th(OR)H$		
R= $CH(t\text{-}Bu)_2$	93.1±1.4	RSC/16
R= $2,6\text{-}(t\text{-}Bu)_2C_6H_3$	91.9±1.4	RSC/16
$[Cp^*_2ThH_2]_2$	93.3±2	RSC/17
$Cp^*_2Th(Me_3CO)H$	93.1	TC/18
$Cp^*_2U[OSi(t\text{-}Bu)Me_2]H$	81.8±1.2	RSC/16
$[Cp^*_2SmH]_2$	55.0	TC/18
	54.6±2.0	RSC/19

[a] Key: RSC = reaction solution calorimetry, TC = theoretical calculations

theory were used to obtain the M-H BDEs in Cp_2MH (M = Sc, Y, La) complexes which increase in the order: Sc-H (50.0 kcal/mol) < Y-H (67.0) < La-H (68.2).[15]

Group 4

Most data for zirconium-hydrogen and hafnium-hydrogen bond dissociation enthalpies were reported by Schock and Marks (Table 3).[20] A series of values of zirconium-hydrogen BDEs in $Cp^*_2ZrH_2$ and $Cp^*_2Zr(OR)H$ were calculated from the enthalpies of reactions of the complexes with C_6F_5OH which yielded $Cp^*_2Zr(L)(OC_6F_5)$ and H_2; the calculated values were based on $D(Zr\text{-}OC_6F_5) = 92.6 \pm 2.4$ kcal/mol.

Although it is not straightforward to draw conclusions from these data, the values seem to indicate that the Zr-H BDEs in $Cp^*_2Zr(L)H$ complexes are

Table 3 Group 4 M-H Bond Dissociation Enthalpy

molecule	BDE, kcal/mol	Method/Ref.[a]
$Cp^*_2ZrH_2$	78.0±1.9 83.7	RSC/20 TC/18
$Cp^*_2Zr(OPh)H$	89.0±2.2	RSC/20
$Cp^*_2Zr(OC_6F_5)H$	85.4±2.4	RSC/20
$Cp^*_2Zr(OCH_2CF_3)H$	83.0±1.9	RSC/20
$Cp^*_2Zr(OBu\text{-}t)H$	83.2±3.1	RSC/20
$Cp^*_2Zr(Ph)H$	78.7±1.7	RSC/20
Cp_2ZrClH	93.3	RSC/21
$Cp^*_2HfH_2$	82.8±1.6	RSC/20
$Cp^*_2Hf(Ph)H$	83.7±2.6	RSC/20

[a] Key: RSC = reaction solution calorimetry, TC = theoretical calculations

higher for L = alkoxy (83-89 kcal/mol) than for L = H (78) or Ph (79), probably due to the tendency of hard alkoxide ligands to stabilize high metal oxidation states.[20] The results also show that Hf-H (83 kcal/mol) is stronger than Zr-H (78) in $Cp^*{}_2MH_2$ complexes.[20]

Groups 5 and 6

The available bond enthalpy data for group 5 organometallic complexes containing metal-hydrogen bonds are still very few. The bond energy of diatomic VH^+ is found to be 50 kcal/mol using a new type of guided-ion-beam mass spectrometer.[9] The V-H BDE value in Cp_2VH has been reported as 48.3 kcal/mol.[15] Relative strengths of early transition metal-hydrogen bonds in substituted niobocenes and tantalocenes (Cp_2MHL, M = Nb, Ta; L = H_2, CO, C_2H_4) has been studied by the use of valence ultraviolet photoelectron spectroscopy in the group of Lichtenberger; the M-H BDE values decrease in the order: $Cp_2MH_3 > Cp_2M(C_2H_4)H > Cp_2M(CO)H$.[22]

The available thermochemical data for group 6 metal-hydrogen bonds are presented in Table 4. In addition to the reaction solution calorimetry technique used to derive the BDE data, the thermochemical cycle in Scheme 1

Scheme 1 Themochemical Cycle for M-H BDE Determination in Solution

$$L_nM\text{-}H_{(sol)} \rightleftharpoons L_nM^-{}_{(sol)} + H^+{}_{(sol)} \qquad \text{(i)}$$

$$L_nM^-{}_{(sol)} \rightleftharpoons L_nM\cdot_{(sol)} + e^- \qquad \text{(ii)}$$

$$H^+{}_{(sol)} + e^- \rightleftharpoons 0.5\,H_{2(g)} \qquad \text{(iii)}$$

$$0.5\,H_{2(g)} \rightleftharpoons H\cdot_{(g)} \qquad \text{(iv)}$$

$$H\cdot_{(g)} \rightleftharpoons H\cdot_{(sol)} \qquad \text{(v)}$$

$$L_nM\text{-}H_{(sol)} \rightleftharpoons L_nM\cdot_{(sol)} + H\cdot_{(sol)} \quad \Delta G^\circ = \text{Bond Dissociation Free Energy}$$

began to be used to estimate metal-hydrogen bond dissociation enthalpies in acetonitrile solution by Tilset and Parker.[28] Such cycles are particularly useful when transient species, for which thermochemical data cannot be obtained by more direct methods, are involved.

The bond dissociation free energy is easily converted to a bond dissociation enthalpy by assuming that $S°(M\text{-}H) \approx S°(M\cdot)$ and that ΔS for $M\text{-}H \rightarrow M\cdot + H\cdot$ is therefore equal to $S°(H\cdot)$ in acetonitrile. However, $S°(H\cdot)$ in acetonitrile equals the entropy changes in steps iv and v of Scheme 1, so only the enthalpy changes for step iv and v affect the bond dissociation enthalpies. The eventual expression for the M-H bond dissociation enthalpy is eq 3.

$$\text{BDE (in kcal/mol)} = 1.37\ pK_a + 23.06\ E°_{ox}(M^-) + 59.5 \qquad (3)$$

The results show that M-H BDE values in $CpM(CO)_3H$ complexes increases as follows: Cr-H (61.5 kcal/mol)[26] < Mo-H (69.2)[33] < W-H (72.3)[33]. The order of bond strength in $LM(CO)_3H$ (L = Cp or Cp*, Tp, Tp'; M = Mo, W) decreases as Cp or Cp* > Tp > Tp', due to the steric effect.[36,37] The BDE values for the 17-e cationic hydrides are reported to be 8-10 kcal lower than those of the neutral complexes in $LM(CO)_2L'H$ (L = Cp, Cp*, Tp, Tp*; M= Cr, Mo, W; L' = CO, PPh_3, PEt_3, $P(OMe)_3$).[28,37]

Table 4 Group 6 M-H Bond Dissociation Enthalpy

molecule	BDE, kcal/mol	Method/Ref.[a]
$HCr(CO)_6^+$	55.0±2.4	ICRS/12
$HCpCr(CO)_2(NO)^+$	49.5±3.3	ICRS/12
$CpCr(CO)_3(Me)(H)^+$	58.4±5.3	ICRS/12
$Cr(CO)_3(Bz)(H)^+$	52.9±3.6	ICRS/12
$CpCr(CO)_3H$	61.7±0.7	CMC, ES/23a
	61.5±0.2	RSC/26, 27
$Cp^*Cr(CO)_3H$	62.3±0.2	RSC/26
$Cp^*Cr(CO)_3H^{+\cdot}$	54.3±1	TCC/28
$CpCr(CO)_2(PPh_3)H$	59.8	RSC/26
$CpCr(CO)_2(PPh_3)H^{+\cdot}$	49.8	TCC/28
$CpCr(CO)_2PEt_3H$	59.9	RSC/26
$CpCr(CO)_2PEt_3H^{+\cdot}$	50.9	TCC/28
$CpCr(CO)_2P(OMe)_3H$	62.7	RSC/26
$CpCr(CO)_2P(OMe)_3H^{+\cdot}$	51.7	TCC/28
$HMo(CO)_6^+$	62.2±2	ICRS/12
Cp_2MoH_2	61.5±2	RSC/29, 30
	60	41
$CpMo(CO)_3H$	65, 66	RSC/23a,c, 31
	67.5±1.4	RSC/23b
	69.2	TCC/33, 34
	≤65	RSC/35
$Cp^*Mo(CO)_3H$	68.5	TCC/33, 36
	69	25
	65.7	TC/18
$TpMo(CO)_3H$	62.2	TCC/37

Table 4. Cont'd

	63.0±1.0	TCC/36
$TpMo(CO)_3H^{+\cdot}$	55.5	TCC/37
$Tp'Mo(CO)_3H$	59.3 60.0±1.0	TCC/37 TCC/36
$Tp'Mo(CO)_3H^{+\cdot}$	53.3	TCC/37
$HW(CO)_6^+$	61.5±2	ICRS/12
Cp_2WH_2	74.4±0.9 72 73	RSC/29, 30 TCC/32, 38 41
$Cp_2W(I)H$	65.3±1	RSC/29, 30
$CpW(CO)_3H$	81.1±1.2 72.3 73 72.5	RSC/23a,39 TCC/33 25 34
$CpW(CO)_2(PMe_3)H$	69.6	TCC/33
$CpW(CO)_2(PMe_3)(H)_2^+$	>76.1	TCC/40
$TpW(CO)_3H$	65.8	TCC/37
$TpW(CO)_3H^{+\cdot}$	57.9	TCC/37
$Tp'W(CO)_3H$	62.2	TCC/37
$Tp'W(CO)_3H^{+\cdot}$	55.3	TCC/37

[a] Key: CMC = Calvet microcalorimetry, ES = equilibrium studies in solution, ICRS = ion cyclotron resonance spectroscopy, RSC = reaction solution calorimetry, TC = theoretical calculations, TCC = thermochemical cycle.

Group 7

The bond dissociation enthalpies of manganese-hydrogen bonds have been studied by several research groups. The Mn-H BDE value of $Mn(CO)_5H_2^+$

Table 5. Group 7 M-H Bond Dissociation Enthalpy

molecule	BDE, kcal/mol	Method/Ref.[a]
$Mn(CO)_5H$	68.0	TCC/25, 33
	68.9	DF/42
	57.4	TC/18
	58.6±2.4	CMC/24
	63	43
	≤65	RSC/41
$Mn(CO)_5H_2^+$	83.5±2.6	EG/12
$HMn(CO)_5(Me)^+$	63.9±2.6	ICRS/12
$HMn(CO)_5(MeC_5H_4)^+$	67.7±3.1	ICRS/12
$HMn_2(CO)_{10}^+$	48.8±3.1	ICRS/12
$Mn(CO)_4(PPh_3)H$	68.4	TCC/25, 33
$Mn(CO)_4(PEtPh_2)H$	71	44
Cp_2Mn-H	50.2	TC/15
Cp_2Tc-H	59.1	TC/15
Cp_2Re-H	59.8	TC/15
$Re(CO)_5H$	74.7	TCC/25, 33
$HRe(CO)_5Me^+$	70.3±3.1	ICRS/12
$HRe_2(CO)_{10}^+$	58.9±2	ICRS/12

[a] Key: CMC = Calvet microcalorimetry, DF = density functional study, EG = equilibrium studies in gas phase, ES = equilibrium studies in solution, ICRS = ion cyclotron resonance spectroscopy, RSC = reaction solution calorimetry, TC = theoretical calculations, TCC = thermochemical cycle.

in the gas phase was reported as 83.5 kcal/mol,[12] which is higher than M-H bonds in other manganese hydrides (Table 5). Only a few rhenium-hydrogen complexes have been studied; they give an average value of 70 kcal/mol.[12,25,33] The M-H BDE is larger for Re than Mn in the following three types of complexes: $M(CO)_5H$ (Re-H, 74.7 kcal/mol > Mn-H, 68.0),[33] $HM(CO)_5Me^+$ (Re-H 70.3 > Mn-H, 63.9),[12] and $HM_2(CO)_{10}^+$ (Re-H 58.9 > Mn-H, 48.8).[12] The M-H BDE in Cp_2MH complexes decreases in the order: Re-H (59.8) > Tc-H (59.1) > Mn-H (50.2).[15]

Group 8

The metal-hydrogen bond dissociation enthalpies of group 8 metals are presented in Table 6. Several experimental techniques were used to derive these data. The bond dissociation enthalpies for the cationic dihydrides were estimated by the group of Morris employing a thermochemical cycle (eq 4).[45]

$$\mathrm{BDE}\ [MH(H_2)^+] = 1.37\, pK_a + 23.06\, E^\circ(MH_2^+/MH_2) + 66 \qquad (4)$$

$$E^\circ \text{ vs } Fc^+/Fc \text{ in THF}$$

The result demonstrates that the M-H BDE increases in the order Fe < Ru < Os, as is seen in three types of complexes, Cp_2MH^+ (Fe-H, 51.4 kcal/mol < Ru-H, 64.8),[12] $CpM(CO)_2H$ (Fe-H, 57.1 < Ru-H, 64.9),[33] $M(CO)_4(H)_2$ (Fe-H, 67.6[33] < Os-H, 78[48]). The M-H BDEs for the cationic dihydrogen $RuHL_2(H_2)^+$ complexes (L = depe, 81 kcal/mol; dppe, 82; dtfpe, 89) are consistently higher than those of the neutral monohydrides; this may be related to the fact that both H-H and Ru-H bonds must be cleaved in these dihydrogen complexes.[45] The trend in M-H BDE (as well as the pK_a) values for dihydrogen $MHL_2(H_2)^+$

(M = Ru, Os) complexes as a function of the metal, Os < Ru, is distinctively different than the trend in the hydride complexes where 5d M-H > 4d M-H. The high H-H bond energy of the Ru^{2+} complexes is probably the reason why M-H for Ru is stronger than Os.[45]

Table 6 Group 8 M-H Bond Dissociation Enthalpy

molecule	BDE, kcal/mol	Method/Ref.[a]
$Fe(CO)_4H_2$	65.1 67.6	12, 41 TCC/25,33
$HFe(CO)_5^+$	71.5±3.6	ICRS/12
$CpFe(CO)_2H$	57.1 53.8	TCC/33 TC/15
Cp_2FeH^+	51.4±5	ICRS/12
$CpFe(CO)_2(Me)(H)^+$	50.2±3.3	ICRS/12
$H_3Ru_3(COCH_3)(CO)_9$	65	41
Cp_2RuH^+	64.8±3.6	ICRS/12
$Cp^*Ru(PMe_3)_2H$	37.4	TC/18
$CpRu(PPh_3)_2H_2^+$	74.2 72	TCC/46 TCC/45
$CpRu(dppm)H_2^+$	78.5 75.5	TCC/46 TCC/45
$CpRu(dppe)H_2^+$	76.8 73.8	TCC/46 TCC/45
$CpRu(dppp)H_2^+$	75.4	TCC/46
$CpRu(CO)_2H$	65.1	TCC/33
$Ru(dmpe)_2H_2$	63.5	PAC/47

Table 6. Cont'd

$RuH(dtfpe)_2H_2^+$ [b]	89	TCC/45
$RuH(dppe)_2H_2^+$	82	TCC/45
$RuH(depe)_2H_2^+$	81	TCC/45
$Os(CO)_4H_2$	78	RSC/48
$OsH(dtfpe)_2H_2^+$ [b]	81	TCC/45
$OsH(dppe)_2H_2^+$	80	TCC/45
$OsH(depe)_2H_2^+$	76	TCC/45

[a] Key: ICRS = ion cyclotron resonance spectroscopy, PAC = photoacoustic calorimetry, RSC = reaction solution calorimetry, TC = theoretical calculations, TCC = thermochemical cycle. [b] dtfpe = $(4\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}CF_3)_2$

Group 9

The available bond enthalpy data for group 9 organometallic metal-hydrogen bonds are listed in Table 7. Several techniques were used to derive these data. The Rh-H bond (62 kcal/mol) is stronger than Co-H (56) in the complexes M(oep)H (oep = octaethylporphyrin).[49] Changing either the phosphine ligand in the Co and Ir complexes or the halide in the Ir complexes does not dramatically change the M-H BDE.

Table 7 Group 9 M-H Bond Dissociation Enthalpy

molecule	BDE, kcal/mol	Method/Ref.[a]
$Co(CO)_4H$	67.7	DF/42
	66.4	TCC/33
	56	EG/12
	57	41
	55.0	TC/15

Table 7. Cont'd

$Co(CO)_3P(OPh)_3H$	65.2	TCC/33
	66	25
$Co(CO)_3(PPh_3)H$	65.0	TCC/33
$Co(CN)_5H^{3-}$	58	41
$CoH_2[P(OMe)_3]_4^+$	<62	41
$CpCo(CO)_2H^+$	58.6±2.9	ICRS/12
$Co(oep)H^b$	≤56	ES/49
$Rh(oep)H^b$	62.0	ES/49
$Rh(Cl)[P(p\text{-tolyl})_3]_3(H)_2$	57.6	51
$CpRh(CO)_2H^+$	68.7±2.9	ICRS/12
$Cp^*Ir(PMe_3)(Cy)H$	74.0	RSC/52
$Cp^*Ir(PMe_3)(H)_2$	74.2±4.3	KS/RSC/PAC/52
	73.6	TC/18
$H_2Ir(CO)_2(PPh_2Me)_2^+$	<62	41
$H_2IrCl(CO)(PPh_3)_2$	64	47
	59	41
$Ir(X)(CO)(PPh_3)_2H_2$		ES/53
X=Cl	59.1	
X=Br	60.5	
X=I	61.7	
$Ir(Cl)(CO)(PPh_3)_2(Cl)H$	58.6	RSC/54
$Ir(Cl)(CO)(PPh_3)_2(Br)H$	56.7	RSC/54
$Ir(Cl)(CO)(PMePh_2)_2(Cl)H$	63.6	RSC/54
$Ir(Cl)(CO)(PR_3)_2H_2$		
$PR_3 = PEt_3$	58.1	ES/55

Table 7. Cont'd

$PR_3 = PCy_3$	58.9	ES/55
$Ir(X)(CO)(PR_3)_2H_2$		ES/53
$X=Cl, PR_3 = P(i\text{-}Pr)_3$	57.4	
$X=Cl, PR_3 = PBuPh_2$	57.9	
$X=Cl, PR_3 = PPh_3$	60.0	
$X=Cl, PR_3 = PCy_3$	57.4	
$X=Cl, PR_3 = PBz_3$	59.6	
$X=Cl, PR_3 = P(p\text{-}tolyl)_3$	58.9	
$X=Cl, PR_3 = P(OPh)_3$	58.4	
$X=Br, PR_3 = P(i\text{-}Pr)_3$	58.6	
$X=Br, PR_3 = PPh_3$	56.2	
$X=Br, PR_3 = PCy_3$	58.4	
$X=Br, PR_3 = P(OPh)_3$	56.9	
$X=I, PR_3 = P(i\text{-}Pr)_3$	54.3	
$X=I, PR_3 = PPh_3$	54.8	
$X=I, PR_3 = PCy_3$	61.2	
$X=I, PR_3 = P(OPh)_3$	53.6	
$Cp^*Ir(PMe_3)(H)(R)$		ES/56
$R = c\text{-}C_5H_9$	51.4	
$R = C_5H_{11}$	58.4	
$R = Ph$	76.8	
$R = Cy$	52.2	
$R = 2,3\text{-}Me_2Bu$	57.4	
$R = CH_2CMe_2Et$	55.7	

[a] Key: EG = equilibrium studies in gas phase, ES = equilibrium studies in solution, DF = density functional study, KS = kinetic studies in solution, PAC = photoacoustic calorimetry, RSC = reaction solution calorimetry, TC = theoretical calculations, TCC = thermochemical cycle. [b] oep = octaethylporphyrin

Group 10

Since only very few M-H BDEs for group 10 metal hydrides are available (Table 8), it is difficult to draw conclusions from these data. The bond enthalpy of the Pt-H bond in *trans*-$Pt(PPh_3)_2(Cl)(H)$ in the gas phase was derived as

73.4±8 kcal/mol,[57] which is much higher than (dppe)Pt(CH_3)H (24.8) in Drago's report.[18]

Table 8 Group 10 M-H Bond Dissociation Enthalpy

molecule	BDE, kcal/mol	Method/Ref.[a]
$HNi(CO)_4^+$	59.3±2.1	ICRS/12
Cp_2NiH^+	51.4±3.1	ICRS/12
$CpNi(NO)H^+$	75.3±3.3	ICRS/12
CpNi(CO)H	50.2	TC/15
(dppe)Pt(CH_3)H	24.8	TC/18
trans-Pt(PPh_3)$_2$(Cl)(H)	73.4	RSC/57

[a] Key: ICRS = ion cyclotron resonance spectroscopy, RSC = reaction solution calorimetry, TC = theoretical calculations.

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A CORRELATION BETWEEN BASICITIES AND NUCLEOPHILICITIES OF CpIr(CO)(PR$_3$) COMPLEXES[†]

A paper submitted to *Inorganic Chemistry*

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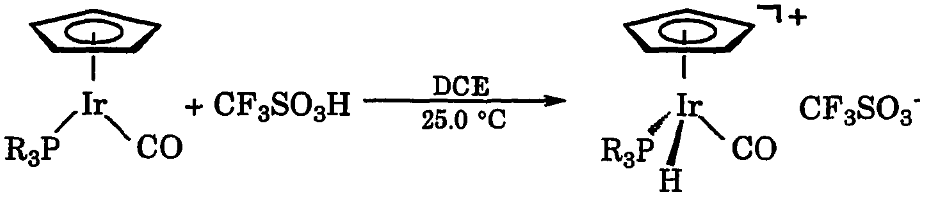
Abstract

Basicities of the series of complexes CpIr(CO)(PR$_3$) [PR$_3$ = P(*p*-C$_6$H$_4$CF$_3$)$_3$, P(*p*-C$_6$H$_4$F)$_3$, P(*p*-C$_6$H$_4$Cl)$_3$, PPh$_3$, P(*p*-C$_6$H$_4$CH$_3$)$_3$, P(*p*-C$_6$H$_4$OCH$_3$)$_3$, PPh$_2$Me, PPhMe$_2$, PMe$_3$, PEt$_3$, PCy$_3$] have been measured by the heat evolved (ΔH_{HM}) when the complex is protonated by CF$_3$SO$_3$H in 1,2-dichloroethane (DCE) at 25.0 °C. The $-\Delta H_{HM}$ values range from 28.0 kcal/mol for CpIr(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$] to 33.2 kcal/mol for CpIr(CO)(PMe$_3$) and are directly related to the basicities of the PR$_3$ ligands in the complexes. The nucleophilicities of the CpIr(CO)(PR$_3$) complexes were established from second order rate constants (k) for their reactions with CH$_3$I to give [CpIr(CO)(PR$_3$)(CH$_3$)]$^+$I$^-$ in CD$_2$Cl$_2$ at 25.0 °C. Values of k range from 0.15×10^{-2} M^{-1}s^{-1} for CpIr(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$] to 44×10^{-2} M^{-1}s^{-1} for CpIr(CO)(PMe$_3$). There is an excellent linear correlation between the basicities (ΔH_{HM}) and nucleophilicities (log k) of the CpIr(CO)(PR$_3$) complexes. Only the complex CpIr(CO)(PCy$_3$) with the bulky tricyclohexylphosphine ligand deviates dramatically from the trend.

Introduction

Basicities of transition-metal complexes[1-3] are of much interest because they are assumed to be indicators of other types of reactivity that depend upon electron-richness at the metal center.[4] As pK_a values of organic acids and bases are useful predictors of their reactivities, so too might one expect the basicities of metal complexes to be a guide to predicting their nucleophilicities, abilities to form hydrogen bonds with alcohols,[5] and tendencies to undergo oxidative-addition as well as simple oxidation and reduction reactions. However, few quantitative data[2d] are available that correlate metal complex basicities with other reactivities of metal complexes.

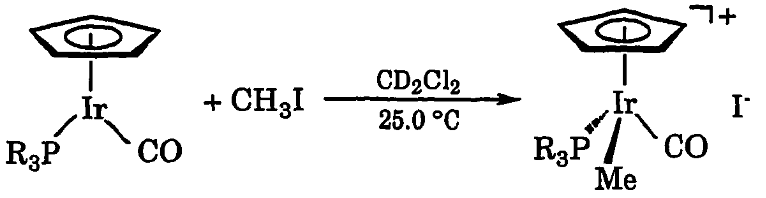
In this paper, we report the first example of a correlation between the basicities and nucleophilicities of a series of CpIr(CO)(PR_3) complexes. The basicities are defined as the enthalpy of protonation of the metal complex (ΔH_{HM}) with triflic acid (CF_3SO_3H) in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1). The nucleophilicities are measured by the rate constants (k) for their



(1)

1 - 11 **$1H^+CF_3SO_3^-$ - $11H^+CF_3SO_3^-$**

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



1 - 11 **$1CH_3^+I^-$ - $11CH_3^+I^-$** (2)

reactions with CH_3I to form $[Cp(CO)(PR_3)Ir(CH_3)]^+I^-$ in CD_2Cl_2 at 25.0 °C (eq 2). These studies provide a quantitative basis for understanding how systematic changes in metal basicity affect rate constants for reactions in which the metal in the complex acts as the nucleophile.

Experimental Section

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

The ^1H NMR spectra were obtained on samples dissolved in $CDCl_3$ or CD_2Cl_2 on a Nicolet-NT 300 MHz spectrometer using TMS ($\delta = 0.00$ ppm) as the internal reference. The $^{31}P\{^1H\}$ NMR spectra of samples in $CDCl_3$ in 10-mm tubes were recorded on a Varian VXR-300 MHz NMR spectrometer using 85% phosphoric acid ($\delta = 0.00$ ppm) as the external reference. Solution infrared spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1-mm spacers.

Synthesis of CpIr(CO)(PR_3). The phosphines $P(p\text{-}C_6H_4Cl)_3$, $P(p\text{-}C_6H_4F)_3$, $P(p\text{-}C_6H_4CF_3)_3$, $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4OMe)_3$, and PCy_3 were purchased from Strem while PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, and PEt_3 were purchased from Aldrich. The starting material, *cis*-$Ir(CO)_2(Cl)[NH_2(p\text{-}C_6H_4Me)]$, was prepared as a purple powder from $IrCl_3{\cdot}xH_2O$ in 86% yield according to a known procedure.[8] Although complexes **7**, **8**, and **9** have been prepared previously by other methods,[3b] all of the other complexes except **11** in this study were synthesized from reactions of *cis*-$Ir(CO)_2(Cl)[NH_2(p\text{-}C_6H_4Me)]$ with the appropriate phosphine (eq 3), followed by reaction with potassium cyclopentadienide (KCp) *in situ* (eq 4). The purity and identity of each

$$\textit{cis}\text{-IrCl(CO)}_2(p\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3) + 2\,\text{PR}_3 \xrightarrow[\text{reflux}]{\text{toluene}} \textit{trans}\text{-IrCl(CO)(PR}_3)_2 \tag{3}$$

$$\textit{trans}\text{-IrCl(CO)(PR}_3)_2 + \text{KCp} \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\textbf{1-10}}{\text{CpIr(CO)(PR}_3)} \tag{4}$$

compound were established by comparison of their infrared and ^1H NMR spectra with those of other $CpIr(CO)(PR_3)$ complexes reported in the literature.[3b]

$CpIr(CO)(PPh_3)$ (4). This compound was prepared in 67% yield from the reaction of KCp[3a] with $IrCl(CO)(PPh_3)_2$[9] according to the previously reported procedure[10]; it was also prepared in 62% yield by the method given in the next paragraph. ^{31}P NMR ($CDCl_3$): δ 16.66 ppm. ^1H NMR (CD_2Cl_2): δ 5.11 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 7.34-7.55 (m, 15 H, Ph). IR (CH_2Cl_2): υ(CO) 1923 cm^{-1}.

$CpIr(CO)[P(p\text{-}C_6H_4Cl)_3]$ (2). A solution of *cis*-$Ir(CO)_2(Cl)[NH_2(p\text{-}C_6H_4Me)]$ (200 mg, 0.51 mmol) in toluene (25 mL) was treated with a slight excess of 2 equiv of tris(*p*-chlorophenyl)phosphine (400 mg, 1.1 mmol). The mixture was refluxed for about 1 h until the IR spectrum showed only the new band (υ(CO) toluene: 1965 cm^{-1}) for *trans*-$IrCl(CO)[P(p\text{-}C_6H_4Cl)_3]_2$ and no bands corresponding to the starting material (υ(CO) toluene: 2074 s, 1991 s cm^{-1}). The color of the reaction solution changed from the initial dark purple to yellow. After cooling the reaction solution to room temperature, it was filtered through a cannula into a flask containing white crystalline KCp;[3a] the KCp was prepared by allowing 25 mg (0.60 mmol) of K to react with freshly cracked CpH (0.06 ml, 0.7 mmol) in THF (25 mL) under reflux for 2 h and removing the solvent under vacuum. The mixture containing *trans*-$IrCl(CO)[P(p\text{-}C_6H_4Cl)_3]_2$ and KCp in toluene was refluxed for about 3 h until the IR spectrum showed only the new band (υ(CO) toluene: 1938 cm^{-1}) for **2** and the complete disappearance of the 1965 cm^{-1} band for *trans*-$IrCl(CO)[P(p\text{-}ClC_6H_4)_3]_2$. After cooling to room temperature the solution was filtered and reduced to ~ 5 mL under vacuum. The residue was passed through a short column (8 x 1.5 cm) of Florisil; eluting with toluene yielded the orange product band which was collected. 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 containing the product was eluted with Et_2O/hexanes (1:10). During slow evaporation of the solvents under vacuum, a yellow precipitate began to form. Cooling to -20 °C yielded 210 mg of **2** (63% based on *cis*-$Ir(CO)_2(Cl)[NH_2(p\text{-}C_6H_4Me)]$) as yellow crystals. ^1H NMR (CD_2Cl_2): δ 5.14 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 7.34-7.50 (m, 12 H, C_6H_4). IR (CH_2Cl_2): υ(CO) 1930 cm^{-1}.

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

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

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

$CpIr(CO)[P(p\text{-}C_6H_4Me)_3]$ (5). 50 min, 1963 cm^{-1}, 1 h; yield, 50%. ^1H NMR (CD_2Cl_2): δ 2.39 (s, 9 H, CH_3), 5.11 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 7.34-7.50 (m, 12 H, C_6H_4). $^{31}P\{^1H\}$ ($CDCl_3$): δ 13.67 (s). IR (CH_2Cl_2): υ(CO) 1921 cm^{-1}.

CpIr(CO)[P(*p*-$C_6H_4OMe)_3$] (6). 20 min, 1961 cm^{-1}, 1 h; yield, 64%. ^{1}H NMR (CD_2Cl_2): δ 3.90 (s, 9 H, CH_3O), 5.12 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 7.3-7.5 (m, 12 H, C_6H_4). IR (CH_2Cl_2): υ(CO) 1919 cm^{-1}.

CpIr(CO)(PPh$_2$Me) (7). 20 min, 1958 cm^{-1}, 30 min; yield, 46%. ^{1}H NMR (CD_2Cl_2): δ 2.30 (d, J_{PH} = 9.9 Hz, 3 H, Me), 5.13 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 7.4-7.7 (m, 10 H, C_6H_5). IR (CH_2Cl_2): υ(CO) 1922 cm^{-1}.

CpIr(CO)(PMe$_2$Ph) (8). 20 min, 1950 cm^{-1}, 30 min; yield, 42%. ^{1}H NMR (CD_2Cl_2): δ 2.02 (d, J_{PH} = 10.2 Hz, 6 H, Me), 5.24 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 7.4-7.7 (m, 5 H, C_6H_5). IR (CH_2Cl_2): υ(CO) 1918 cm^{-1}.

CpIr(CO)(PMe$_3$) (9). 10 min, 1945 cm^{-1}, 30 min; yield, 42%. ^{1}H NMR (CD_2Cl_2): δ 1.77 (d, J_{PH} = 10.2 Hz, 9 H, Me), 5.30 (d, J_{PH} = 0.9 Hz, 5 H, Cp). IR (CH_2Cl_2): υ(CO) 1916 cm^{-1}.

CpIr(CO)(PEt$_3$) (10). 30 min, 1940 cm^{-1}, 40 min; yield, 40%. ^{1}H NMR (CD_2Cl_2): δ 1.77 (m, 6 H, CH_2), 1.02 (m, 9 H, CH_3), 5.26 (d, J_{PH} = 0.9 Hz, 5 H, Cp). ^{31}P{^{1}H} {$CDCl_3$}: δ 6.63 (s). IR (CH_2Cl_2): υ(CO) 1912 cm^{-1}.

CpIr(CO)(PCy$_3$) (11). To a flask containing KCp (5 mmol) was added a dark purple solution of *cis*-Ir(CO)$_2$(Cl)[NH$_2$(*p*-C_6H_4Me)] (400 mg, 1.0 mmol) in toluene (25 mL). The mixture was refluxed 14 h until the IR spectrum showed two new bands (υ(CO) toluene: 2035 s, 1966 s cm^{-1}) for CpIr(CO)$_2$^{11} and no bands corresponding to the starting material (υ(CO) toluene: 2074 s, 1991 s cm^{-1}). The color of the reaction solution changed from the initial dark purple to yellow. After cooling to room temperature, the yellow solution was filtered and reduced to 5 mL under vacuum. This concentrated solution was passed through a short column (8 x 1.5 cm) of neutral alumina packed in hexanes; eluting with hexanes yielded a yellow band which was collected. After concentrating the solution volume to 5 mL under vacuum, 15 mL of decane was added. To the yellow solution was added 850 mg of tricyclohexylphosphine (PCy_3) (1.5 mmol). The mixture was refluxed overnight until the IR spectrum showed a new band (υ(CO) decane: 1928 cm^{-1}) for **11** and the complete disappearance of $CpIr(CO)_2$. After cooling to room temperature, the solution was added to a neutral alumina column (15 x 1.5 cm). Eluting with hexanes (150 mL) removed decane and unreacted PCy_3. The yellow product band was eluted with Et_2O/hexanes (1:5). During slow evaporation of the solvents under vacuum, a yellow precipitate began to form. Cooling to -20 °C yielded 220 mg of **11** (40% based on *cis*-$Ir(CO)_2(Cl)[NH_2(p\text{-}C_6H_4Me)]$) as yellow crystals: ^1H NMR (CD_2Cl_2): δ 5.23 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.3-2.1 (m, 33 H, Cy). IR (CH_2Cl_2): υ(CO) 1909 cm^{-1}.

Protonation Reactions. Compounds **1-11** were protonated for NMR characterization of the $[CpIr(CO)(PR_3)(H)]CF_3SO_3$ products by dissolving approximately 5 mg of the complex in 0.50 mL of CD_2Cl_2 in an NMR tube under nitrogen. To the solution was added 1 equiv of CF_3SO_3H with a gastight microliter syringe through a rubber septum. The color of the solution changed from yellow to colorless immediately upon mixing. Yields of the protonated products as determined by IR and ^1H NMR spectroscopy are quantitative. They were characterized by their spectra as compared with those of **2H$^+$**, **4H$^+$**, and **7-9H$^+$** which were previously reported.[3b]

4H$^+$ and **5H$^+$** were isolated as white solids by evaporating their solutions and recrystallizing the residues from CH_2Cl_2/Et_2O at 25 °C. Spectroscopic data at room temperature for compounds **1H$^+$-11H$^+$** are listed below.

$\{CpIr(CO)[P(p\text{-}C_6H_4CF_3)_3](H)\}CF_3SO_3$ ($1H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 12 H, C_6H_4), 5.94 (d, J_{PH} = 0.9 Hz, 5 H, Cp), -14.26 (d, J_{PH} = 25.2 Hz, 1 H, Ir-H). $^{31}P\{^1H\}$ ($CDCl_3$): δ 5.11 (s). IR (CH_2Cl_2): ν(CO) 2067 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4Cl)_3](H)\}CF_3SO_3$ ($2H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 12 H, C_6H_4), 5.94 (d, J_{PH} = 0.9 Hz, 5 H, Cp), -14.45 (d, J_{PH} = 24.4 Hz, 1 H, Ir-H). IR (CH_2Cl_2): ν(CO) 2063 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4F)_3](H)\}CF_3SO_3$ ($3H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 12 H, C_6H_4), 5.86 (d, J_{PH} = 0.9 Hz, 5 H, Cp), -14.41 (d, J_{PH} = 24.6 Hz, 1 H, Ir-H). $^{31}P\{^1H\}$ ($CDCl_3$): δ 0.99 (s). IR (CH_2Cl_2): ν(CO) 2068 cm^{-1}.

$[CpIr(CO)(PPh_3)(H)]CF_3SO_3$ ($4H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.5-7.8 (m, 15 H, C_6H_5), 5.88 (d, J_{PH} = 0.9 Hz, 5 H, Cp), -14.44 (d, J_{PH} = 24.1 Hz, 1 H, Ir-H); $^{31}P\{^1H\}$ ($CDCl_3$): δ 3.65 (s). IR (CH_2Cl_2): ν(CO) 2063 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4Me)_3](H)\}CF_3SO_3$ ($5H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 12 H, C_6H_4), 5.79 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.45 (s, 3 H, Me), -14.46 (d, J_{PH} = 23.7 Hz, 1 H, Ir-H). $^{31}P\{^1H\}$ ($CDCl_3$): δ 1.29 (s). IR (CH_2Cl_2): ν(CO) 2060 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4OMe)_3](H)\}CF_3SO_3$ ($6H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 12 H, C_6H_4), 5.78 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 3.91 (s, 9 H, MeO), -14.52 (d, J_{PH} = 24.0 Hz, 1 H, Ir-H). IR (CH_2Cl_2): ν(CO) 2058 cm^{-1}.

$[CpIr(CO)(PPh_2Me)(H)]CF_3SO_3$ ($7H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 10 H, C_6H_5), 5.90 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.70 (d, J_{PH} = 12.0 Hz, 3 H, Me), -14.66 (d, J_{PH} = 23.2 Hz, 1 H, Ir-H). IR (CH_2Cl_2): ν(CO) 2061 cm^{-1}.

$[CpIr(CO)(PPhMe_2)(H)]CF_3SO_3$ ($8H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 5 H, C_6H_5), 5.89 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.36 (d, J_{PH} = 11.4 Hz, 3 H, Me), 2.39 (d, J_{PH} = 11.4 Hz, 3 H, Me), -15.03 (d, J_{PH} = 25.1 Hz, 1 H, Ir-H). IR (CH_2Cl_2): υ(CO) 2057 cm^{-1}.

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

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

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

Reactions of 1-11 with CH$_3$I: Compounds **1-11** were reacted (eq 2) with CH_3I for ^{1}H NMR characterization of the [CpIr(CO)(PR$_3$)(CH$_3$)]I products by dissolving approximately 5 mg of the complex in 0.50 mL of CD_2Cl_2 in an NMR tube under nitrogen. To the solution was added 10 equiv of CH_3I with a gastight microliter syringe through a rubber septum. The color of the solution changed from yellow to colorless during the time of the study (2 s to 4 h). Both NMR and IR spectra showed the disappearance of the starting material and the appearance of new bands for [CpIr(CO)(PR$_3$)(CH$_3$)]I. **4CH$_3^+$I$^-$** and **9CH$_3^+$I$^-$** were isolated as white solids by evaporating their solutions and recrystallizing them from CH_2Cl_2/Et_2O at 25 °C. Spectroscopic data for **1CH$_3^+$I$^-$-11CH$_3^+$I$^-$**, which are very similar to those previously reported[10] for **4CH$_3^+$I$^-$**, are listed below.

$\{CpIr(CO)[P(p\text{-}C_6H_4CF_3)_3](CH_3)\}I$ ($1CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.6-7.8 (m, 12 H, C_6H_4), 6.09 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.18 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2054 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4Cl)_3](CH_3)\}I$ ($2CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.4-7.7 (m, 12 H, C_6H_4), 5.97 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.13 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2051 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4F)_3](CH_3)\}I$ ($3CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.4-7.7 (m, 12 H, C_6H_4), 5.99 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.15 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2046 cm^{-1}.

$[CpIr(CO)(PPh_3)(CH_3)]I$ ($4CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.4-7.7 (m, 15 H, C_6H_5), 5.87 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.15 (d, J_{PH} = 5.1 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2049 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4Me)_3](CH_3)\}I$ ($5CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.4-7.7 (m, 12 H, C_6H_4), 5.87 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.46 (s, 9 H, Me), 1.13 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2046 cm^{-1}.

$\{CpIr(CO)[P(p\text{-}C_6H_4OMe)_3](CH_3)\}I$ ($6CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.3-7.6 (m, 12 H, C_6H_4), 5.87 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 3.90 (s, 9 H, MeO), 1.14 (d, J_{PH} = 5.1 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2045 cm^{-1}.

$[CpIr(CO)(PPh_2Me)(CH_3)]I$ ($7CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.4-7.7 (m, 10 H, C_6H_5), 5.92 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.57 (d, J_{PH} = 10.5 Hz, 3 H, Me), 1.07 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2047 cm^{-1}.

$[CpIr(CO)(PPhMe_2)(CH_3)]I$ ($8CH_3^+I^-$). ${}^1H$ NMR (CD_2Cl_2): δ 7.4-7.7 (m, 5 H, C_6H_5), 5.95 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.42 (d, J_{PH} = 11.4 Hz, 3 H, Me), 2.32 (d, J_{PH} = 11.4 Hz, 3 H, Me), 1.06 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2045 cm^{-1}.

[CpIr(CO)(PMe$_3$)(CH$_3$)]I (9CH$_3$$^+I^-$). ^{1}H NMR (CD$_2Cl_2$): δ 6.06 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 2.07 (d, J_{PH} = 11.7 Hz, 9 H, Me), 1.05 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH$_3$). IR (CH$_2$Cl$_2$): υ(CO) 2041 cm^{-1}.

[CpIr(CO)(PEt$_3$)(CH$_3$)]I (10CH$_3$$^+I^-$). ^{1}H NMR (CD$_2Cl_2$): δ 6.06 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.77 (m, 6 H, CH$_2$), 1.05 (m, 9 H, Me), 1.14 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH$_3$). IR (CH$_2$Cl$_2$): υ(CO) 2041 cm^{-1}.

[CpIr(CO)(PCy$_3$)(CH$_3$)]I (11CH$_3$$^+I^-$). ^{1}H NMR (CD$_2Cl_2$): δ 6.06 (d, J_{PH} = 0.9 Hz, 5 H, Cp), 1.3 - 2.1 (m, 33 H, Cy), 1.14 (d, J_{PH} = 3.0 Hz, 3 H, Ir-CH$_3$). IR (CH$_2$Cl$_2$): υ(CO) 2037 cm^{-1}.

Calorimetric Studies of Reaction 1. Determinations of the heats of protonation (ΔH_{HM}) of the CpIr(CO)(PR$_3$) complexes with 0.1 M CF$_3$SO$_3$H in 1,2-dichloroethane (DCE) solvent at 25 °C were performed using a Tronac Model 458 isoperibol calorimeter as originally described[12] and then modified.[3a] Typically a run consisted of three sections:[13] initial heat capacity calibration, titration, and final heat capacity calibration. Each section was preceded by a baseline acquisition period. A 3-min or 2-min titration period was used for the compounds in this study. During the titration period, approximately 1.2 or 0.8 mL of a 0.1 M CF$_3$SO$_3$H solution (standardized to a precision of ±0.0002 M) in DCE solvent was added at a constant rate (0.3962 mL/min) to 50.0 mL of a 2.6 or 1.7 mM solution of the complex (5-10% excess) in DCE at 25.0 °C.

The ΔH_{HM} values for each complex were measured using two different standardized acid solutions and are reported as the average of at least four titrations and as many as six. The heat of dilution (ΔH_{dil}) of the acid in DCE

(-0.2 kcal/mol)[3a] was used to correct the reaction enthalpies. The error in ΔH_{HM} is reported as the average deviation from the mean of all the determinations.

The accuracy of the calorimeter was monitored before each set of ΔH_{HM} determinations by titrating 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (-37.0 ± 0.3 kcal/mol; literature value,[12] -37.2 ± 0.4 kcal/mol).

Kinetic Studies of Reaction 2. In a typical experiment, 2-10 mg of $CpIr(CO)(PR_3)$ and 10 mg (0.0410 mmol) of the internal standard Ph_3CH (recrystallized from ethanol[7]) were introduced into a 5 mm NMR tube. To the tube was added a 0.50 mL solution of CH_3I in CD_2Cl_2 with a gastight syringe. The ^1H NMR spectra of samples thermostatted at 298 K were taken on the VXR 300 NMR spectrometer using the methine proton of $Ph_3C\mathit{H}$ (5.56 ppm) as the internal reference. A 15 s pulse delay was used to ensure complete relaxation of all the protons. Integrals of peaks at ~6.0 ppm (Cp, product), 5.56 ($Ph_3C\mathit{H}$), ~5.2 (Cp, reactant), 2.15 (free CH_3I), and ~1.14 ($Ir\text{-}CH_3$, product) were obtained from each of the 15-21 spectra per sample recorded over a period of three half-lives. The sum of the integrals of all reactants and products was constant throughout each kinetic run. The initial concentrations of $[Ir]_0$ were calculated using eq 5, and the initial concentrations of $[CH_3I]_0$ were calculated using eq 6,

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

$$[MeI]_0 = \frac{(I_{MeI} + I_{Ir\text{-}Me})\,[Ph_3CH]}{3 \times I_S} \qquad (6)$$

where $I_{Cp}{}^{p}$ = integral of product Cp signal, $I_{Cp}{}^{r}$ = integral of reactant Cp signal, [Ph_3CH] = concentration of internal standard Ph_3CH, M, I_S = integral of the methine proton of $Ph_3C\mathit{H}$, I_{MeI} = integral of reactant MeI signal; $I_{Ir\text{-}Me}$ = integral of product Ir-CH_3 signal. The $[Ir]_0$ and $[CH_3I]_0$ concentrations in Table 1 are averages of the concentrations obtained from 15-21 spectra taken during the kinetic runs.

The expressions (eqs 7 and 8) used for the calculation of the rate constant k_{obs} and the second-order rate constant k, were derived as shown below:

For the reaction $A + B \longrightarrow C$

$$-\frac{d[A]}{dt} = k\,[A]\,[B]$$

where $[A]_0 = [A] + [C]$, $[B]_0 = [B] + [C]$

therefore, $[B]_0 - [A]_0 = [B] - [A] = b$ and

when $[B]_0 / [A]_0 = a$, $b = (a\text{-}1)\,[A]_0$

(1) When a > 10

$$-\frac{d[A]}{dt} = k_{obs}\,[A]\,; \quad \text{where } k_{obs} = k\,[B]_0$$

$$\ln\frac{[A]_0}{[A]} = k_{obs}\,t$$

$$\ln\left(1 + \frac{[C]}{[A]}\right) = k_{obs}\,t$$

as $[C] / [A] = I_{Cp}{}^{p} / I_{Cp}{}^{r}$,

$$\text{therefore, } \ln\left(1 + \frac{I_{Cp}{}^{p}}{I_{Cp}{}^{r}}\right) = k_{obs}\,t \qquad (7)$$

The slope of a plot of $\ln(1 + I_{Cp}{}^{p}/I_{Cp}{}^{r})$ vs time is k_{obs}; and $k = k_{obs} / [MeI]_0$.

(2) When $a < 10$

$$-\frac{d[A]}{dt} = k\,[A]\,(b + [A])$$

$$-\frac{d[A]}{[A]\,(b + [A])} = k\,dt$$

$$\ln \frac{(b + [A])}{[A]} - \ln \frac{(b + [A]_0)}{[A]_0} = bkt$$

$$\ln \frac{(b + [A])}{[A]} = \ln a + bkt$$

substitute b with $b = (a\text{-}1)\,([A] + [C])$,

$$\ln \frac{[A] + (a\text{-}1)\,([A] + [C])}{[A]} = \ln a + (a\text{-}1)\,[A]_0\,kt$$

since $[C] / [A] = I_{Cp}{}^{p} / I_{Cp}{}^{r}$,

$$\ln [a + (a\text{-}1)\frac{I_{Cp}{}^{p}}{I_{Cp}{}^{r}}] = \ln a + (a\text{-}1)\,[Ir]_0\,kt \qquad (8)$$

The second-order rate constant k is calculated from the slope of a plot of $\ln [1 + (a\text{-}1)I_{Cp}{}^{p}/I_{Cp}{}^{r}]$ vs time, where the slope is $\{(a\text{-}1)\,[Ir]_0\}$.

Results

Syntheses of Iridium Complexes 1-11. In spite of known syntheses for CpM(CO)(PR_3) (M = Co, Rh) complexes[14] and (C_5H_4R)Ir(CO)(PPh_3) (R = $COCH_3$, CH_3, C(O)C_6H_5, CHO),[15] only the preparations of complexes **2, 4, 7-9** have been reported previously using different synthetic routes often in relatively low yields.[3b,10] We developed a general method (eqs 3 and 4) to synthesize all of the complexes, except **11**, from KCp and *trans*-IrCl(CO)(PR_3)$_2$. The reported synthetic procedure for the preparation of "Vaska's complex"[16] *trans*-IrCl(CO)(PPh_3)$_2$ involves refluxing $IrCl_3$ and PPh_3 in N,N-dimethylformamide.[9] The preparation of other *trans*-IrCl(CO)(PR_3)$_2$ complexes where PR_3 is a phosphine other than PPh_3, however, cannot be accomplished by this method. Although other methods[17] have been reported in the literature, most of them require many steps and give low overall yields, as for *trans*-IrCl(CO)(PEt_3)$_2$.[17a] We developed a simple, reliable method (eq 3) for the preparation of the *trans*-IrCl(CO)(PR_3)$_2$ complexes which are used *in situ* to make the final products **1-10** (eq 4). While this work was in progress, Rahim and Ahmed[24] reported the synthesis of some of the *trans*-IrCl(CO)(PR_3)$_2$ complexes by essentially the same method. The starting complex *cis*-IrCl(CO)$_2$[NH_2(*p*-C_6H_4Me)][18] is available from $IrCl_3 \bullet xH_2O$ in high yield in a "one-pot" reaction[19] and the *trans*-IrCl(CO)(PR_3)$_2$ complexes are produced in high yield. The subsequent reaction (eq 4) of *trans*-IrCl(CO)(PR_3)$_2$ with KCp gave the CpIr(CO)(PR_3) complexes in overall isolated yields of 40-73%. When the phosphine is tricyclohexylphosphine, the *trans*-Ir(CO)(PCy_3)$_2$ does not react with KCp in refluxing toluene to give **11**, presumably because of the bulky PCy_3 ligands. However, complex **11** was synthesized (eqs 9 and 10) in 40% yield by reacting PCy_3 with $CpIr(CO)_2$, which was prepared *in situ* from the reaction of *cis*-$Ir(CO)_2[NH_2(p\text{-}C_6H_4Me)]$ with KCp.

$$\textit{cis}\text{-}IrCl(CO)_2(p\text{-}NH_2C_6H_4CH_3) + KCp \xrightarrow[\text{reflux}]{\text{toluene}} CpIr(CO)_2 \qquad (9)$$

$$CpIr(CO)_2 + PCy_3 \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\textbf{11}}{CpIr(CO)(PCy_3)} \qquad (10)$$

Complexes **1-11** have the half-sandwich geometry shown in eq 1 as confirmed for **4** by an X-ray crystallographic determination.[20] The compounds were characterized by ^1H NMR and IR spectroscopy (see Experimental Section). Only compounds **9-11** are air-sensitive in the solid state. As a precaution, all compounds were stored under N_2, and solutions were prepared using dry deaerated solvents.

Characterization of Products in Reactions 1 and 2. Quantitative formation of the three-legged piano-stool complexes **$1H^+CF_3SO_3^-$-$11H^+CF_3SO_3^-$** occurs upon addition of 1 equiv of CF_3SO_3H to the neutral complexes **1-11** (eq 1) as evidenced by ^1H NMR and IR spectroscopy. The Ir-H resonances in the ^1H NMR spectra occur as doublets between -14.26 ppm (**$1H^+$**) and -14.64 ppm (**$11H^+$**) with $^2J_{PH}$ = 24-25 Hz due to coupling with the phosphine phosphorus atom. Protonation causes the Cp proton resonances to shift ~0.8 ppm downfield; the ν(CO) bands move ~140 cm^{-1} to higher frequency (see Experimental section). The IR and ^1H NMR spectra of these complexes are very similar to those of **$2H^+$**, **$4H^+$**, and **7-$9H^+$**, which have been previously reported.[3b] The protonated complexes are air-sensitive in solution. Complexes **$4H^+CF_3SO_3^-$** and **$5H^+CF_3SO_3^-$** were isolated as white solids from the reaction of **4** and **5** with CF_3SO_3H in Et_2O.

As established previously[10] for the reaction of CpIr(CO)(PPh$_3$), all of the CpIr(CO)(PR$_3$) complexes (**1-11**) in this study react (eq 2) with CH$_3$I in CD$_2$Cl$_2$ to give the methyl complexes **1CH$_3^+$-11CH$_3^+$** quantitatively, as observed by ^{1}H NMR spectroscopy. The Ir-CH$_3$ ^{1}H NMR resonances in these compounds occur as doublets between δ 1.18 ppm (**1CH$_3^+$**) and 1.05 ppm (**9CH$_3^+$**) with $^2J_{PH}$ = ~3 Hz due to coupling with the phosphine phosphorus atom. Their Cp proton signals are ~0.8 ppm downfield of those in the starting complexes (**1-11**). The ν(CO) bands move ~130 cm^{-1} to higher frequency (see Experimental section) upon methylation, as expected for the formation of a cationic complex. The IR and ^{1}H NMR spectra of these complexes are similar to those of **4CH$_3^+$** which was characterized previously.[10] Complexes **4CH$_3^+$I$^-$** and **9CH$_3$I$^-$** were isolated as white solids.

Calorimetric Studies. The heats of protonation (ΔH_{HM}) determined by calorimetric titration of the CpIr(CO)(PR$_3$) complexes with 0.1 M CF$_3$SO$_3$H in 1,2-dichloroethane (DCE) at 25.0 °C according to eq 1 are presented in Table 2. Plots of temperature vs amount of acid added were linear, indicating that the protonations occur rapidly and stoichiometrically.[13] There was no decomposition of either the neutral or protonated species during the titration as evidenced by the normal pre- and post-titration curves. Infrared spectra of the titrated solutions showed ν(CO) bands characteristic of the protonated products **1H$^+$-11H$^+$**. The ΔH_{HM} value for **4** (30.0± 0.1 kcal/mol) agrees well with the literature value of (30.1± 0.2).[3b]

Kinetic Studies. Rate constants for the reactions (eq 2) of **1-11** with CH$_3$I in CD$_2$Cl$_2$ at 25.0 °C were determined by ^{1}H NMR spectrometry. When a 10-fold excess of CH$_3$I is used, the reactions are pseudo-first order, and plots of the observed rate constants (k_{obs}) against methyl iodide concentrations give good straight lines with near-zero intercepts (Figure 1). The observed rate constants (k_{obs}) and the second-order rate constants ($k = k_{obs} / [MeI]_0$) are listed in Table 1. The rates of the reactions were not noticeably affected by wrapping the flasks in aluminum foil. For reactions which are not run under pseudo-first order conditions, only the k values are obtained (eq 8) and listed in Table 1. The rate constants (k) range from 0.15 x 10^{-2} $M^{-1}s^{-1}$ for CpIr(CO)[P(*p*-$C_6H_4CF_3)_3$] to 44 x 10^{-2} $M^{-1}s^{-1}$ for CpIr(CO)(PMe_3). The values of k (Table 1) in the four to six runs of each complex are within 10% of the average value listed in Table 2. The k for **4** ((2.9 ± 0.2) 10^{-2} $M^{-1}s^{-1}$) agrees well with the literature value ((2.5 ± 0.2) 10^{-2} $M^{-1}s^{-1}$) as determined by monitoring the disappearance of the ν(CO) band of the starting material.[10]

Discussion

Basicities of CpIr(CO)(PR_3) Complexes 1-11. As has been noted in previous studies of basicities (ΔH_{HM} or pK_a)[1,4] of transition metal complexes, increasing the basicities of the ligands bound to a metal increases the basicity of the metal. In the CpIr(CO)(PR_3) series of complexes, we use ΔH_{HP} for the protonation of the free phosphine (eq 11) as the measure of the phosphine basicity. Earlier[3b] we reported a correlation ($-\Delta H_{HM} = 23.9 - 0.298\Delta H_{HP}$)

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\,°C]{DCE} HPR_3^+CF_3SO_3^-,\ \Delta H_{HP} \qquad (11)$$

between the basicity of the phosphine ligand and the basicity of five CpIr(CO)(PR_3) complexes (eq 1). In this study, we add four additional compounds to the correlation (Fig. 2). Including all nine compounds (**1**-**9**), the correlation (eq 12) is the same within experimental error as that obtained previously.

$$-\Delta H_{HM} = 23.9 + 0.300(-\Delta H_{HP}), \quad r = 0.996 \qquad (12)$$

The basicities of the phosphines extend over a wide range from the weakly basic $P(p\text{-}C_6H_4CF_3)_3$ ($-\Delta H_{HP}$ = 13.6 kcal/mol) to the very basic PEt_3 ($-\Delta H_{HP}$ = 33.7 kcal/mol).[4] However, the ΔH_{HM} values only range from -28.0 kcal/mol for $CpIr(CO[P(p\text{-}C_6H_4CF_3)_3]$ (**1**) to -33.2 kcal/mol for $CpIr(CO)(PMe_3)$ (**9**). The relatively small change in metal basicity with a much larger change in phosphine basicity is reflected in the 0.300 coefficient for the ΔH_{HP} term in eq 12; this coefficient shows that a 1.0 kcal/mol change in phosphine basicity results in only a 0.300 kcal/mol change in metal basicity. Possible reasons for this insensitivity of metal basicity to phosphine ligand basicity were discussed earlier.[3i]

Two compounds, $CpIr(CO)(PEt_3)$ (**10**) and $CpIr(CO)(PCy_3)$ (**11**), were not included in the correlation (eq 12) because they appeared to deviate significantly from it (Fig. 2). Both of these complexes are less basic by about 1.1-1.2 kcal/mol than expected based on their PR_3 basicity. The bulky PCy_3 ligand (cone angle 170°)[21] might be expected to reduce the basicity of $CpIr(CO)(PCy_3)$ due to steric crowding in the more highly coordinated $CpIr(CO)(PCy_3)(H)^+$ product (eq 1), which would make protonation less favorable. The PEt_3 ligand in **10** is not as large as PCy_3 in **11**, yet the cone angle for PEt_3 is variously reported to be 132°[21a], 137°[21b], and 166°[21g,h]. The smaller than expected $-\Delta H_{HM}$ value for **10** suggests that PEt_3 does induce a steric effect which is consistent with the largest cone angle (166°).[21g,h]

Rates of Reaction of CpIr(CO)(PR$_3$) with MeI (eq 2). All of the compounds **1-11** react (eq 2) with CH_3I by a second order rate law: Rate = k[CpIr(CO)(PR$_3$)][CH$_3$I]. The same rate law was observed[10] in a more limited study of the reaction of CpIr(CO)(PPh$_3$) with CH_3I. This rate law suggests that the mechanism of reaction is one that involves nucleophilic attack of the iridium in the complex on the carbon of the CH_3I which results in displacement of the I^- and formation of the $[CpIr(CO)(PR_3)(CH_3)]^+I^-$ product. Since the nucleophilicity of the Ir is expected to depend on the electron-richness of the metal and the basicity (ΔH_{HM}, eq 1) of the metal also reflects electron-richness at the metal center, one might expect a correlation between the rate constant (k) for the reaction in eq 2 and the basicity (ΔH_{HM}, eq 1). Indeed, for CpIr(CO)(PR$_3$) complexes **1-9** there is an excellent correlation between log k and $-\Delta H_{HM}$ (Fig. 3 and eq 13). Changing the basicity (ΔH_{HM}) of

$$\log k = -15.8 + 0.47(-\Delta H_{HM}), \quad r = 0.993 \qquad (13)$$

CpIr(CO)(PR$_3$) from 28.0 kcal/mol for **1** ($PR_3 = P(p\text{-}C_6H_4CF_3)_3$) to 33.2 for **9** ($PR_3 = PMe_3$) increases the rate of reaction 2 by approximately 300-fold.

Again the PEt$_3$ and PCy$_3$ complexes (**10** and **11**) are not included in the correlation (eq 13). The PEt$_3$ complex (**10**) appears to deviate only slightly from the line (Fig. 3). However, the PCy$_3$ complex (**11**) is approximately 46 times slower than is predicted from eq 13. This large reduction in iridium nucleophilicity is almost certainly due to the bulkiness of the PCy$_3$ ligand. The effects of PCy$_3$ and other bulky phosphines on rates of CO substitution in CpRh(CO)$_2$ complexes by PR$_3$ nucleophiles were reported earlier by Basolo and co-workers.[25] The rates of these reactions were also dramatically slower for the bulky phosphines.

Graham and co-workers[10] previously reported a related kinetic study of the reaction of $CpCo(CO)(PR_3)$ with CH_3I to give $[CpCo(CO)(PR_3)(CH_3)]^+I^-$ in CH_2Cl_2 at 25.0 °C. The second-order rate constants decreased with the PR_3 ligand, $PPhMe_2$ (3.0×10^{-2} $M^{-1}s^{-1}$) > PPh_2Me (1.5×10^{-2}) > PPh_3 (0.26×10^{-2}) > PCy_3 (0.055×10^{-2}), in the same order as observed in our $CpIr(CO)(PR_3)$ series. These data also demonstrate the unusually poor nucleophilicity of the PCy_3 complex which reacts more slowly than any of the other $CpCo(CO)(PR_3)$ complexes. In fact, the steric effect of bulky ligands is greater for the Co complexes than the Ir complexes; this may be seen in the ratio (Ir/Co) of rate constants k for the $CpM(CO)(PR_3)$ complexes which increase with the bulkiness of the ligand: $PPhMe_2$ (6.6) ~ PPh_2Me (6.6) < PPh_3 (11) < PCy_3 (15). With the least bulky phosphines, the Ir complex reacts 6.6 times faster than the Co. However, as the bulkiness of the phosphine increases, the rate decreases more for the Co complexes than the Ir. This is consistent with the smaller size of Co which makes its nucleophilicity more sensitive to bulky ligands.

Conclusions

The basicities of the $CpIr(CO)(PR_3)$ complexes as measured by their heats of protonation ($-\Delta H_{HM}$, eq 1) range from 28.0 kcal/mol for **1** ($PR_3 = P(p\text{-}C_6H_4CF_3)_3$) to 33.2 for **9** ($PR_3 = PMe_3$). This difference ($\Delta\Delta H_{HM}$) of 5.2 kcal/mol corresponds to complex **9** being 6,500 times more basic than **1** in terms of their equilibrium constants for protonation; this assumes that ΔS is the same for protonations of both **1** and **9**, which means that $\Delta\Delta H \sim \Delta\Delta G = -RT\ln(K_9/K_1)$. For these same complexes, **9** is 300 times more nucleophilic than **1** in their reactions with CH_3I (eq 2). Thus, a large change in metal basicity results in a modest change in its nucleophilicity. For nine CpIr(CO)(PR_3) compounds (**1**-**9**), there is an excellent correlation between $-\Delta H_{HM}$ and the rate constants (log k). Only CpIr(CO)(PCy_3) (**11**) deviates significantly from this correlation, presumably due to the bulkiness of the tricyclohexylphosphine ligand which makes the complex a much weaker nucleophile than is expected from its basicity. It is also observed that the CpIr(CO)(PR_3) complexes are all more nucleophilic than their Co analogs[10] CpCo(CO)(PR_3) as reflected in their second order rate constants, k_{Ir} and k_{Co}, for their reactions with CH_3I; this difference increases with the bulkiness of the PR_3 ligand. In addition, there is linear correlation ($\log k_{Ir} = 0.470 + 0.784 \log k_{Co}$, $r = 0.999$, Figure 4) between $\log k_{Ir}$ for CpIr(CO)(PR_3) and $\log k_{Co}$ for CpCo(CO)(PR_3). The slope (0.784), which is less than 1.0, in this correlation reflects the greater effect of bulky PR_3 ligands on the nucleophilicity of the Co complexes as compared with their Ir analogs.

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Table 1 Reaction Rates of $CpIr(CO)(PR_3)$ with CH_3I in CD_2Cl_2 at 25.0 °C (eq 2)

$CpIr(CO)(PR_3)$ PR_3=	10^3 $[Ir]_0$ M	10^3 $[CH_3I]_0$ M	a^a	10^4 $k_{obs}{}^b$ s^{-1}	10^2 k^c $M^{-1}s^{-1}$
$P(p\text{-}C_6H_4CF_3)_3$	67	350	5.2		0.15
	21	320	15	4.3	0.13
	6.9	110	16	1.6	0.15
	6.9	160	23	2.4	0.15
$P(p\text{-}C_6H_4Cl)_3$	2.4	58	25	3.7	0.62
	2.6	67	25	4.2	0.63
	2.8	120	40	7.6	0.61
	2.5	180	60	11	0.61
$P(p\text{-}C_6H_4F)_3$	4.2	74	18	8.0	1.10
	2.6	51	20	6.2	1.22
	1.6	65	40	8.1	1.24
	0.54	52	100	7.3	1.35
PPh_3	4.1	36	8.7		2.7
	3.1	37	12	12	3.3
	2.3	39	15	11	2.8
	2.7	53	20	15	2.9
	3.3	104	30	30	2.9
$P(p\text{-}C_6H_4Me)_3$	31	50	1.6		6.9
	5.2	54	10	36	6.7
	1.2	29	25	20	6.9
	2.0	54	27	38	6.9
	2.2	66	30	45	6.8
	2.4	91	38	62	6.8

Table 1. Cont'd

$P(p\text{-}C_6H_4OMe)_3$	4.9	43	8.8		7.3
	6.3	56	8.9		6.7
	8.7	82	9.4		6.9
	4.4	72	16	50	7.0
PPh_2Me	8.4	7.0	0.8		11
	8.0	8.8	1.1		9.7
	4.2	22	5.1		10
	2.5	38	15	38	10
	2.5	41	17	29	9.4
	3.3	57	18	53	9.4
PMe_2Ph	5.8	4.7	0.8		24
	7.6	6.7	0.9		21
	9.6	8.6	0.9		18
	9.2	8.3	0.9		20
	11	9.7	0.9		18
	5.4	9.5	1.8		21
PMe_3	7.4	8.0	1.1		46
	6.9	7.9	1.2		43
	5.7	7.9	1.4		43
	3.6	12.8	3.5		42
PEt_3	8.3	41	4.9		15
	4.9	54	11	67	12
	3.5	39	11	78	20

Table 1. Cont'd

	3.9	48	12	118	25
PCy_3	30	83	2.8		0.82
	7.4	25	3.4		0.86
	12	114	9.6	8.0	0.78
	9.8	150	15	12	0.78

[a]Ratio of $[\mathrm{MeI}]_0/[\mathrm{Ir}]_0$. [b]Calculated using eq 7. [c]Calculated from k_{obs} or using eq 8.

Table 2. Heats of Protonation and Rate Constants for $CpIr(CO)(PR_3)$ Complexes

$CpIr(CO)(PR_3)$ PR_3 =	cone angle Θ (°)[a]	$-\Delta H_{HP}$[b] (kcal/mol)	$-\Delta H_{HM}$[c, d] (kcal/mol)	$10^2 k/M^{-1}s^{-1}$ [e]	log k
$P(p\text{-}C_6H_4CF_3)_3$ (**1**)	145	13.6 (2)	28.0 (2)	0.15 (1)	-2.82
$P(p\text{-}C_6H_4Cl)_3$ (**2**)	145	17.9 (2)	29.2 (2)[f]	0.62 (1)	-2.21
$P(p\text{-}C_6H_4F)_3$ (**3**)	145	19.6 (2)	29.8 (2)	1.23 (7)	-1.91
PPh_3 (**4**)	145	21.2 (1)	30.0 (1)	2.9 (2)	-1.54
$P(p\text{-}C_6H_4CH_3)_3$ (**5**)	145	23.2 (3)	31.1 (3)	6.8 (1)	-1.17
$P(p\text{-}C_6H_4OCH_3)_3$ (**6**)	145	24.1 (2)	31.2 (2)	7.0 (2)	-1.15
PPh_2Me (**7**)	136	24.7 (2)	31.5 (1)[f]	10.0 (4)	-1.00
$PPhMe_2$ (**8**)	122	28.4 (2)	32.5 (2)[f]	20 (2)	-0.70
PMe_3 (**9**)	118	31.6 (2)	33.2 (3)[f]	44 (2)	-0.36
PEt_3 (**10**)	132[g]	33.7 (3)	32.9 (2)	18 (4)	-0.74
PCy_3 (**11**)	170	33.2 (4)	32.7 (2)	0.81 (3)	-2.09

[a] Reference 21a. [b] Reference 4, eq 11. [c] For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C, eq 1. [d] Numbers in parentheses are average deviations from the mean of at least four titrations. [e] Average of values in Table 1; numbers in parentheses are average deviations from the mean. [f] From ref. 3b. [g] Other values in the literature are 137[21b] and 166[21g,h].

Figure Captions

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

Figure 2. Correlation (eq 12) of metal basicity ($-\Delta H_{HM}$, eq 1) for CpIr(CO)(PR_3) with phosphine basicity ($-\Delta H_{HP}$, eq 11).

Figure 3. Correlation (eq 13) of rate constants (log k for eq 2) with metal basicity ($-\Delta H_{HM}$ for eq 1) for CpIr(CO)(PR_3) at 25.0 °C.

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

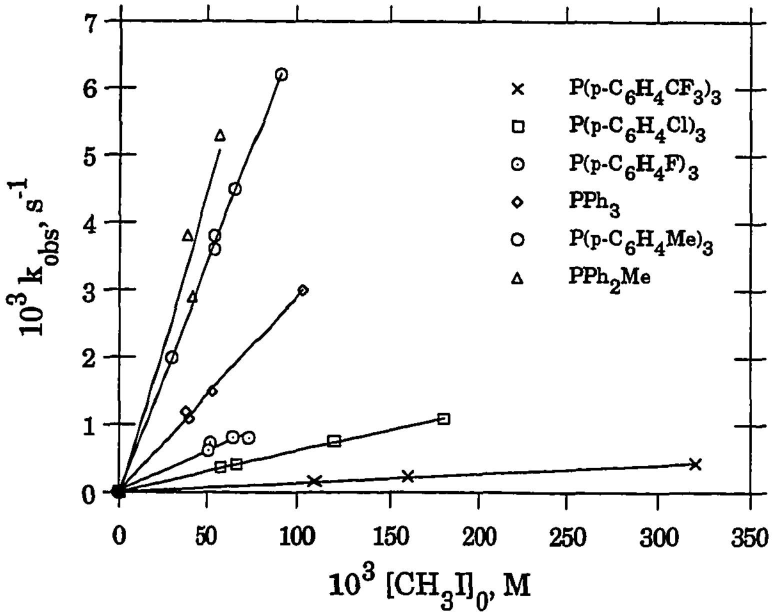

Figure 1. Plot of k_{obs} vs $[CH_3I]_0$ for reactions of $CpIr(CO)(PR_3)$ with CH_3I at 25 °C in CD_2Cl_2 (eq 2).

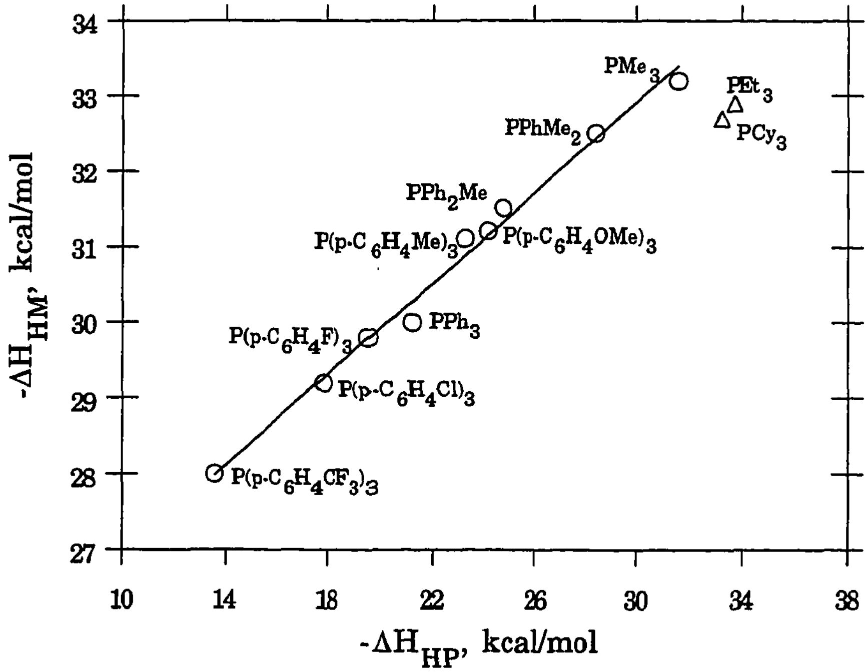

Figure 2. Correlation (eq 12) of metal basicity ($-\Delta H_{HM}$, eq 1) for $CpIr(CO)(PR_3)$ with phosphine basicity ($-\Delta H_{HP}$, eq 11).

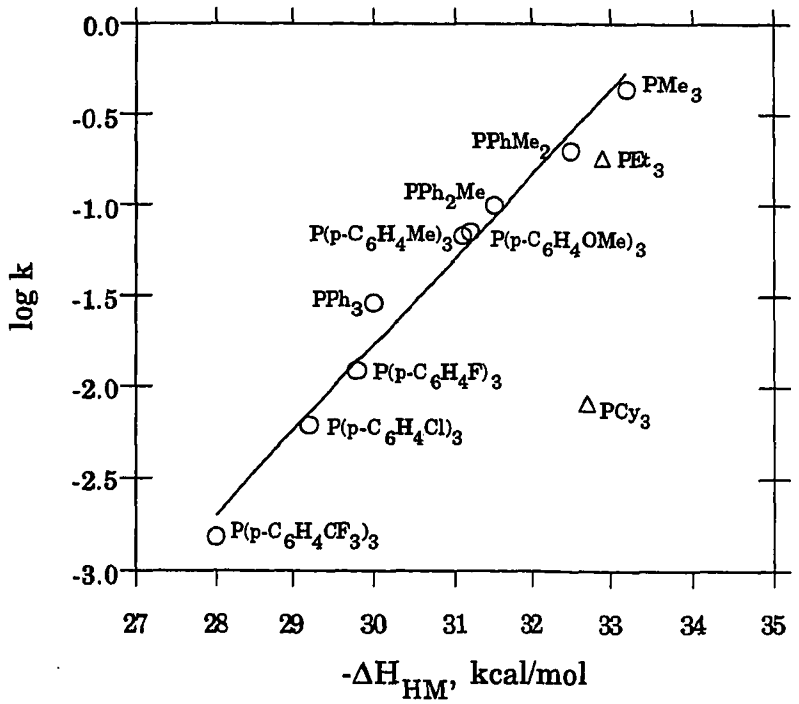

Figure 3. Correlation (eq 13) of rate constants (log k for eq 2) with metal basicity ($-\Delta H_{HM}$ for eq 1) for $CpIr(CO)(PR_3)$ at 25.0 °C.

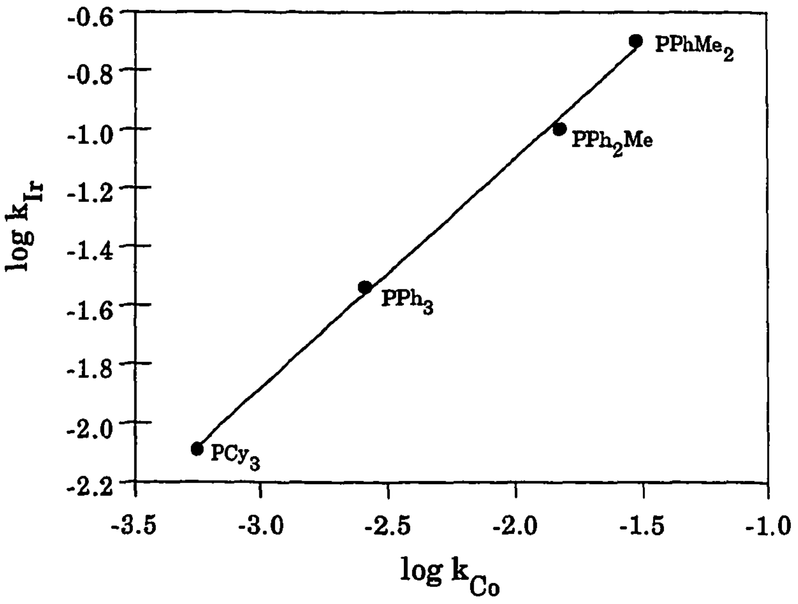

Figure 4. Correlation between log k_{Ir} for CpIr(CO)(PR_3) and log k_{Co} for CpCo(CO)(PR_3) for their reactions with CH_3I in CH_2Cl_2 at 25.0 °C (eq 2).

EFFECTS OF PENTAMETHYLCYCLOPENTADIENYL AND PHOSPHINE LIGANDS ON THE BASICITIES AND NUCLEOPHILICITIES OF $Cp^*Ir(CO)(PR_3)$ COMPLEXES

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Abstract

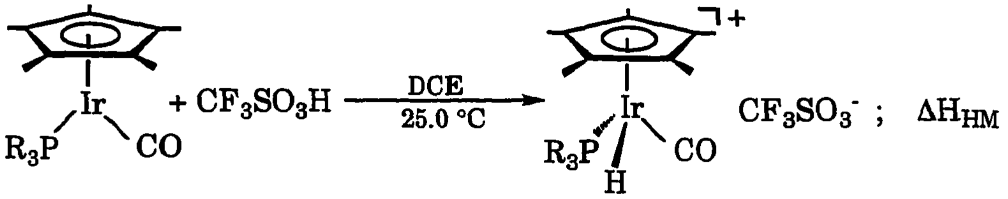
The basicities and nucleophilicities of a series of η^5-pentamethylcyclopentadienyl complexes $Cp^*Ir(CO)(PR_3)$ (PR_3 = $P(p\text{-}C_6H_4CF_3)_3$, $P(p\text{-}C_6H_4Cl)_3$, PPh_3, PPh_2Me, PMe_3) have been determined and compared with values for their $CpIr(CO)(PR_3)$ analogs. Their basicities were measured calorimetrically by the heat evolved (ΔH_{HM}) when the metal in the complexes was protonated by CF_3SO_3H in 1,2-dichloroethane (DCE). The $-\Delta H_{HM}$ values range from 33.8 kcal/mol for the weakest base $Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$ to 38.0 kcal/mol for the strongest $Cp^*Ir(CO)(PMe_3)$. Their nucleophilicities are defined by rate constants (k) for the reactions of the $Cp^*Ir(CO)(PR_3)$ complexes with CH_3I to give $[Cp^*Ir(CO)(PR_3)(CH_3)]^+I^-$ in CH_2Cl_2. The rate constants vary from 0.048 $M^{-1}s^{-1}$ for the weakest nucleophile $Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$ to 23.4 $M^{-1}s^{-1}$ for the strongest $Cp^*Ir(CO)(PMe_3)$. In general, the pentamethylcyclopentadienyl complexes react 40 times faster than the cyclopentadienyl analogs. However, they do not react as fast as predicted from electronic properties of the complexes which suggests that the steric size of the Cp* ligand reduces the nucleophilicities of $Cp^*Ir(CO)(PR_3)$ complexes. In addition, heats of protonation (ΔH_{HP}) of tris(2-methoxyphenyl)phosphine,

tris(2,6-dimethoxyphenyl)phosphine, and tris(2,4,6-trimethylphenyl)phosphine were measured and used to estimate pK_a values for these phosphines.

Introduction

There has been much interest in the electronic and steric effects of the cyclopentadienyl ligand and its methyl-substituted derivatives on the properties of transition metal complexes.[1-4] A few studies have been performed with the aim of comparing the reactivities[5-8] of pentamethylcyclopentadienyl complexes with those of the cyclopentadienyl analogs.

We recently reported studies of the basicities and nucleophilicities of a series of $CpIr(CO)(PR_3)$ complexes.[9] The basicities were determined calorimetrically by the heat evolved (ΔH_{HM}) when the metal in the complexes was protonated by CF_3SO_3H in 1,2-dichloroethane (DCE); and the nucleophilicities were established by rate constants (k) for the reactions of the $CpIr(CO)(PR_3)$ complexes with CH_3I to form $[CpIr(CO)(PR_3)(CH_3)]^+I^-$. We found that there is a linear correlation between (ΔH_{HM}) and log k for the $CpIr(CO)(PR_3)$ complexes except for $CpIr(CO)(PCy_3)$ which contains the bulky tricyclohexylphosphine ligand. We now report the synthesis of a series of

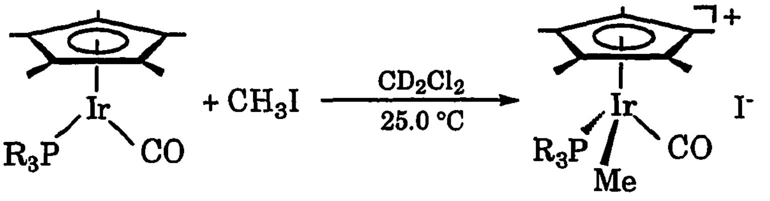


(1)

1 - 5 **$1H^+CF_3SO_3^-$ - $5H^+CF_3SO_3^-$**

PR_3: $P(p\text{-}C_6H_4CF_3)_3$ (**1**, **$1H^+$**), $P(p\text{-}C_6H_4Cl)_3$ (**2**, **$2H^+$**), PPh_3 (**3**, **$3H^+$**), PPh_2Me (**4**, **$4H^+$**), PMe_3 (**5**, **$5H^+$**)

pentamethylcyclopentadienyl iridium(I) complexes, Cp*Ir(CO)(PR$_3$) (PR$_3$ = P(*p*-C$_6$H$_4$CF$_3$)$_3$, P(*p*-C$_6$H$_4$Cl)$_3$, PPh$_3$, PPh$_2$Me, PMe$_3$), their heats of protonation (eq 1),[6] and rates of reaction with CH$_3$I (eq 2). A comparison of the ΔH_{HM} and k values for the series of CpIr(CO)(PR$_3$) and Cp*Ir(CO)(PR$_3$) complexes allows



(2)

1 - 5 **1CH$_3^+$I$^-$ - 5CH$_3^+$I$^-$**

PR$_3$: P(*p*-C$_6$H$_4$CF$_3$)$_3$ (**1**, **1CH$_3^+$**), P(*p*-C$_6$H$_4$Cl)$_3$ (**2**, **2CH$_3^+$**), PPh$_3$ (**3**, **3CH$_3^+$**), PPh$_2$Me (**4**, **4CH$_3^+$**), PMe$_3$ (**5**, **5CH$_3^+$**)

us to evaluate quantitatively the effects of the Cp and Cp* ligands on the basicities and nucleophilicities of this family of complexes. We also examine the basicities (ΔH_{HP}) of tris(2-methoxyphenyl)phosphine [P(2-C$_6$H$_4$OMe)$_3$] (**6**), tris (2,6-dimethoxyphenyl)phosphine {P[(2,6-C$_6$H$_3$(OMe)$_2$]$_3$} (**7**), tris (2,4,6-trimethoxyphenyl)phosphine {P[2,4,6-C$_6$H$_2$(OMe)$_3$]$_3$} (**8**), and tris (2,4,6-trimethylphenyl)phosphine [P(2,4,6-C$_6$H$_2$Me$_3$)$_3$] (**9**) by measuring their heats of protonation (ΔH_{HP}) in DCE solvent (eq 3).

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HPR_3^+CF_3SO_3^- \ ; \quad \Delta H_{HP} \qquad (3)$$

Experimental Section

General Procedure. All preparative reactions, chromatography, and manipulations were carried out under an atmosphere of nitrogen or argon with use of vacuum line, Schlenk, syringe, or drybox techniques similar to those described in the literature.[10] The solvents were purified under nitrogen as described below using standard methods.[11] Toluene, benzene, decane, hexanes, and methylene chloride were refluxed over CaH_2 and then distilled. Diethyl ether was distilled from sodium benzophenone. 1,2-Dichloroethane was purified by washing with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and water again; the solvent was then predried over anhydrous $MgSO_4$, stored in amber bottles over molecular sieves (4 Å), and then distilled from P_4O_{10} under argon immediately before use. Triflic acid (CF_3SO_3H) was purchased from 3M Co. and purified by fractional distillation under argon before use. Methyl iodide was distilled over P_4O_{10} and stored in a brown bottle away from sunlight in contact with a small amount of powdered copper.[11] Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under vacuum (10^{-5} mm Hg) for 12 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2. Tris(2-methoxyphenyl)phosphine, tris(2,6-dimethoxyphenyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, and tris(2,4,6-trimethylphenyl)phosphine were purchased from Aldrich and used without further purification. The phosphines $P(p\text{-}C_6H_4Cl)_3$, $P(p\text{-}C_6H_4CF_3)_3$, and PPh_2Me were purchased from Strem while PPh_3 and PMe_3 were purchased from Aldrich. The starting material, $[Cp^*IrCl_2]_2$ was prepared as an orange powder in 85% yield from the reaction of $IrCl_3{\cdot}xH_2O$ with Cp*H (Aldrich) in MeOH under reflux for 48 h according to a known procedure.[12,13] Cp*Ir(CO)$_2$ was synthesized as yellow crystals from Fe$_3$(CO)$_{12}$ (Aldrich) and [Cp*IrCl$_2$]$_2$ by refluxing in benzene for 24 h as previously reported.[13,14] Yield: 80%. ^{1}H NMR (CDCl$_3$): δ 2.18 (s, Cp*). IR (CH$_2$Cl$_2$): υ(CO) 2009 (s), 1938 (s) cm^{-1}.

The ^{1}H NMR spectra were obtained on samples dissolved in CDCl$_3$ or CD$_2$Cl$_2$ on a Nicolet-NT 300 MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. The ^{31}P{^{1}H} NMR spectra of samples in CDCl$_3$ in 10-mm tubes were recorded on a Varian VXR-300 MHz NMR spectrometer using 85% phosphoric acid (δ = 0.00 ppm) as the external reference. Solution infrared spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1-mm spacers. Elemental microanalyses were performed by National Chemical Consulting, Inc., Tenafly, NJ.

Synthesis of Cp*Ir(CO)(PR$_3$). All of the Cp*Ir(CO)(PR$_3$) complexes in this study were synthesized in reactions of Cp*Ir(CO)$_2$ with the appropriate phosphine in decane. The purity and identity of each compound was established by comparing its infrared and ^{1}H NMR spectra with the previously reported literature values for Cp*Ir(CO)(PEt$_3$).[15] Below is given the general procedure for these preparations.

To a yellow solution of Cp*Ir(CO)$_2$ (200 mg, 0.50 mmol) in decane (10 mL) was added 1.5 equiv of PR$_3$ (0.75 mmol). The mixture was refluxed for 2 - 24 h until the IR spectrum showed only the new band for Cp*Ir(CO)(PR$_3$) and the complete disappearance of Cp*Ir(CO)$_2$ (υ(CO) decane: 2058 s, 1918 s cm^{-1}). After cooling to room temperature, yellow to orange crystals began to precipitate. The crystals were filtered and washed with hexanes (3 x 2 mL). The combined filtrates were chromatographed on a neutral alumina column

(15 x 1.5 cm). Eluting with hexanes (150 mL) removed decane and free PR_3; a yellow band containing additional $Cp^*Ir(CO)(PR_3)$ was eluted with Et_2O/hexanes (1:5). During slow evaporation of the solvents under vacuum, a yellow precipitate began to form. Cooling to -20 °C yielded more crystals. The combined yellow product was obtained in 75 - 90% yield. Analytically pure and X-ray quality crystals of **2** and **3** were obtained by dissolving the crystals in a minimum amount of CH_2Cl_2 and layering the solution with a 5-fold volume of hexanes, and then cooling to -20 °C for 24 h.

Syntheses of Compounds 1 - 5. Below are given reaction times, υ(CO) values of the products in decane, yields, and spectral data for all $Cp^*Ir(CO)(PR_3)$ complexes prepared by the above method.

$Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$ (1). Reaction time, 24 h; 1944 cm^{-1}; yield, 75%. ^1H NMR (CD_2Cl_2): δ 1.82 (d, J_{PH} = 1.5 Hz, 15 H, Cp*), 7.6 (m, 12 H, C_6H_4). $^{31}P\{^1H\}$ ($CDCl_3$): δ 21.69 (s). IR (CH_2Cl_2): υ(CO) 1920 cm^{-1}.

$Cp^*Ir(CO)[P(p\text{-}C_6H_4Cl)_3]$ (2). Reaction time, 24 h; 1939 cm^{-1}; yield, 83%. ^1H NMR (CD_2Cl_2): δ 1.82 (d, J_{PH} = 1.5 Hz, 15 H, Cp*), 7.4 (m, 12 H, C_6H_4). $^{31}P\{^1H\}$ ($CDCl_3$): δ 20.76 (s). IR (CH_2Cl_2): υ(CO) 1917 cm^{-1}. Anal. Calcd for $C_{29}H_{27}IrOPCl_3$: C, 48.30; H, 3.77. Found: C, 48.43; H, 3.84.

$Cp^*Ir(CO)(PPh_3)$ (3). Reaction time, 4 h; 1935 cm^{-1}; yield, 90%. ^1H NMR (CD_2Cl_2): δ 1.81 (d, J_{PH} = 1.5 Hz, 15 H, Cp*), 7.4 (m, 15 H, C_6H_5). $^{31}P\{^1H\}$ ($CDCl_3$): δ 20.47 (s). IR (CH_2Cl_2): υ(CO) 1912 cm^{-1}. Anal. Calcd for $C_{29}H_{30}IrOP$: C, 56.38; H, 4.90. Found: C, 56.46; H, 4.90.

$Cp^*Ir(CO)(PPh_2Me)$ (4). Reaction time, 2 h; 1928 cm^{-1}; yield, 78%. ^1H NMR (CD_2Cl_2): δ 1.82 (d, J_{PH} = 1.5 Hz, 15 H, Cp*), 7.6 (m, 10 H, C_6H_5). $^{31}P\{^1H\}$ ($CDCl_3$): δ 25.18 (s). IR (CH_2Cl_2): υ(CO) 1910 cm^{-1}.

Cp*Ir(CO)(PMe$_3$) (5). Reaction time, 2 h; 1928 cm^{-1}; yield, 75%. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.08 (d, J_{PH} = 1.5 Hz, 15 H, Cp*), 1.58 (d, J_{PH} = 9.9 Hz, 9 H, Me). IR (CH$_2$Cl$_2$): υ(CO) 1909 cm^{-1}.

Protonation of Complexes 1-5. Compounds **1-5** were protonated for NMR characterization by dissolving approximately 5 mg of the complex in 0.50 mL of CD$_2$Cl$_2$ (or CDCl$_3$) in an NMR tube under nitrogen. To the solution was added 1 equiv of CF$_3$SO$_3$H with a gas-tight microliter syringe through a rubber septum. The color of the solution changed from yellow to colorless immediately upon mixing. Both NMR and IR spectra showed the disappearance of the starting material and the appearance of new bands for the [Cp*Ir(CO)(PR$_3$)(H)]CF$_3$SO$_3$ product. The spectroscopic data are similar to those of [CpIr(CO)(PR$_3$)(H)]CF$_3$SO$_3$[9,14] except the ^{1}H chemical shifts of the Ir-H resonances are downfield and the υ(CO) values are lower than those in the Cp complexes, which is consistent with the stronger electron donating ability of Cp* compared with Cp.[3,4] Yields of the protonated products as determined by IR and ^{1}H NMR spectroscopy are quantitative.

Compound **3H$^+$CF$_3$SO$_3^-$** was isolated as a white solid precipitate when **3** (50 mg) was protonated with CF$_3$SO$_3$H (1 equiv) in Et$_2$O (5 mL) solution. Analytically pure and X-ray quality crystals of **3H$^+$CF$_3$SO$_3^-$** were obtained by dissolving the white solid in a minimum amount of CH$_2$Cl$_2$ and layering the solution with a 3-fold volume of diethyl ether, and then cooling to -20 °C for 24 h. Spectroscopic data at room temperature for compounds **1H$^+$-5H$^+$** are presented below.

{Cp*Ir(CO)[P(*p*-$C_6H_4CF_3$)$_3$](H)}CF_3SO_3 ($1H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.6 - 7.8 (m, 12 H, C_6H_4), 1.99 (s, 15 H, Cp*), -14.05 (d, J_{PH} = 27.6 Hz, 1 H, Ir-H). IR (CH_2Cl_2): υ(CO) 2051 cm^{-1}.

{Cp*Ir(CO)[P(*p*-C_6H_4Cl)$_3$](H)}CF_3SO_3 ($2H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.4 - 7.6 (m, 12 H, C_6H_4), 1.96 (s, 15 H, Cp*), -14.28 (d, J_{PH} = 27.6 Hz, 1 H, Ir-H). IR (CH_2Cl_2): υ(CO) 2045 cm^{-1}.

{Cp*Ir(CO)[P(C_6H_5)$_3$](H)}CF_3SO_3 ($3H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3 - 7.5 (m, 15 H, C_6H_5), 1.93 (s, 15 H, Cp*), -14.28 (d, J_{PH} = 26.1 Hz, 1 H, Ir-H). IR (CH_2Cl_2): υ(CO) 2042cm^{-1}. Anal. Calcd for $C_{30}H_{31}IrF_3O_4PS$: C, 46.93; H, 4.07. Found: C, 46.91; H, 4.09.

[Cp*Ir(CO)(PPh_2Me)(H)]CF_3SO_3 ($4H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.6 (m, 10 H, C_6H_5), 2.00 (s, 15 H, Cp*), 2.50 (d, J_{PH} = 12.0 Hz, 3 H, Me), -14.66 (d, J_{PH} = 27.2 Hz, 1 H, Ir-H). IR (CH_2Cl_2): υ(CO) 2040 cm^{-1}.

[Cp*Ir(CO)(PMe_3)(H)]CF_3SO_3 ($5H^+CF_3SO_3^-$). ^{1}H NMR (CD_2Cl_2): δ 2.09 (s, 15 H, Cp*), 1.91 (d, J_{PH} = 12.0 Hz, 9 H, Me), -15.30 (d, J_{PH} = 29.1 Hz, 1 H, Ir-H). IR (CH_2Cl_2): υ(CO) 2038 cm^{-1}.

Reaction of 1-5 with CH_3I. Compounds **1-5** were reacted with CH_3I for NMR characterization of the [Cp*Ir(CO)(PR_3)(CH_3)]I products by dissolving approximately 5 mg of the complex in 0.5 mL of CD_2Cl_2 in a 5 mm NMR tube under nitrogen. To the solution was added 10 equiv of CH_3I with a gas-tight microliter syringe through a rubber septum. The color of the solution changed from yellow to colorless during the time of the study (2 s to 30 min). Both NMR and IR spectra showed the disappearance of the starting material and the appearance of new bands for [Cp*Ir(CO)(PR_3)(CH_3)]I. The spectroscopic data are similar to those for [CpIr(CO)(PR_3)(CH_3)]I[9,17] except the υ(CO) values are lower for the Cp* compounds, which indicates that Cp* is a stronger donor than Cp. Yields of the methylated products as determined by IR and ^{1}H NMR spectroscopy are quantitative.

Compound **$3CH_3^+I^-$** was isolated as a white solid by the reaction of **3** (50 mg) with CH_3I (10 equiv) in Et_2O (5 mL) solution. Analytically pure and X-ray quality crystals of **$3CH_3^+I^-$** were formed by dissolving the white solid in a minimum amount of CH_2Cl_2 and layering the solution with a 3-fold volume of diethyl ether, and then cooling to -20 °C for 24 h.

Spectroscopic data at room temperature for compounds **$1CH_3^+$-$5CH_3^+$** are listed below.

{Cp*Ir(CO)[P(*p*-$C_6H_4CF_3)_3$](CH$_3$)}I ($1CH_3^+I^-$). ^{1}H NMR (CD_2Cl_2): δ 7.6-7.8 (m, 12 H, C_6H_4), 1.84 (d, J_{PH} = 2.4 Hz, 15 H, Cp*), 0.75 (d, J_{PH} = 5.7 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2032 cm^{-1}.

{Cp*Ir(CO)[P(*p*-$C_6H_4Cl)_3$](CH$_3$)}I ($2CH_3^+I^-$). ^{1}H NMR (CD_2Cl_2): δ 7.4-7.7 (m, 12 H, C_6H_4), 1.81 (d, J_{PH} = 2.4 Hz, 15 H, Cp*), 0.70 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2032 cm^{-1}.

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

[Cp*Ir(CO)(PPh$_2$Me)(CH$_3$)]I ($4CH_3^+I^-$). ^{1}H NMR (CD_2Cl_2): δ 7.3-7.5 (m, 10 H, C_6H_5), 1.85 (d, J_{PH} = 2.1 Hz, 15 H, Cp*), 2.37 (d, J_{PH} = 10.5 Hz, 3 H, Me), 0.68 (d, J_{PH} = 5.4 Hz, 3 H, Ir-CH_3). IR (CH_2Cl_2): υ(CO) 2030 cm^{-1}.

[Cp*Ir(CO)(PMe$_3$)(CH$_3$)]I (5CH$_3$$^+I^-$). ^{1}H NMR (CD$_2Cl_2$): δ 2.05 (d, J_{PH} = 2.1 Hz, 15 H, Cp*), 1.82 (d, J_{PH} = 10.8 Hz, 9 H, Me), 0.61 (d, J_{PH} = 6.0 Hz, 3 H, Ir-CH$_3$). IR (CH$_2$Cl$_2$): υ(CO) 2030 cm^{-1}.

Protonation of Phosphines. Phosphines **6-9** were protonated for NMR characterization by dissolving approximately 5 mg of the phosphine in 0.50 mL of CDCl$_3$ in an NMR tube under nitrogen. To the solution was added 1 equiv of CF$_3$SO$_3$H with a gas-tight microliter syringe through a rubber septum. Both ^{1}H and ^{31}P NMR spectra showed the disappearance of the starting material and the appearance of new bands for the [HPR$_3$]CF$_3$SO$_3$. The ^{1}H NMR data for **8** are the same as those reported previously.[16] Yields of the protonated products as determined by ^{1}H NMR spectroscopy are quantitative. Spectroscopic data at room temperature for **6-8** and **6H$^+$-8H$^+$** are listed below.

P(2-C$_6$H$_4$OMe)$_3$ (6). ^{1}H NMR (CDCl$_3$): δ 3.74 (s, 9 H), 6.65 (m, 3 H), 6.85 (m, 6 H), 7. 32 (m, 3 H).

P[(2,6-C$_6$H$_3$(OMe)$_2$]$_3$ (7). ^{1}H NMR (CDCl$_3$): δ 3.47 (s, 18 H), 6.45 (dd, 8.4 Hz, 3.0 Hz, 6 H), 7.12 (td, 8.1 Hz, 0.6 Hz, 3 H). ^{31}P NMR (CDCl$_3$): δ 10.17 (s).

P[2,4,6-C$_6$H$_2$(OMe)$_3$]$_3$ (8). ^{1}H NMR (CDCl$_3$): δ 3.49 (s, 18 H), 3.78 (s, 9 H), 6.03 (d, 2.4 Hz, 6 H). ^{31}P NMR (CDCl$_3$): δ 8.99 (s).

[HP(2-C$_6$H$_4$OMe)$_3$] CF$_3$SO$_3$ (6H$^+$CF$_3$SO$_3$$^-$). ^{1}H NMR (CDCl$_3$): δ 3.82 (s, 9 H), 7.05 (m, 9 H), 7. 64 (m, 3 H), 8.65 (d, J_{PH} = 530 Hz, 1 H).

{HP[(2,6-C$_6$H$_3$(OMe)$_2$]$_3$}CF$_3$SO$_3$ (7H$^+$CF$_3$SO$_3$$^-$). ^{1}H NMR (CDCl$_3$): δ 3.68 (s, 18 H), 6.64 (dd, 8.4 Hz, 5.7 Hz, 6 H), 7.59 (t, 8.4 Hz, 3 H), 8.50 (d, J_{PH} = 533 Hz, 1 H). ^{31}P NMR (CDCl$_3$): δ -50.17 (s).

$\{HP[2,4,6\text{-}C_6H_2(OMe)_3]_3\}$ CF_3SO_3 ($8H^+CF_3SO_3^-$). ^1H NMR ($CDCl_3$): δ 3.69 (s, 18 H), 3.88 (s, 9 H), 6.17 (bs, 6 H), 8.35 (d, J_{PH} = 541 Hz, 1 H). ^{31}P NMR ($CDCl_3$): δ -52.23 (s).

It has been reported[16] that **8** (pK_a = 11.2, cone angle = 184°) reacts with CH_2Cl_2 to form $ClCH_2PR_3^+Cl^-$ in $t_{1/2} < 15$ min, with (i-Pr)Br in 1 h, and with (i-Pr)Cl in 15 h. We found that **8** reacts with DCE solvent within 50 min at room temperature; reaction of **7** with DCE cannot be detected for 20 h; **6** and **9** are stable in DCE. The NMR results are given below.

Product of the Reaction of 7 with DCE. ^1H NMR ($CDCl_3$): δ 3.65 (s, 18 H), 6.67 (dd, 8.4 Hz, 5.4 Hz, 6 H), 7.59 (t, 8.4 Hz, 3 H), 3.74 (bs, 4 H). ^{31}P NMR ($CDCl_3$): δ 2.32 (s).

Product of the Reaction of 8 with DCE. ^1H NMR ($CDCl_3$): δ 3.66 (s, 18 H), 3.92 (s, 9 H), 6.16 (d, J_{PH} = 4.8 Hz, 6 H), 3.74 (bs, 4 H). ^{31}P NMR ($CDCl_3$): δ 8.98 (s).

Calorimetric Studies. Determinations of the heats of protonation (ΔH_{HM}) of the $Cp^*Ir(CO)(PR_3)$ complexes with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25 °C were performed using a Tronac Model 458 isoperibol calorimeter as originally described[18] and then modified.[14] Typically a run consisted of three sections:[19] initial heat capacity calibration, titration, and final heat capacity calibration. Each section was preceded by a baseline aquisition period. A 2-min titration period was used for all complexes. A 5-mL aliquot of a freshly prepared solution of the complex (weighed in a N_2-filled glovebox) in DCE (approximately 0.020 M) was injected into the reaction Dewar vessel via syringe, followed by 45 mL of DCE. During the titration period, approximately 0.8 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE solvent was added at a constant rate (0.3962 mL/min) to 50.0 mL of a 1.7 mM solution of the complex (5-10% excess) in DCE at 25.0 °C. Infrared spectra of the titrated solution showed υ(CO) bands for the Cp*Ir(CO)(PR$_3$)H$^+$ products and weak bands for the excess Cp*Ir(CO)(PR$_3$) reactants.

The ΔH_{HM} values for each complex were measured using two different standardized acid solutions and are reported as the average of at least four titrations and as many as six. The heat of dilution (ΔH_{dil}) of the acid in DCE (-0.2 kcal/mol)[20] was used to correct the reaction enthalpies. The error in ΔH_{HM} is reported as the average deviation from the mean of all the determinations (Table 1).

The accuracy of the calorimeter was established before each set of ΔH_{HM} determinations by titrating 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (-37.0 ± 0.3 kcal/mol; literature value,[18] -37.2 ± 0.4 kcal/mol).

Determinations of the heats of protonation (ΔH_{HP}) of the phosphines **6-9** with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C were performed in the same manner as described above. A 3-min titration period was used for these studies. The phosphine solutions were prepared by adding the solid compound to the argon-filled Dewar flask. The flask was then attached to the calorimeter's insert assembly and flushed with argon; then 50 mL of DCE was added by syringe.

Kinetic Studies of the Reactions (eq 2) of Cp*Ir(CO)(PR$_3$) (PR$_3$ = P(*p*-C$_6$H$_4$CF$_3$)$_3$, P(*p*-C$_6$H$_4$Cl)$_3$) with CH$_3$I. In a typical experiment, 2-10 mg of Cp*Ir(CO)(PR$_3$) and 10 mg (0.0410 mmol) of the internal standard Ph$_3$CH (recrystallized from ethanol[11]) were introduced into a 5 mm NMR tube. To the tube at 25.0 °C was added a 0.50 mL solution of CH_3I in CD_2Cl_2. The ^1H NMR spectrum was taken with the VXR 300 NMR spectrometer using the methine proton of Ph_3CH (5.56 ppm) as the internal reference. A 15 s pulse delay was used to ensure complete relaxation of all the protons. Integrals of peaks at ~1.9 ppm (Cp*, product), 5.56 (Ph_3CH), ~1.8 (Cp*, reactant), 2.15 (free CH_3I), and ~0.7 (Ir-CH_3, product) were obtained from each of the 15-18 spectra recorded over a period of three half times. The sum of the integrals of all reactants and products was constant throughout each kinetic run. The initial concentrations of $[Ir]_0$ were calculated by eq 4, while the initial concentrations of $[CH_3I]_0$ were calculated by eq 5 using integrations of proton NMR resonances of each species,

$$[Ir]_0 = \frac{(I_{Cp*}{}^{p} + I_{Cp*}{}^{r})[Ph_3CH]}{15 \times I_S} \tag{4}$$

$$[MeI]_0 = \frac{(I_{MeI} + I_{Ir\text{-}Me})\,[Ph_3CH]}{3 \times I_S} \tag{5}$$

where $I_{Cp*}{}^{p}$ = integral of product Cp* signal, $I_{Cp*}{}^{r}$ = integral of reactant Cp* signal, $[Ph_3CH]$ = concentration of internal standard Ph_3CH, M, I_S = integral of the methine proton of Ph_3CH, I_{MeI} = integral of reactant CH_3I signal, and $I_{Ir\text{-}Me}$ = integral of product Ir-Me signal. The $[Ir]_0$ and $[CH_3I]_0$ concentrations in Table 2 are averages of the concentrations obtained from 15-18 spectra. Second-order rate constants k were calculated from eq 6 as described previously.[9] The reproducibility of rate constants is ±10% or better.

When a < 10 ; $$\ln\left[a + (a-1)\frac{I_{Cp^*}{}^{p}}{I_{Cp^*}{}^{r}}\right] = \ln a + (a-1)\,[\mathrm{Ir}]_0\,kt \qquad (6)$$

where $a = [CH_3I]_0 / [Ir]_0$

Kinetic Studies of the Reactions (eq 2) of Cp*Ir(CO)(PR$_3$) (PR$_3$ = PPh$_3$, PPh$_2$Me, PMe$_3$) with CH$_3$I. Since the rates of reaction of these three compounds were too fast to be measured by ^{1}H NMR spectroscopy, we used the following technique. All the kinetic experiments were carried out at 25.0 ± 0.2 °C under argon using a Shimadzu UV-3101PC spectrophotometer equipped with an internal timer and a thermostated cell-holder. The rates of reaction were monitored directly by following the disappearance of the band at 312 nm for the Cp*Ir(CO)(PR$_3$) complexes. Since the ratio $[CH_3I]_0 / [Ir]_0$ was greater than 10, the absorbance (A)-time data were fitted to the pseudo-first-order eq 7

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}\cdot t) \qquad (7)$$

by use of the programs Spectracalc or GraFit in order to obtain k_{obs} values.[21] The k values were calculated from the expression: $k = k_{obs} / [\,MeI]_0$. The rates of the reactions were not noticeably affected by wrapping the flasks in aluminum foil.

Results

Syntheses of Iridium Complexes 1-5. The complexes Cp*Ir(CO)(PR$_3$) (PR$_3$ = PEt$_3$, P(OMe)$_3$, P(O-i-Pr)$_3$) were previously prepared by refluxing Cp*Ir(CO)$_2$ with the phosphine or phosphite in toluene.[15] However, of the phosphines used in the present study only PMe$_3$ gave the product (**5**) under these conditions. For all of the other phosphines, it was necessary to use the higher boiling solvent decane (b.p. 174 °C) (eq 8).

$$Cp^{*}Ir(CO)_2 + PR_3 \xrightarrow[\text{reflux}]{\text{decane}} Cp^{*}Ir(CO)(PR_3) \tag{8}$$

PR_3 = P(*p*-$C_6H_4CF_3)_3$, **1**, 75%; P(*p*-$C_6H_4Cl)_3$, **2**, 83%; PPh_3, **3**, 90%;
PPh_2Me, **4**, 78%; PMe_3, **5**, 75%

Complexes **1-5** have the half-sandwich geometry shown in eq 1; this was confirmed for **2** by an X-ray crystallographic determination;[22] its structure is similar to that of $CpIr(CO)(PPh_3)$.[23] The compounds were characterized by ^1H NMR and IR spectroscopy (see Experimental Section). All of compounds **1-5** are air-sensitive in the solid state; so, they were stored under N_2, and solutions were prepared using dry deaerated solvents.

Characterization of Reaction Products in Equations 1 and 2. Quantitative formation of the three-legged piano-stool complexes $\mathbf{1H^+CF_3SO_3^-}$ - $\mathbf{5H^+CF_3SO_3^-}$ occurs upon addition of 1 equiv of CF_3SO_3H to the neutral complexes **1 - 5** (eq 1) as established by ^1H NMR and IR spectroscopy. The Ir-H resonances in their ^1H NMR spectra occur as doublets between -14.05 ppm ($\mathbf{1H^+}$) and -15.30 ppm ($\mathbf{5H^+}$) with $^2J_{PH}$ = 26-29 Hz due to coupling with the phosphine phosphorus, which is typical of hydrides.[24] The υ(CO) band in $\mathbf{1H^+}$-$\mathbf{5H^+}$ is ~ 130 cm^{-1} higher than that in the **1-5** complexes (see Experimental section). The protonated complexes are air-sensitive in solution. Their IR and ^1H NMR spectra are similar to those of $[CpIr(CO)(PR_3)H]^+CF_3SO_3^-$[9,14] which have been previously characterized. The complex **$3H^+CF_3SO_3^-$** was isolated as a white solid from the reaction of **3** with CF_3SO_3H in Et_2O.

The reactions of **1 - 5** with CH_3I in CD_2Cl_2 quantitatively result in colorless solutions of **$1CH_3^+$ - $5CH_3^+$** (eq 2) as observed by ^1H NMR spectroscopy. The Ir-CH_3 ^1H NMR resonances occur as doublets between 0.75 ppm (**$1CH_3^+$**) and 0.61 ppm (**$5CH_3^+$**) with $^2J_{PH}$ = ~ 5-6 Hz due to coupling with the phosphine phosphorus. The υ(CO) bands are ~ 120 cm^{-1} higher than those of the neutral precursor complexes **1-5** (see Experimental section). The somewhat higher (~10 cm^{-1}) υ(CO) values for $Cp^*Ir(CO)(PR_3)(H)^+$ than $Cp^*Ir(CO)(PR_3)(CH_3)^+$ indicates that the H^+ ligand is more electron-withdrawing than CH_3^+. The IR and ^1H NMR spectra of **$1CH_3^+$ - $5CH_3^+$** are similar to those of $CpIr(CO)(PR_3)(CH_3)^+$ which have been characterized previously.[9] Complexes **$2CH_3^+$** and **$3CH_3^+$** were isolated as white solids.

Calorimetric Studies. The heats of protonation (ΔH_{HM}) determined by calorimetric titration of the $Cp^*Ir(CO)(PR_3)$ complexes with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) at 25.0 °C according to eq 1 are presented in Table 1. 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 were linear for these compounds.[19] Titrations of the very air sensitive complexes **4** and **5** 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 was only ~ 5% of the titration slope indicating that the heat contributed by decomposition is small and the effect on the ΔH_{HM} values is probably within the experimental error.

The heats of protonation (ΔH_{HP}) of the phosphines **6**, **7** and **9** according to eq 3 are also presented in Table 1. The titration of phosphine **8** was unsuccessful due to its reaction with the DCE solvent, as was evident from the release of heat before the acid titration began. The product of this reaction was probably $\{(ClCH_2CH_2)P[2,4,6\text{-}C_6H_2(OMe)_3]_3\}^+Cl^-$.

Kinetic Studies. Rate studies of the reactions (eq 2) of complexes **1-5** with CH_3I showed that they obeyed the rate law: Rate = $k[Cp^*Ir(CO)(PR_3)][CH_3I]$. For the reactions of **3-5** where a 10-fold excess of CH_3I was used, plots (Figure 1) of pseudo-first-order rate constants k_{obs} vs $[CH_3I]_0$ gave straight lines with near-zero intercepts. The observed rate constants (k_{obs}) and the second-order rate constants ($k = k_{obs} / [MeI]_0$) are listed in Table 2; average k values are collected in Table 3. The values of k were generally reproducible within ±10%.

Discussion

Basicities of $Cp^*Ir(CO)(PR_3)$ Complexes 1-5. As has been noted in previous studies of basicities (ΔH_{HM} or pK_a)[6,25] of transition metal complexes, increasing the basicities of the ligands bound to a metal increases the basicity of the metal. In the $CpIr(CO)(PR_3)$ series of complexes,[9,14] the $-\Delta H_{HM}$ values range from 28.0 kcal/mol for $CpIr(CO)[P(p\text{-}C_6H_4CF_3)_3]$ to 33.2 for $CpIr(CO)(PMe_3)$ and there is a linear correlation (eq 9) between the metal basicity (ΔH_{HM}) and phosphine basicity (ΔH_{HP}, eq 3). In the $Cp^*Ir(CO)(PR_3)$

$$-\Delta H_{HM} = 23.9 + 0.300(-\Delta H_{HP}),\ \text{in kcal/mol} \tag{9}$$

series of complexes, the basicities ($-\Delta H_{HM}$, eq 1) of the complexes generally increase with the basicities of phosphine ligands (Table 1):

$P(p\text{-}C_6H_4CF_3)_3$ (33.8 kcal/mol) < $P(p\text{-}C_6H_4Cl)_3$ (36.9) < PPh_3, PPh_2Me (37.1) < PMe_3 (38.0)

However, there is a poor correlation between ΔH_{HM} and ΔH_{HP} resulting from the very similar ΔH_{HM} values for the complexes (**2**, **3**, **4**) with the $P(p\text{-}C_6H_4Cl)_3$ (36.9 kcal/mol), PPh_3 (37.1), and PPh_2Me (37.1) ligands, respectively. The ΔH_{HM} values for these compounds have been measured many times with up to four different acid concentrations, each standardized independently. In all cases, the ΔH_{HM} values are reproducible within our normal error limits (±0.2 or 0.3). We do not understand why the ΔH_{HM} values do not correlate with ΔH_{HP}, especially because excellent correlations are observed in $CpIr(CO)(PR_3)$,[9,14] and other series of phosphine complexes $Fe(CO)_3(PR_3)_2$,[14] $W(CO)_3(PR_3)_3$,[26] and $CpOs(PR_3)_2Br$.[27]

The availability of $-\Delta H_{HM}$ for $Cp^*Ir(CO)(PPh_3)$ (37.1 kcal/mol) allows one to determine the effect on Ir basicity of replacing a CO ligand in $Cp^*Ir(CO)_2$ (21.4 kcal/mol)[14] by PPh_3. The large increase in $-\Delta H_{HM}$ by 15.7 kcal/mol indicates that the equilibrium constant for protonation of $Cp^*Ir(CO)(PPh_3)$ is 3.5×10^{11} larger than for $Cp^*Ir(CO)_2$; this estimate [$\Delta\Delta H_{HM} = \Delta\Delta G = -RT \ln (K_2/K_1)$] assumes that ΔS is the same for the protonation of both complexes. The $\Delta\Delta H_{HM}$ difference (15.7 kcal/mol) confirms an earlier indirect estimate (14.4 kcal/mol) for the difference in basicities between $Cp'Ir(CO)(PPh_3)$ and $Cp'Ir(CO)_2$ complexes.[11] The effect of replacing a CO ligand by a phosphine on metal basicity has also been observed in pK_a values for the following pairs of compounds determined in MeCN: $HCo(CO)_4$ (8.3) vs $HCo(CO)_3(PPh_3)$ (15.4),[28] $HMn(CO)_5$ (14.1) vs $HMn(CO)_4(PPh_3)$ (20.4),[28] $CpW(CO)_3H$ (16.1) vs $CpW(CO)_2(PMe_3)H$ (26.6),[28] $CpCr(CO)_3H$ (13.3) vs $CpCr(CO)_2(PPh_3)H$

(21.8),[29a,b] and $CpW(CO)_3H^{+\cdot}$ (-3.3) vs $CpW(CO)_2(PMe_3)H^{+\cdot}$ (5.1).[30] It is evident, however, from these data that substitution of CO by PR_3 does not cause the same magnitude of increase in metal basicity in all metal complexes.

Effects of Cp* and Cp on Metal Basicity (ΔH_{HM}) in Cp'Ir(CO)(PR_3). In order to understand the effects of Cp* and Cp on the basicitities of the CpIr(CO)(PR_3) complexes, we examined differences ($\Delta\Delta H_{HM}$ in Table 3) between ΔH_{HM} values for Cp*Ir(CO)(PR_3) and their CpIr(CO)(PR_3) analogs. The values of $\Delta\Delta H_{HM}$ range from 4.8 to 7.7 kcal/mol following no obvious trend. The average value (6.2 kcal/mol) is similar to that (5.7) for the Cp'Ir(COD) compounds,[20] where Cp' is Cp* or Cp. Other $\Delta\Delta H_{HM}$ values for Cp* vs Cp complexes are $Cp'Ru(PMe_3)_2Cl$ (9.0 kcal/mol)[27] and $Cp'Ru(PPh_3)_2H$ (5.5).[27] This effect of the Cp' ligand on metal basicity has also been found in pK_a values for the following pairs of compounds determined in MeCN: $Cp^*Mo(CO)_3H$ (17.1) vs $CpMo(CO)_3H$ (13.9),[28] $Cp^*Fe(CO)_2H$ (26.3) vs $CpFe(CO)_2H$ (20.2),[28] $Cp^*Cr(CO)_3H$ (16.1) vs $CpCr(CO)_3H$ (13.3),[29c] and $Cp^*Mo(CO)_3H^{+\cdot}$ (-2.5) vs $CpMo(CO)_3H^{+\cdot}$ (-6.0).[30] Thus, the basicity enhancement caused by the replacement of Cp by Cp* depends on the metal and the ligands in the complex.

Effects of Cp* and Cp on Rate Constants for the Reaction (eq 2) of Cp'Ir(CO)(PR_3) with CH_3I. The reactions of compounds **1-5** with CH_3I (eq 2) obey a second order rate law: Rate = k[Cp*Ir(CO)(PR_3)] [CH_3I]. Analogous reactions of CpIr(CO)(PR_3) followed the same rate law.[9,17] This rate law suggests that the mechanism of these reactions involves nucleophilic attack of the iridium in the complex on the carbon of the CH_3I which results in displacement of the I^- and formation of the $[Cp^*Ir(CO)(PR_3)(CH_3)]^+I^-$ product.

Thus, we consider the rate constants (k) a measure of the nucleophilicities of the complexes.

In order to understand the effects of Cp* and Cp on these nucleophilicities, we plot (Fig. 2) log k values (Table 3) versus the basicities ($-\Delta H_{HP}$) of the PR_3 ligands in the complexes. These correlations (eq 10 and 11)

$$\log k = -3.43 + 0.155(-\Delta H_{HP}),\ r=0.99,\ \text{for}\ Cp^{*}Ir(CO)(PR_3) \qquad (10)$$

$$\log k = -4.64 + 0.140(-\Delta H_{HP}),\ r=0.99,\ \text{for}\ CpIr(CO)(PR_3) \qquad (11)$$

show that the metal becomes more nucleophilic as its PR_3 ligand becomes more basic. Within experimental error, the slopes, i.e., the coefficients for the $-\Delta H_{HP}$ terms in eq 10 and 11, are the same for both the Cp* and Cp complexes. Thus, for all $Cp'Ir(CO)(PR_3)$ pairs of complexes, the rate constant for the reaction of the Cp* complex is approximately 40 times larger than that for the analogous Cp complex. This presumably reflects the greater electron-donating ability of the Cp* ligand, as was also noted in the ΔH_{HM} values above.

In order to determine if the Cp* ligand exerts a steric effect in addition to its electronic effect, we compare the nucleophilicities (log k) of the Cp* and Cp compounds in relation to measures of their electron-richness ($E_{1/2}$) or basicity ($-\Delta H_{HM}$). In Fig. 3(a) are plotted (open circles) for $CpIr(CO)(PR_3)$ log k vs $E_{1/2}$ (given as the reduction potential)[31] for the oxidation of the complex to $CpIr(CO)(PR_3)^+$; as expected, there is a correlation (eq 12) between the ease of

$$\log k = 3.69 - 10.66(E_{1/2}),\ r = 0.99,\ \text{for}\ CpIr(CO)(PR_3) \qquad (12)$$

oxidation and nucleophilicity. Also shown on the plot are points (solid circles) for the $Cp^{*}Ir(CO)(PR_3)$ complexes. Clearly, log k values for all of the Cp* complexes are smaller than predicted from their $E_{1/2}$ values and the $CpIr(CO)(PR_3)$ correlation (eq 12). This suggests that the steric size of the Cp* ligand is reducing the nucleophilicity of the Ir center from its expected value based on the electron-richness of the metal ($E_{1/2}$). Similarly, a plot (Fig. 3(b)) of log k vs $-\Delta H_{HM}$ for the $CpIr(CO)(PR_3)$ complexes (open circles) gives a linear correlation (eq 13),[9] which shows that the nucleophilicities of the

$$\log k = -15.8 + 0.47(-\Delta H_{HM}),\ r = 0.99, \text{ for } CpIr(CO)(PR_3) \qquad (13)$$

$CpIr(CO)(PR_3)$ complexes increase as their basicities increase. However, the nucleophilicities (log **k**) of the $Cp^*Ir(CO)(PR_3)$ complexes (solid circles) are again all substantially below those predicted by the $CpIr(CO)(PR_3)$ correlation (eq 13). Thus, it appears that while the $Cp^*Ir(CO)(PR_3)$ complexes are more nucleophilic than their Cp analogs, they are less nucleophilic than predicted by electronic considerations ($E_{1/2}$ and $-\Delta H_{HM}$) alone. This result strongly suggests that it is the steric properties of the Cp* ligand which make its $Cp^*Ir(CO)(PR_3)$ complexes less nucleophilic than predicted. It is evident from Fig.3 that log k values for the $Cp^*Ir(CO)(PR_3)$ complexes not less than the predicted values (eqs 12 and 13) by a constant amount. Thus, the steric effect of Cp* on log k is also a function of the phosphine ligands and perhaps other properties of the complexes.

Basicities (ΔH_{HP}) of Phosphines. Basicities (Table 2) of the tris(methoxyphenyl)phosphines increase in the order:

$P(4\text{-}C_6H_4OMe)_3$ (24.1 kcal/mol)[18] < $P(2\text{-}C_6H_4OMe)_3$ (**6**, 25.5) << $P[(2,6\text{-}C_6H_3(OMe)_2]_3$ (**7**, 33.8) < $P[2,4,6\text{-}C_6H_2(OMe)_3]_3$ (**8**, 36.7)

The $-\Delta H_{HP}$ value of $P[2,4,6\text{-}C_6H_2(OMe)_3]_3$ (**8**) could not be determined experimentally because of its reaction reacts with DCE under the conditions of the calorimetric titrations. However, it can be estimated using eq 14,

$$-\Delta H_{HP} = 1.82pK_a(H_2O) + 16.3, \text{ in kcal/mol} \qquad (14)$$

which correlates[18] ΔH_{HP} and pK_a values of 12 phosphines. With this equation, the reported pK_a (11.2)[32] of **8** can be used to estimate the $-\Delta H_{HP}$ value (36.7 kcal/mol). Thus, **8** is much more basic than pyridine (29.3 kcal/mol)[6] but is not as basic as Et_3N (39.3).[6] The electron-donating ability of the methoxy groups makes **7** (33.8 kcal/mol) as basic as PEt_3 (33.7),[18] although its cone angle is much larger (close to **8**, 184°)[16] than that (132°) for PEt_3.[33a] The pK_a (9.61) of **7** calculated with eq 14 is in reasonable agreement with that (9.33)[32] obtained by a titration method. The calculated pK_a (5.05) of **6** is also similar to that (4.47) determined by titration.[32]

The basicities ($-\Delta H_{HP}$) of the tris(methylphenyl)phosphines increase in the order: $P(2\text{-}C_6H_4Me)_3$ (22.6 kcal/mol)[18] <$P(4\text{-}C_6H_4Me)_3$ (23.2)[18] << $P(2,4,6\text{-}C_6H_2Me_3)_3$ (**9**, 29.4). The pK_a for $P(2,4,6\text{-}C_6H_2Me_3)_3$ estimated with use of eq 14 is 7.20. The basicity ($-\Delta H_{HP}$) of **9** is intermediate between that of $PPhMe_2$ (28.4 kcal/mol) and PMe_3 (31.6).[6]

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Table 1. Heats of Protonation of $Cp^*Ir(CO)(PR_3)$ Complexes (ΔH_{HM}) and Phosphines (ΔH_{HP})

Compound	$-\Delta H_{HM}$ kcal/mol[a, b]	$-\Delta H_{HP}$ kcal/mol[a, b]
$Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$, **1**	33.8 (2)	13.6 (2)[c]
$Cp^*Ir(CO)[P(p\text{-}C_6H_4Cl)_3]$, **2**	36.9 (2)	17.9 (2)[c]
$Cp^*Ir(CO)(PPh_3)$, **3**	37.1 (2)	21.2 (1)[c]
$Cp^*Ir(CO)(PPh_2Me)$, **4**	37.1 (3)	24.7 (0)[c]
$Cp^*Ir(CO)(PMe_3)$, **5**	38.0 (2)	31.6 (2)[c]
$P(2\text{-}C_6H_4OMe)_3$, **6**		25.5 (2)
$P[2,6\text{-}C_6H_3(OMe)_2]_3$, **7**		33.8 (2)
$P(2,4,6\text{-}C_6H_2Me_3)_3$, **9**		29.4 (2)

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

Table 2. Rates of Reaction (eq 2) of $Cp^*Ir(CO)(PR_3)$ with CH_3I at 25.0 °C

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

Table 2. Cont'd

	0.10	2.12	21	5.32	25.1
	0.10	2.67	27	6.60	24.7
	0.10	3.20	32	8.20	25.6
	0.10	3.73	37	9.00	24.1

[a]Average concentrations obtained from 15-18 spectra calculated using eq 4. [b]Average concentrations obtained from 15-18 spectra calculated using eq 5. [c]Ratio of $[MeI]_0$ / $[Ir]_0$. [d]Calculated using eq 7. [e]Calculated from k_{obs} or using eq 6. [f]Reaction rate monitored by ^1H NMR in CD_2Cl_2. [g]Reaction rate monitored by UV-Vis spectroscopy at 312 nm in CH_2Cl_2.

Table 3. Comparison of ΔH_{HM} [a] and k [b] Values for Cp*Ir(CO)(PR_3) and CpIr(CO)(PR_3) Complexes

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

[a] $-\Delta H_{HM}$ in kcal/mol. [b] k in $M^{-1}s^{-1}$. [c] For Cp*Ir(CO)(PR_3). [d] For CpIr(CO)(PR_3); see reference 9.

Figure Captions

Figure 1. Dependence of k_{obs} on $[CH_3I]_0$ for the reactions of $Cp^*Ir(CO)(PR_3)$ with CH_3I in CH_2Cl_2 at 25.0 °C

Figure 2. Plot of log k for eq 2 vs $-\Delta H_{HP}$ for PR_3 (eq 3). Comparison of the effect of Cp* and Cp ligands on the nucleophilicities of $Cp'Ir(CO)(PR_3)$ complexes.

Figure 3. (a) Plot of log k (for eq 2) vs $E_{1/2}$. (b) Plot of log k (for eq 2) vs $-\Delta H_{HM}$ (for eq 1). Open circles for $CpIr(CO)(PR_3)$. Solid circles for $Cp^*Ir(CO)(PR_3)$.

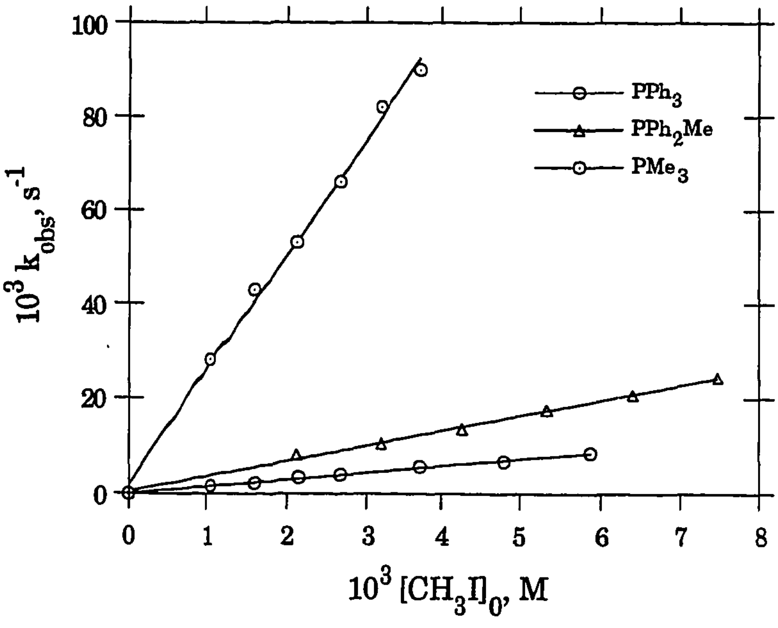

Figure 1. Dependence of k_{obs} on $[CH_3I]_0$ for the reactions of Cp*Ir(CO)(PR_3) with CH_3I in CH_2Cl_2 at 25.0 °C

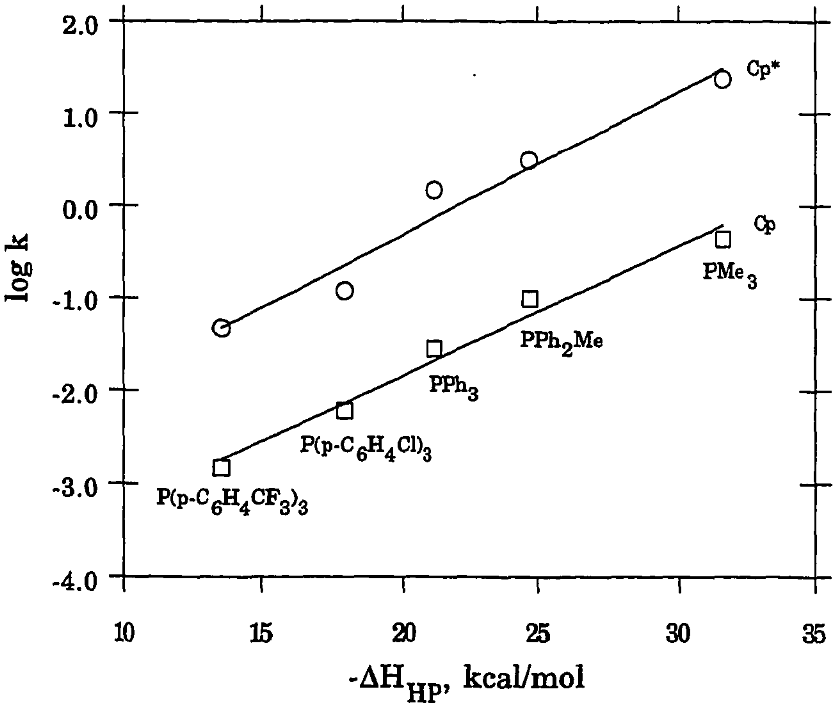

Figure 2. Plot of log k for eq 2 vs $-\Delta H_{HP}$ for PR_3 (eq 3). Comparison of the effect of Cp* and Cp ligands on the nucleophilicities of Cp'Ir(CO)(PR_3) complexes.

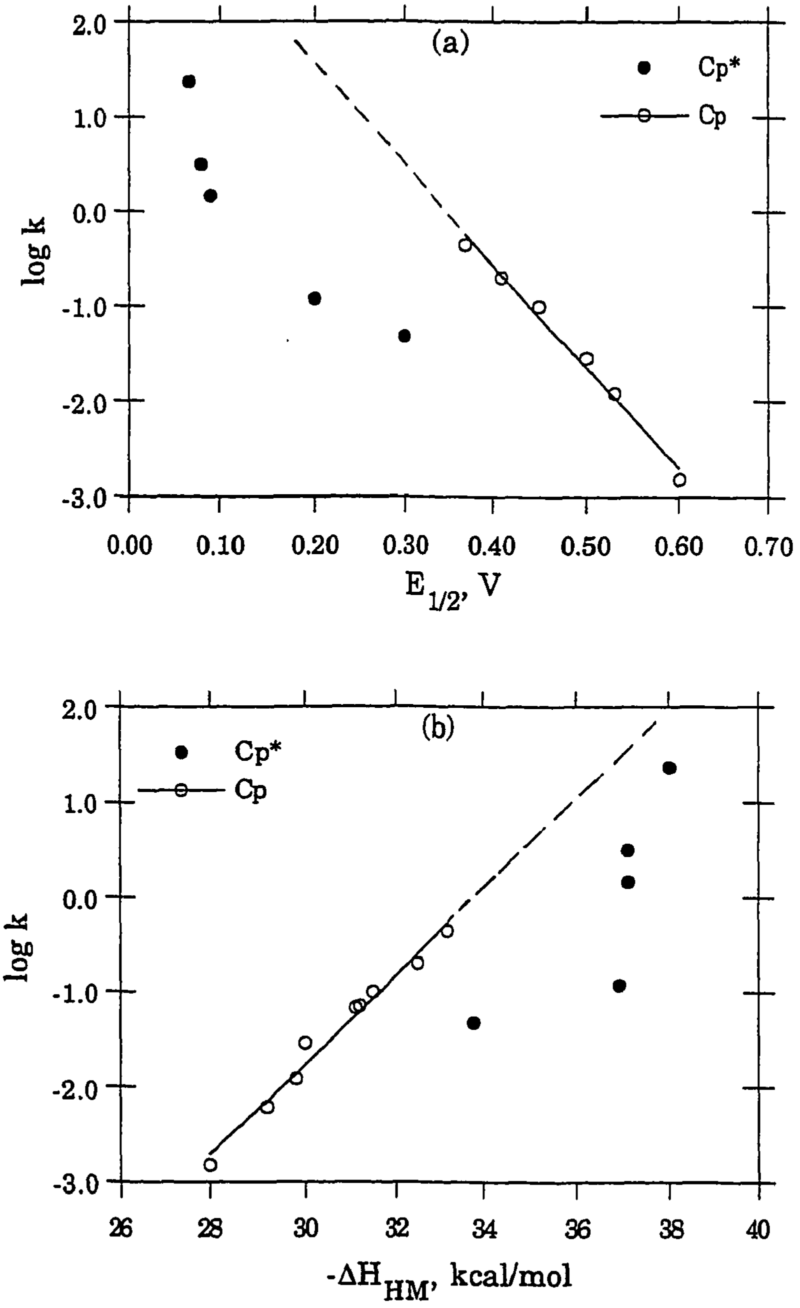

Figure 3. (a) Plot of log k (for eq 2) vs $E_{1/2}$. (b) Plot of log k (for eq 2) vs $-\Delta H_{HM}$ (for eq 1). Open circles for $CpIr(CO)(PR_3)$. Solid circles for $Cp^*Ir(CO)(PR_3)$.

METAL-HYDROGEN BOND DISSOCIATION ENTHALPIES IN SERIES OF COMPLEXES OF EIGHT DIFFERENT TRANSITION METALS

A paper submitted to *Journal of the American Chemical Society*

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Abstract

Homolytic bond dissociation enthalpies (BDEs) of the mononuclear cationic metal hydride complexes HML_n^+, where ML_n = $Cr(CO)_2(dppm)_2$, $Mo(CO)_2(L\text{-}L)_2$, $W(CO)_3(PR_3)_3$, $W(CO)_2(dppm)_2$, $W(CO)_3(tripod)$, $W(CO)_3(triphos)$, $Cp^*Re(CO)_2(PR_3)$, $Fe(CO)_3(PR_3)_2$, $Fe(CO)_3(L\text{-}L)$, Cp^*_2Ru, $CpRu(PMe_3)_2I$, $CpRu(L\text{-}L)H$, $CpRu(PPh_3)_2H$, Cp^*_2Os, $CpOs(PR_3)_2Br$, $CpOs(PPh_3)_2Cl$, $CpOs(PPh_3)_2H$, $CpIr(CO)(PR_3)$, $CpIr(CS)(PPh_3)$, $(C_5Me_nH_{5-n})Ir(COD)$, $Cp^*Ir(CO)(PR_3)$, and $Cp^*Ir(CO)_2$ have been estimated by use of a thermochemical cycle that requires a knowledge of the heats of protonation (ΔH_{HM}) and oxidation potentials ($E_{1/2}$) of the neutral metal complexes (ML_n). Excellent correlations were found between $-\Delta H_{HM}$ and $E_{1/2}$ within related series of complexes. The BDE values obtained by this method fall in the range 56-75 kcal/mol. For related complexes of a given metal, the energy required for homolytic M-H bond cleavage (BDE) increases linearly as $-\Delta H_{HM}$ for heterolytic M-H bond cleavage increases. The M-H BDE values are greater for third-row than second-row and first-row metals, the difference being 1-12 kcal/mol. Other trends in BDE values are also discussed.

Introduction

There is great interest in transition-metal hydrides, both because of their unusual reactivities and their potential as homogeneous catalysts for hydrogenation and other reactions of organic substrates.[1] In order to understand the mechanisms and thermodynamics of these catalytic reactions, a knowledge of metal-hydrogen bond enthalpies is essential. Cleavage of the M-H bond in transition metal hydrides can yield a hydrogen atom (H·), a proton (H^+), or a hydride (H^-) ion. The energy associated with H· cleavage (eq 1) is

$$\text{M-H} \longrightarrow \text{M}\cdot + \text{H}\cdot\ ; \quad \text{BDE} \qquad (1)$$

defined as the homolytic bond dissociation enthalpy (BDE). The heterolytic cleavage of the M-H bond (eq 2) may be described by either a pK_a or ΔH_{HM} value. The energies for H· and H^+ cleavage from neutral M-H complexes have

$$\text{M-H} \longrightarrow \text{M}^- + \text{H}^+;\ \Delta H_{HM} \text{ or } pK_a \qquad (2)$$

been determined by several research groups using a variety of experimental techniques.[2,3,4] One approach makes use of a thermochemical cycle which involves an oxidation potential, a bond dissociation enthalpy (BDE), and a pK_a value; it allows the estimation of thermodynamic quantities such as pK_a and BDE that are either difficult or impossible to obtain directly. Early work of Breslow[5] used this thermochemical cycle to estimate pK_a values of weak carbon acids in aprotic solvents. More recently, Arnold[6] made use of three different thermochemical cycles to estimate pK_a values of radical cations; and

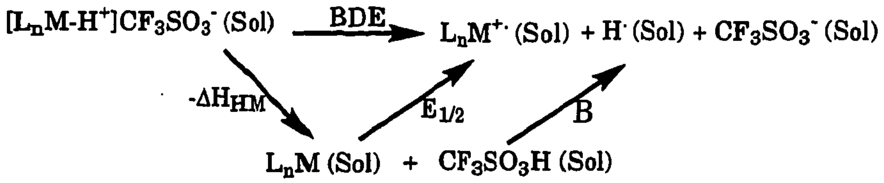
Bordwell[7] estimated a large number of C-H, O-H, and N-H bond dissociation enthalpies (BDE) as well as pK_a's of radical cations. Arnett[8] has combined solution calorimetry and electrochemistry to estimate homolytic and heterolytic bond energies for a number of C-C, C-O, C-S, and C-N bonds. Similar cycles were proposed by Tilset and Parker[3] to estimate metal-hydride BDE and pK_a values for transition-metal hydrides and their cation radicals. In the latter studies, the BDE and pK_a values are related to each other by eq 3.

$$\mathrm{BDE\ (M\text{-}H)} = 1.37\mathrm{p}K_a + 23.06E^\circ_{ox}(\mathrm{M}^-) + 59.5 \qquad (3)$$

The 59.5 kcal/mol constant applies to E°_{ox} values that are measured relative to ferrocene (Fc/Fc$^+$) in acetonitrile/ Bu_4NPF_6 (0.1M) solution. The BDE values determined by this method are based on the known bond dissociation energy of $CpCr(CO)_3H$, which was determined calorimetrically ($D_{Cr\text{-}H}$ = 61.5 ± 0.2 kcal/mol).[9]

In contrast to the situation for neutral M-H complexes, there are few data available for cationic metal-hydrides. In this paper, we present estimates of M-H bond dissociation enthalpies (BDEs) for 18-electron metal hydride cations (L_nMH^+); these include series of complexes of eight transition metals (M = Cr, Mo, W, Re, Fe, Ru, Os, Ir). All of the estimates are based on the

Scheme 1



Solvent: 1,2-dichloroethane (DCE)
Temp: 25.0 °C

thermochemical cycle in Scheme 1, which requires a knowledge of the heats of protonation (ΔH_{HM}) and oxidation potentials ($E_{1/2}$) of the neutral metal complexes (ML_n). The -ΔH_{HM} values were reported previously in a series of papers from this group.[4] In the present paper are given measured $E_{1/2}$ values for the ML_n complexes and calculated BDE values for the M-H bond in fifty-one L_nMH^+ complexes.

Experimental Section

General Procedure. All preparative reactions, chromatography, and manipulations were carried out under an atmosphere of nitrogen or argon with use of vacuum line, Schlenk, syringe or drybox techniques similar to those described in the literature.[10] The solvents were purified under nitrogen as described below using standard methods.[11] Toluene, benzene, decane, hexanes, and methylene chloride were refluxed over CaH_2 and then distilled. Diethyl ether was distilled from sodium benzophenone. 1,2-Dichloroethane (DCE) was purified by washing with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and water again; the solvent was then predried over anhydrous $MgSO_4$, stored in amber bottles over molecular sieves (4 Å), and then distilled from P_4O_{10} under argon immediately before use. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under vacuum (10^{-5} mm Hg) for 12 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2.

The ^1H NMR spectra were obtained on samples dissolved in $CDCl_3$ or CD_2Cl_2 on a Nicolet-NT 300 MHz spectrometer using TMS ($\delta = 0.00$ ppm) as the internal reference. Solution infrared spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1-mm spacers.

Materials. The complexes, decamethylruthenocene (Cp^*_2Ru) and decamethylosmocene (Cp^*_2Os), were purchased from Strem and used without purification. Ferrocene (Cp_2Fe) was purchased from Aldrich and purified by chromatography on a column of neutral alumina, eluting with hexanes. The compounds cis-$Cr(CO)_2(dppm)_2$,[12] cis-$Mo(CO)_2(L\text{-}L)_2$ (L-L = arphos, dppe, dppm),[12] fac-$W(CO)_3(PR_3)_3$ (PR_3 = $PMePh_2$, $PEtPh_2$, PEt_2Ph, PMe_3, PEt_3),[13] $W(CO)_3$(tripod),[14] $W(CO)_3$(triphos),[14] $Cp^*Re(CO)_2(PMe_2Ph)$,[13] $Cp^*Re(CO)_2(PMe_3)$,[13] $CpRu(PMe_3)_2I$,[15] $CpOs(PPh_3)_2Br$,[15] $CpOs(PPh_3)_2Cl$,[15] $CpOs(PPh_2Me)_2Br$,[15] $CpIr(CO)(PR_3)$ [PR_3 = $P(p\text{-}C_6H_4CF_3)_3$, $P(p\text{-}C_6H_4F)_3$, PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, PEt_3, PCy_3),[16] $CpIr(CS)(PPh_3)$,[17] $(C_5Me_nH_{5-n})Ir(COD)$ (n = 0, 1, 3, 4, 5),[18] $Cp^*Ir(CO)(PR_3)$ [PR_3 = $P(p\text{-}C_6H_4CF_3)_3$, $P(p\text{-}C_6H_4Cl)_3$, PPh_3, PPh_2Me, PMe_3],[19] and $Cp^*Ir(CO)_2$[19] were available from previous studies and were purified, if neccessary, before use. Ligand abbreviations are given in Table 1. The compounds $W(CO)_2(dppm)_2$,[12] $Fe(CO)_3(PR_3)_2$ (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3),[17] $Fe(CO)_3(L\text{-}L)$ (L-L = dppp, dppm),[20] $CpOs(PMe_3)_2Br$,[15] and $CpOs(PPh_3)_2H$[15] were prepared according to literature procedures. We are grateful for gifts of CpRu(dppm)H, CpRu(dppe)H, and $CpRu(PPh_3)_2H$ from Dr. R. H. Morris, University of Toronto.

Electrochemical Measurements. The electrochemical measurements were performed using a BAS-100 electrochemical analyzer (Bioanalytical Systems Inc., Purdue Research Park, West Lafayette, IN) equipped with a three-electrode assembly. The platinum working electrode (BAS, 1 mm) was polished with two BAS polishing aluminas (0.3 and 0.05 μ) for one min each and then rinsed with distilled deionized water between polishings; it was rinsed ultrasonically in ethanol for about 5 min before use. A platinum wire (BAS) was used as the auxiliary electrode, and a SCE was used as the reference electrode. The glass electrochemical cell was dried in an oven at 110°C for 4 h, allowed to cool to room temperature in a desiccator, and flushed with nitrogen for 10 min.

In a typical experiment, an amount of the metal complex sufficient to make 10.0 mL of a 1.0 mM solution was weighed into a small Schlenk flask capped with a rubber septum in a N_2-filled glovebox. To the electrochemical cell under nitrogen was added 330 mg (to make 0.10 M) of tetrabutylammonium tetrafluoroborate ($TBABF_4$; 99% pure, Aldrich, recrystallized twice from a 5:1 mixture of diethyl ether:ethanol and dried under vacuum overnight) and 10.0 mL of the solution of the compound in DCE via a syringe. The solution was purged with nitrogen for one min and stirred for 5 min under nitrogen to ensure complete dissolution. The electrochemical measurements were taken immediately after preparation of the solution. This is especially important for the $Cp^*Ir(CO)(PR_3)$ and $CpOs(PPh_3)_2H$ complexes due to their extreme air sensitivity.

The techniques used to determine $E_{1/2}$ were cyclic voltammetry (CV), second harmonic alternating current voltammetry (SHACV),[21] and Osteryoung square wave voltammetry (OSWV);[22] all were performed on the BAS-100 instrument. The ferrocenium/ferrocene redox couple served as the external standard for all measurements, and its $E_{1/2}$ value was checked against the reference electrode before and after each experiment. The $E_{1/2}$

value of Cp^*_2Ru was also checked against the reference electrode before and after each set of measurements, and the $E_{1/2}$ value of Cp^*_2Os was checked occasionally.

CV measurements were made at a scan speed of 100 mV/s. SHACV measurements were made at a scan rate of 5 mV/s and a frequency of 25 Hz. OSWV measurements were made at a scan speed of 60 mV/s (scan frequency 15 Hz and step voltage 4 mV). The square wave voltammetric responses for all of the compounds are peak-shaped and highly symmetrical. In general, the reproducibility of the CV measurements for a scan rate of 100 mV/s was ±10 mV. Reproducibilities of the SHACV measurements were ±20 mV, and ±15 mV for the OSWV measurements.

Results

Electrochemical Measurements. Our use of CV, SHACV[21], and OSWV[22] techniques for the measurement of $E_{1/2}$ values for a variety of organometallic complexes follows Arnett's application of these methods to organic molecules.[8] Smith[21] has also suggested that simple, direct measurement of $E_{1/2}$ should be possible by SHACV even with an EC mechanism where the half-life of the electrode reaction product is in the sub-millisecond range. To illustrate the results obtained by these techniques we show CV, SHACV, and OSWV traces (Figure 1) for the measurement of $E_{1/2}$ for $CpIr(CO)(PPh_2Me)$. The CV trace shows that the oxidation ($E_{ox} = 0.49$ V) is irreversible, whereas the SHACV trace is symmetrical with a sharply delineated $E_{1/2}$ value of 0.46 ± 0.02, and OSWV yields a highly symmetrical peak with $E_{1/2} = 0.44 \pm 0.01$. In general, for complexes that are irreversible by

CV, their $E_{1/2}$ values determined by SHACV and OSWV are the same within ±20 mV. The $E_{1/2}$ values for the reversible oxidation of Cp^*_2Ru obtained from CV (0.684 V), SHACV (0.676 V), and OSWV (0.682 V) are in excellent agreement, and the $E_{1/2}$ values for the reversible oxidation of Cp_2Fe (CV, 0.595; SHACV, 0.598; OSWV, 0.589) are also consistent. These and other comparisons of $E_{1/2}$ values demonstrate that the SHACV and OSWV methods are useful for measuring $E_{1/2}$ values. The error in $E_{1/2}$ for reversible oxidations is 20 mV or less;[3,8] the maximum error in $E_{1/2}$ for oxidations followed by subsequent reaction is ± 80 mV due to possible kinetic shifts.[21c]

The $E_{1/2}$ values, given as reduction potentials vs. SCE at room temperature (23 °C), for the oxidation of all of the complexes in DCE solution are listed in Table 1. The methods by which the $E_{1/2}$ values were determined are also indicated. All of the $E_{1/2}$ values presented in this paper are referenced to the SCE electrode; for those who wish to reference these values to the ferrocene-ferrocenium couple (Fc/Fc^+), the following equation may be used: $E_{1/2}$ (vs. Fc/Fc^+) = $E_{1/2}$ (vs. SCE) -0.59 V. The following data are also presented in Table 1: (a) the heats of protonation ($-\Delta H_{HM}$)[4] of the neutral organometallic compounds (eq 4);

$$L_nM + CF_3SO_3H \xrightarrow[25.0°C]{ClCH_2CH_2Cl} [L_nM(H)](CF_3SO_3)\ ; \qquad \Delta H_{HM} \qquad (4)$$

(b) the heats of protonation ($-\Delta H_{HP}$)[13, 23] of the free phosphines (PR_3) present

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ °C]{ClCH_2CH_2Cl} HPR_3^+CF_3SO_3^-\ ; \qquad \Delta H_{HP} \qquad (5)$$

in the metal complexes (eq 5); and (c) the bond dissociation enthalpies (BDE) obtained from the $-\Delta H_{HM}$ and $E_{1/2}$ values as described below.

Table 2 lists reduction potentials ($E_{1/2}$) for the oxidation of Cp_2Fe, $Cp^*{}_2Ru$, and $CpIr(CO)(PPh_3)$ in DCE solvent as a function of temperature. The observation that $E_{1/2}$ is not temperature dependent indicates that $\Delta S_{redox} \approx 0$ within experimental error for these systems.[8c, f]

Previous Electrochemical Studies of the Compounds. Electrochemical studies of several of complexes related to those in Table 1 have been reported previously. It is evident that $E_{1/2}$ values obtained in different laboratories depend on the experimental conditions. These prior electrochemical studies established that these oxidations are one-electron processes.

cis-$Cr(CO)_2(dppe)_2$ undergoes a one-electron *cis*°/*cis*+ oxidation at -0.59 V (vs Fc/Fc^+) in 0.1 M Bu_4NClO_4 dichloromethane solution.[24a,b] *cis*-$Cr(CO)_2(dppm)_2$ undergoes a one-electron *cis*°/*cis*+ oxidation at 0.01 V (vs Ag/AgCl) in 0.1 M Et_4NClO4 acetone solution.[24c] The $E_{1/2}$ value for *cis*-$Cr(CO)_2(dppm)_2$ in 0.1 M Bu_4NBF_4 1,2-dichloroethane solution in the present study is -0.71 V (vs Fc/Fc^+).

cis-$Mo(CO)_2(dppm)_2$ and *cis*-$Mo(CO)_2(dppe)_2$ undergo one-electron oxidations at 0.30 V and 0.31 V (vs Ag/AgCl), respectively, in 0.1 M Et_4NClO_4 acetone solution.[24c] *cis*-$Mo(CO)_2(dppe)_2$ undergoes a one-electron oxidation at 0.30 V in 0.1 M Bu_4NPF_6/CH_2Cl_2 solution.[25] The $E_{1/2}$ values for the *cis*-$Mo(CO)_2(L\text{-}L)_2$ in the present study occur at 0.28 V for L-L = arphos, 0.24 V for dppe, and 0.18 V for dppm.

The tungsten compound *cis*-$W(CO)_2(dppe)_2$ undergoes a one-electron *cis*°/*cis*+ oxidation at 0.31 V (vs Ag/AgCl) in 0.1 M Et_4NClO_4 acetone solution.[24c] The $E_{1/2}$ value for *cis*-$W(CO)_2(dppm)_2$ in 0.1 M Bu_4NBF_4/DCE solution in the present study is 0.14 V (vs SCE).

The iron complexes $Fe(CO)_3(PR_3)_2$ (PR_3 = PPh_3, 0.33 V; $PMePh_2$, 0.28 V; $(PR_3)_2$ = dppm, 0.16 V) are reported to undergo one-electron oxidations.[26] The compounds $Fe(CO)_3(PR_3)_2$ in Table 1 also undergo reversible one-electron oxidations at the following potentials: 0.55 V for L = PPh_3, 0.49 V for $PMePh_2$, 0.45 V for PMe_2Ph, 0.41 V for PMe_3, and 0.40 V for dppm.

The hydrides $CpRu(PR_3)_2H$ [$(PR_3)_2$ = $(PPh_3)_2$, dppm, dppe, dppp] undergo one-electron oxidations at -0.3 to +0.1 V vs. Fc/Fc^+ in 0.2 M Bu_4NPF_6/CH_2Cl_2 solution;[3,27] these are similar to the $E_{1/2}$ values obtained in the present study for $CpRu(PR_3)_2H$ [$(PR_3)_2$ = $(PPh_3)_2$, 0.23 V; dppm, 0.37 V; dppe, 0.31 V; all vs. Fc/Fc^+].

The compounds Cp^*_2M (M = Ru, Os) undergo one-electron oxidations at 0.12 V for Ru and -0.06 V for Os vs Fc/Fc^+ in MeCN,[29] which are similar to 0.10 V for Ru and -0.08 V for Os vs Fc/Fc^+ in DCE in the present study.

It is well-known that high solution resistance in nonaqueous solvents can lead to large peak separations which can vary from solvent to solvent and with the reference electrode used.[27] Using two solvents under the same conditions, ferrocene was found to exhibit the following peak separations: ΔE_p = 80-95 mV in CH_3CN and ΔE_p = 100-120 mV in CH_2Cl_2.[28] Under our experimental conditions, the peak separations in DCE for reversible compounds, such as Cp_2Fe, Cp^*_2Ru, and Cp^*_2Os, were found to be 80-115 mV. Because separations between the oxidation E_{ox} (by CV) and $E_{1/2}$ (by SHACV or OSWV) peaks for all the compounds undergoing irreversible oxidations by CV are in the 40-60 mV range, this indicates that they are one-electron processes.

Bond Dissociation Enthalpy (BDE) Calculations. Our method of estimating bond dissociation enthalpies of M-H bonds in L_nMH^+ complexes is closely analogous to that of Tilset and Parker.[3] It differs in that we use the heat of protonation (ΔH_{HM}) in place of pK_a. It uses the thermochemical cycle in Scheme 1, which is summarized in eq 6. The constant 33.3 kcal/mol in this

$$\mathrm{BDE}\ (\mathrm{M\text{-}H^+}) = -\Delta H_{HM} + 23.06E_{1/2}\,(\mathrm{M}) + 33.3 \quad \text{in kcal/mol} \tag{6}$$

equation was calculated using our measured $-\Delta H_{HM}$ (26.6 kcal/mol) and $E_{1/2}$ (0.51 V) data and the known BDE value (71.7 kcal/mol)[29] for $Cp^*_2OsH^+$. The BDE of 71.7 kcal/mol for $Cp^*_2OsH^+$ was determined in MeCN by Tilset using

$$\mathrm{BDE}\ (\mathrm{M\text{-}H^+}) = 1.37pK_a + 23.06E_{1/2}\,(\mathrm{M}) + 59.5 \quad \text{in kcal/mol}$$

the equation where the pK_a is 9.9±0.1 measured against the anilinium ion and $E_{1/2}$ is -0.055 V vs Fc/Fc+. Since all BDE values (Table 1) were calculated using equation 6, any error in our method of calculating the 33.3 constant would affect all BDE values in the same way.

It is important to understand the possible errors in the three terms of eq 6. The ΔH_{HM} measurements in DCE are generally reproducible within ±0.3 kcal/mol or less.[4] The estimated maximum error in electrode potentials ($E_{1/2}$) is ±20 mV (0.5 kcal/mol) for reversible oxidations. The estimated maximum error for irreversible oxidations is ±80 mV which corresponds to ±2 kcal/mol.[21c] Taking these uncertainties into account, our method should yield M-H BDE values with a relative accuracy of approximately ±1 kcal/mol or less for complexes with reversible oxidations and ±3 kcal/mol or less for those with irreversible oxidations.

Discussion

Correlations Between $E_{1/2}$ and $-\Delta H_{HM}$. Since the $E_{1/2}$ of a metal complex is a measure of its ability to lose an electron and the heat of protonation ($-\Delta H_{HM}$) is a measure of its ability to share an electron-pair with a proton, one might reasonably expect there to be a correlation between $E_{1/2}$ and $-\Delta H_{HM}$ values. On the other hand, oxidation and protonation reactions are fundamentally different processes; oxidation leads to a radical cation while protonation results in a structural rearrangement which is required by the addition of a proton ligand to the coordination sphere. In fact, there are excellent correlations between $E_{1/2}$ and $-\Delta H_{HM}$ within a family of compounds. Figure 2 shows the excellent correlation between $E_{1/2}$ and $-\Delta H_{HM}$ for the series of $CpIr(CO)(PR_3)$ complexes. There are similar correlations in the other series of complexes (Figure 3), which are expressed in the following equations (7-11):

$$E_{1/2} = 0.75 - 0.015(-\Delta H_{HM}) \quad \text{for} \quad Fe(CO)_3(PR_3)_2 \tag{7}$$

where $PR_3 = PPh_3, PPh_2Me, PPhMe_2, PMe_3$

$$E_{1/2} = 0.68 - 0.016(-\Delta H_{HM}) \quad \text{for} \quad cis\text{-}Mo(CO)_2(L\text{-}L)_2 \tag{8}$$

where L-L = arphos, dppe, dppm

$$E_{1/2} = 0.79 - 0.020(-\Delta H_{HM}) \quad \text{for} \quad fac\text{-}W(CO)_3(PR_3)_3 \tag{9}$$

where $PR_3 = PPh_2Me, PPh_2Et, PPhEt_2, PMe_3, PEt_3$

$$E_{1/2} = 0.95 - 0.022(-\Delta H_{HM}) \quad \text{for} \quad CpOs(PR_3)_2X \tag{10}$$

where $(PR_3)_2X = (PPh_3)_2Br, (PPh_2Me)_2Br, (PMe_3)_2Br, (PPh_3)_2H$

$E_{1/2} = 1.63 - 0.042(-\Delta H_{HM})$ for $(C_5Me_nH_{5-n})Ir(COD)$ (11a)
where n = 0, 1, 3, 4, 5

$E_{1/2} = 1.82 - 0.044(-\Delta H_{HM})$ for $CpIr(CO)(PR_3)$ (11b)
where $PR_3 = P(p\text{-}C_6H_4CF_3)_3$, $P(p\text{-}C_6H_4F)_3$, PPh_3, PPh_2Me, $PPhMe_2$, PMe_3

The correlation coefficients for eq 8-11b are > 0.99; however, for the Cp*Ir(CO)(PR_3) complexes, the correlation coefficient is only 0.90, so an equation is not included. Slopes of the plots (Figs. 2 and 3), which are the $-\Delta H_{HM}$ coefficients in eqs 7-11, vary considerably from one family of compounds to another. Clearly, slopes of the two series of iridium complexes, $(C_5Me_nH_{5-n})Ir(COD)$ and $CpIr(CO)(PR_3)$, are greater than those of the Os, W, Mo, and Fe series. Although it is not obvious why this is true, a possible explanation involves steric crowding in the more highly coordinated complexes. The iridium complexes are the least sterically crowded; presumably protonation is not sterically hindered by bulky P(aryl)$_3$ or Cp' ligands. On the other hand, the six-coordinate $CpOs(PR_3)_2X$, *fac*-$W(CO)_3(PR_3)_3$, and *cis*-$Mo(CO)_2(L\text{-}L)_2$ complexes are more crowded, and one would expect their protonations to be inhibited by crowding of the bulky PR_3 and X ligands. Generally, in these series, it is the complexes with the mostly weakly donating phosphines and also the largest cone angles[30] that are the least basic. The $-\Delta H_{HM}$ values of these complexes are presumably especially small because of their steric resistance to protonation. Were there no steric factor, $-\Delta H_{HM}$ values of the less basic complexes would be more positive and the slopes of the lines would therefore be larger. Of course, the reasons for the different slopes in Figs. 2 and 3 could involve many other factors since structural changes resulting from oxidation and protonation could affect each series of complexes differently. Nevertheless, the correlations (Figs. 2 and 3, eq 7-11) of $E_{1/2}$ with $-\Delta H_{HM}$ are useful for estimating $E_{1/2}$ and $-\Delta H_{HM}$ values within families of compounds.

Comparison of BDE Values in Table 1 with Those in the Literature. In the present study, we report M-H BDE values for 51 different cationic metal hydride complexes (Table 1). We have used the thermochemical cycle in Scheme 1 and eq 6 to obtain our results which are based on the assumptions described in the Results section. In the literature are reported M-H BDE values for other complexes based on different methods and assumptions. The purpose of this section is to compare our results with those from related studies. Because errors and assumptions in each of the various studies may be quite different, it is difficult to draw conclusions unless the differences in BDE values are quite large.

(1) Cr-H BDE Values. The only BDE value for a Cr complex in Table 1 is that (56.0 kcal/mol) of $Cr(CO)_2(dppm)_2H^+$. This compares with values for the complexes $Cp'Cr(CO)_2(L)H$ which are all very similar to each other ($CpCr(CO)_3H$, 61.5 kcal/mol; $Cp^*Cr(CO)_3H$, 62.3; $CpCr(CO)_2(PPh_3)H$, 59.8; $CpCr(CO)_2(PEt_3)H$, 59.9; $CpCr(CO)_2[P(OMe)_3]H$, 62.7).[9] The BDE values for the 17-e cationic hydrides are reported to be 8-10 kcal lower than those of the neutral complexes, ($Cp^*Cr(CO)_3H^{+\cdot}$, 54.3 kcal/mol; $CpCr(CO)_2(PPh_3)H^{+\cdot}$, 49.8; $CpCr(CO)_2(PEt_3)H^{+\cdot}$, 50.9; $CpCr(CO)_2[P(OMe)_3]H^{+\cdot}$, 51.7).[3d] The BDE (56.0) of our cationic $Cr(CO)_2(dppm)_2H^+$ is between values for the neutral complexes and the 17-e cationic hydrides. The lower BDE for $Cr(CO)_2(dppm)_2H^+$ than $Cp'Cr(CO)_2(L)H$ is consistent with the lower basicity of $Cr(CO)_2(dppm)_2$ than

$Cp'Cr(CO)_2(L)^-$; a correlation between basicity and BDE is discussed in the next section. The BDE value of the Cr-H bond in gas phase $CpCr(CO)_3(Me)H^+$ obtained by ion cyclotron resonance spectroscopy studies is 58 ± 5 kcal/mol,[2e] which is close to that (56.0 kcal/mol) of $Cr(CO)_2(dppm)_2H^+$.

(2) **Mo-H BDE Values**. The BDE values (Table 1) for $Mo(CO)_2(arphos)_2H^+$ (63.6 kcal/mol), $Mo(CO)_2(dppe)_2H^+$ (66.2), and $Mo(CO)_2(dppm)_2H^+$ (67.2) compare with literature values for Cp_2MoH_2 (61.5 kcal/mol),[32a] $CpMo(CO)_3H$ (69.4),[32] $Cp^*Mo(CO)_3H$ (68.5),[3c, 31d] $TpMo(CO)_3H$ (62.2),[31d] $Tp'Mo(CO)_3H$ (59.3),[3f, 31d] and $Mo(CO)_6H^+$ in the gas phase (62).[2e] In general, the Mo-H BDE values are higher than those of Cr-H.

(3) **W-H BDE Values**. The BDE values for the tungsten complexes in Table 1 range from 59.5 kcal/mol for the least basic complex $W(CO)_3(PMePh_2)_3H^+$ to 68.0 for the most basic complex $W(CO)_2(dppm)_2H^+$. Most of the literature values for tungsten hydride complexes fall in the same range: $Cp_2W(I)(H)$ (65.3 kcal/mol),[31a] $CpW(CO)_3H$ (65.0),[3c] $CpW(CO)_2(PMe_3)H$ (69.6),[3c] $TpW(CO)_3H$ (65.8),[3f] $Tp'W(CO)_3H$ (62.2).[3f]

(4) **Re-H BDE Values**. The BDE values (Table 1) for $Cp^*Re(CO)_2(PMe_2Ph)H^+$ (71.0 kcal/mol) and for $Cp^*Re(CO)_2(PMe_3)H^+$ (71.8 kcal/mol) compare with the Re-H BDE values of 74.7 kcal/mol for $Re(CO)_5H$[3c] and 70 ± 3 kcal/mol for $Re(CO)_5(Me)H^+$ in the gas phase.[2e]

(5) **Fe-H BDE Values.** The BDE values for $Fe(CO)_3(PR_3)_2H^+$ complexes in Table 1 range from 60.0 kcal/mol for the complex $Fe(CO)_3(PPh_3)_2H^+$ to 66.1 for $Fe(CO)_3(PMe_3)_2H^+$. The highest value is 66.5 for the most basic $Fe(CO)_3(dppm)H^+$. These compare with the following literature results:

$Fe(CO)_4H_2$ (67.6 kcal/mol) and $CpFe(CO)_2H$ (57.1 kcal/mol).[3c] The reported BDE of Fe-H in gas phase Cp_2FeH^+ is 51± 5 kcal/mol.[2e]

(6) Ru-H BDE Values. The BDE values for the Ru complexes in Table 1 are 66.8 kcal/mol for $CpRu(PMe_3)_2(I)(H)^+$, 70.7 for $CpRu(dppm)(H_2)^+$, 69.4 for $CpRu(dppe)H_2^+$, and 68.3 for $CpRu(PPh_3)_2(H)_2^+$. These compare with 75.5 for $CpRu(dppm)(H_2)^+$, 73.8 for $CpRu(dppe)H_2^+$, and 72.0 for $CpRu(PPh_3)_2(H)_2^+$ reported in the literature.[27] It is not entirely clear why our values are approximately 4 kcal/mol less than those reported previously. Both approaches make use of thermochemical cycles but we use ΔH_{HM} values rather pK_a's; thus, the assumptions are different for the two methods. The reported Ru-H BDE values are 65 kcal/mol for $CpRu(CO)_2H$,[3a] 63.5 for $Ru(dmpe)_2(H)_2$,[34] and 64.8 ± 3.6 kcal/mol for gas phase Cp_2RuH^+.[2e]

(7) Os-H BDE Values. Of the BDE values for the Os complexes in Table 1 the lowest is 63.2 kcal/mol for $CpOs(PPh_3)_2(Br)H^+$ and the highest is 73.6 for $CpOs(PPh_3)_2(H)_2^+$. These compare with values for $OsH(L)_2(\eta^2\text{-}H_2)^+$ (L = depe, 76 kcal/mol; dppe, 80; dtfpe, 81).[27] The lower Os-H BDE values for the $CpOs(PR_3)_2(X)H^+$ complexes may be related to the fact that both H-H and Os-H bonds must be cleaved in the $OsH(L)_2(\eta^2\text{-}H_2)^+$ complexes. This rationale, however, is inconsistent with the very similar BDE values for $CpRu(dppm)(\eta^2\text{-}H_2)^+$ (70.7 kcal/mol) which exists as an $\eta^2\text{-}H_2$ complex and $CpRu(PPh_3)_2(H)_2^+$ (68.3) which is a dihydride.

(8) Ir-H BDE Values. The BDE values (Table 1) for all of the compounds in the $CpIr(CO)(PR_3)H^+$ series are nearly the same (75 kcal/mol); likewise, the values for the $(C_5Me_nH_{5-n})Ir(COD)H^+$ series are all approximately 72 kcal/mol. Neither the basicity nor the steric size of the PR_3 or $C_5Me_nH_{5-n}$

ligands significantly affects the BDE values of the compounds in these series. These BDE values are all similar to those for Cp*Ir(PMe$_3$)(Cy)H (74.0) and Cp*Ir(PMe$_3$)(H)$_2$ (74.2).[33] The average Ir-H BDE for the two Ir-H bonds in hydrogenated Vaska's-type compounds Ir(X)(CO)(PR$_3$)$_2$H$_2$ is 58 kcal/mol;[35] this value varies by no more than 3 kcal/mol with different X and PR$_3$ ligands.

Correlations between BDE and -ΔH_{HM}. Since there are correlations (eqs 7-11) between $E_{1/2}$ and -ΔH_{HM}, which are used to calculate BDE values from eq 6, there must be a correlation between BDE and -ΔH_{HM} values within series of compounds. Since $E_{1/2}$ values increase as -ΔH_{HM} decreases, the terms in eq 6 at least partially cancel one another; as a result, changes in BDEs may be small within a family of compounds. The correlations between $E_{1/2}$ and -ΔH_{HM} allow one to predict BDE values from known -ΔH_{HM} results. If we use eq 12 to represent eq 7-11 and substitute $E_{1/2}$ in eq 6 by $E_{1/2}$ in eq 12, we obtain eq 13 with a new constant z. Thus, for a series of compounds, BDE values may be

$$E_{1/2} = a(-\Delta H_{HM}) + x, \text{ where constants a and x depend upon} \quad (12)$$

the specific series of compounds

$$BDE = (1 + 23.06\ a)(-\Delta H_{HM}) + z \quad (13)$$

predicted just from their ΔH_{HM} values. The forms of eq 13 for each of the series of compounds represented in eq 7-11 are expressed in eq 14-18.

$$BDE = 50.4 + 0.67(-\Delta H_{HM}) \quad \text{for} \quad Fe(CO)_3(PR_3)_2H^+ \quad (14)$$

$$BDE = 48.9 + 0.62(-\Delta H_{HM}) \quad \text{for} \quad Mo(CO)_2(L\text{-}L)_2H^+ \quad (15)$$

$$BDE = 51.6 + 0.52(-\Delta H_{HM}) \quad \text{for} \quad W(CO)_3(PR_3)_3H^+ \quad (16)$$

$$\mathrm{BDE} = 55.2 + 0.50(-\Delta H_{HM}) \quad \text{for} \quad \mathrm{CpOs(PR_3)_2(X)H^+} \qquad (17)$$

$$\mathrm{BDE} = 71.1 + 0.038(-\Delta H_{HM}) \quad \text{for} \quad \mathrm{(C_5Me_nH_{5-n})Ir(COD)H^+} \qquad (18a)$$

$$\mathrm{BDE} = 75.2 + 0.008(-\Delta H_{HM}) \quad \text{for} \quad \mathrm{CpIr(CO)(PR_3)H^+} \qquad (18b)$$

The slopes for the $(C_5Me_nH_{5-n})Ir(COD)H^+$ and $CpIr(CO)(PR_3)H^+$ complexes in eq 11 lead to (1+23.06a) values in eq 13 of near zero, which means that the BDE values are essentially constant for these series of Ir compounds; that is, the BDE values do not change with changes in the ligands. The correlations between BDE and $-\Delta H_{HM}$ values for the Fe, Mo, W, Os, and Ir complexes expressed in eqs 14-18 are shown in Figure 4.

It should be noted in all series of compounds, except those of Ir, that the BDE values increase as the $-\Delta H_{HM}$ values increase; that is, as heterolytic bond cleavage ($-\Delta H_{HM}$) (eq 2) requires more energy, so does homolytic bond cleavage (BDE) (eq 1). However, for the Ir complexes, the BDE values do not increase even though heterolytic bond cleavage enthalpies ($-\Delta H_{HM}$) do.

Other Trends in Bond Dissociation Enthalpies (BDE). It is evident (Table 1) for a series of complexes with the same ligands that the BDE values increase with increasing atomic weight of the metal in the same group. Thus, for the complexes $M(CO)_2(dppm)_2H^+$ (M = Cr, Mo, W), the M-H BDE increases in the order Cr-H (56.0 kcal/mol) < Mo-H (67.2) < W-H (68.0); this is the same trend observed for the $CpM(CO)_3H$ complexes: Cr-H, 62 < Mo-H, 70 < W-H, 73.[3f] Similarly, the M-H BDE is larger for Os than Ru in the two types of complexes, $Cp^*_2MH^+$ (Ru-H, 68.0 < Os-H, 71.7) and $CpM(PPh_3)_2(H)_2^+$ (Ru-H, 68.3 < Os-H, 73.6). Thus, these data support previous reports of increasing M-H BDE values as a 3d metal is replaced by its 4d and 5d congeners.[2e,3]

In order to determine whether a cationic metal hydride complex has a significantly different BDE than a comparable neutral complex, we compare the BDE of $Cp^*Re(CO)_2(PMe_3)H^+$ (71.8 kcal/mol) with that of the isoelectronic and isosteric $CpW(CO)_2(PMe_3)H$ (69.6 kcal/mol).[3h] For this comparison, it would be desirable to use $Cp^*W(CO)_2(PMe_3)H$; however, its BDE has not been reported but its value is likely to be very similar to that of $CpW(CO)_2(PMe_3)H$ because replacement of Cp by Cp* changes M-H BDE values very little as seen in the complexes $CpMo(CO)_3H$ (69.2 kcal/mol)[3c] and $Cp^*Mo(CO)_3H$ (68.5)[3c], as well as $CpIr(CO)(PPh_3)$ (74.9) and $Cp^*Ir(CO)(PPh_3)$ (72.4). Thus, our comparison shows that the BDE values of $Cp^*Re(CO)_2(PMe_3)H^+$ (71.8 kcal/mol) and $Cp^*W(CO)_2(PMe_3)H$ (~ 69.6) are very similar, which suggests that the extra positive charge in a cationic metal hydride complex does not by itself substantially strengthen or weaken a M-H bond. This is also seen in BDE values for $CpFe(CO)_2H$ (57.1 ± 3)[3c] and $CpCo(CO)_2H^+$ (58.6 ± 3)[2e] in the gas phase.

Another obvious trend in the data in Table 1 is that the heterolytic bond cleavage energy ($-\Delta H_{HM}$) for a compound is substantially less than that (BDE) for homolytic bond cleavage. However, it is important to realize that heterolytic cleavage actually involves transfer of a proton (H^+) from the metal to the $CF_3SO_3^-$ base (eq 4). Thus, the $-\Delta H_{HM}$ values depend on the base that accepts the proton.

Summary

In the course of determining bond dissociation enthalpies (BDE) of fifty-one 18-electron cationic transition metal hydride complexes (L_nMH^+), oxidation potentials ($E_{1/2}$) for each of the conjugate Lewis base complexes (L_nM) were measured. Within a family of compounds having the same metal and types of ligands, there is an excellent correlation between the ease of oxidation ($E_{1/2}$) and the basicity ($-\Delta H_{HM}$) of the metal; the more easily oxidized the metal, the more basic it is toward protonation. Because $E_{1/2}$ and $-\Delta H_{HM}$ are used in the calculations of M-H BDE values for the L_nMH^+ complexes, there are also correlations between the BDE and $-\Delta H_{HM}$ values. Thus, within a family of compounds, it is possible to estimate M-H BDE values from $-\Delta H_{HM}$. In all series of compounds, heterolytic cleavage ($-\Delta H_{HM}$) of the M-H bond is much more sensitive to the nature of the ligands in the complex than is homolytic cleavage (BDE).

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Table 1. $-\Delta H_{HM}$, $-\Delta H_{HP}$, $E_{1/2}$, and BDE Values of Organometallic Compounds

Compound ^{h}	$-\Delta H_{HM}$ ^{a} kcal/mol	$-\Delta H_{HP}$ ^{b} kcal/mol	$E_{1/2}$, V ^{c} vs SCE	BDE ^{d} kcal/mol
$Cr(CO)_2(dppm)_2$	25.5	22.0	-0.12^{f,g}	56.0
$Mo(CO)_2(arphos)_2$	23.8	23.2	0.28^{f}	63.6
$Mo(CO)_2(dppe)_2$	27.4	22.8	0.24^{f}	66.2
$Mo(CO)_2(dppm)_2$	29.7	22.0	0.18^{f}	67.2
$W(CO)_3(PMePh_2)_3$	15.1	24.7	0.48^{e,f}	59.5
$W(CO)_3(PEtPh_2)_3$	16.9	25.2	0.45^{e}	60.6
$W(CO)_3(PEt_2Ph)_3$	18.3	27.8	0.41^{e,f}	61.0
$W(CO)_3(PMe_3)_3$	19.5	31.6	0.40^{f}	62.0
$W(CO)_3(PEt_3)_3$	25.0	33.7	0.28^{e,g}	64.7
$W(CO)_2(dppm)_2$	31.5	22.0	0.14^{g}	68.0
$W(CO)_3(tripod)$	10.5		0.72^{g}	60.4
$W(CO)_3(triphos)$	16.7		0.63^{g}	64.5
$Cp^*Re(CO)_2(PMe_2Ph)$	18.3	28.4	0.84^{e,g}	71.0
$Cp^*Re(CO)_2(PMe_3)$	20.1	31.6	0.80^{e,g}	71.8
$Fe(CO)_3(PPh_3)_2$	14.1	21.2	0.55^{e,g}	60.0
$Fe(CO)_3(PMePh_2)_2$	17.6	24.7	0.49^{e,g}	62.2
$Fe(CO)_3(PMe_2Ph)_2$	21.2	28.4	0.45^{e,g}	64.9
$Fe(CO)_3(PMe_3)_2$	23.3	31.6	0.41^{e,g}	66.1
$Fe(CO)_3(dppp)$	21.1	23.4	0.31^{e,g}	61.5
$Fe(CO)_3(dppm)$	24.0	22.0	0.40^{e,g}	66.5
Cp^*_2Ru	19.0		0.68^{e,f,g}	68.0
$CpRu(PMe_3)_2I$	20.6	31.6	0.56^{g}	66.8
$CpRu(dppm)H$	28.9	22.0	0.37^{g}	70.7

Table 1. Cont'd

CpRu(dppe)H	29.0	22.8	0.31^{g}	69.4
$CpRu(PPh_3)_2H$	29.7	21.2	$0.23^{e,g}$	68.3
$Cp^*{}_2Os$	26.6		$0.51^{e,f,g}$	71.7
$CpOs(PPh_3)_2Br$	16.3	21.2	$0.59^{e,g}$	63.2
$CpOs(PPh_3)_2Cl$	19.7	21.2	$0.58^{e,g}$	66.4
$CpOs(PPh_2Me)_2Br$	20.2	24.7	$0.51^{e,g}$	65.3
$CpOs(PMe_3)_2Br$	29.4	31.6	$0.34^{e,g}$	70.5
$CpOs(PPh_3)_2H$	37.3	21.2	0.13^{g}	73.6
$CpIr(CO)[P(p\text{-}C_6H_4CF_3)_3]$	28.0	13.6	$0.60^{f,g}$	75.1
$CpIr(CO)[P(p\text{-}C_6H_4F)_3]$	29.8	19.6	0.53^{f}	75.2
$CpIr(CO)(PPh_3)$	30.0	21.2	$0.50^{f,g}$	74.9
$CpIr(CO)(PPh_2Me)$	31.5	24.7	$0.45^{f,g}$	75.2
$CpIr(CO)(PMe_2Ph)$	32.4	28.4	0.41^{g}	75.2
$CpIr(CO)(PMe_3)$	33.2	31.6	0.37^{g}	75.0
$CpIr(CO)(PEt_3)$	32.9	33.7	$0.35^{f,g}$	74.3
$CpIr(CO)(PCy_3)$	32.7	33.2	0.35^{g}	74.2
$CpIr(CS)(PPh_3)$	26.5	21.2	0.51^{g}	71.6
CpIr(COD)	22.8		0.69^{g}	72.0
$(C_5MeH_4)Ir(COD)$	24.1		0.61^{g}	71.5
$(1,2,3\text{-}C_5Me_3H_2)Ir(COD)$	26.4		0.54^{g}	72.2
$(C_5Me_4H)Ir(COD)$	27.5		0.47^{g}	71.6
Cp*Ir(COD)	28.5		0.45^{g}	72.2
$Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$	33.8	13.6	0.30^{g}	74.0
$Cp^*Ir(CO)[P(p\text{-}C_6H_4Cl)_3]$	36.9	17.9	0.20^{g}	74.8

Table 1. Continued

$Cp^*Ir(CO)(PPh_3)$	37.1	21.2	0.09[g]	72.4
$Cp^*Ir(CO)(PPh_2Me)$	37.1	24.7	0.08[g]	72.3
$Cp^*Ir(CO)(PMe_3)$	38.0	31.6	0.07[g]	72.9
$Cp^*Ir(CO)_2$	21.4		0.72[g]	71.3

[a]For eq 4, ref 4, 16, and 19. [b]For protonation of the free phosphine ligand in the complex (eq 5); for the first protonation of bidentate ligands. See ref 13 and 23. [c]All $E_{1/2}$ values were obtained by CV at a scan rate of 100 mV/s; SHACV at a scan rate of 5 mV/s and a frequencey of 25 Hz, and OSWV at a scan rate of 60 mV/s (scan frequency 15 Hz and step voltage 4 mV). All solutions are 1.0 mM in 1,2-dichloroethane at 23 °C using platinum as the working and auxiliary electrodes and SCE as the reference electrode with 0.10 M Bu_4NBF_4 as the electrolyte. [d]BDE (M^+-H) calculated using eq 6. [e]Reversible in CV. [f]$E_{1/2}$ measured by SHACV. [g]$E_{1/2}$ measured by OSWV. [h]Ligand abbreviations: Cp* = C_5Me_5; Cp = C_5H_5; COD = cyclooctadiene; dppm = $Ph_2PCH_2PPh_2$; dppe = $Ph_2P(CH_2)_2PPh_2$; dppp = $Ph_2P(CH_2)_3PPh_2$; arphos = $Ph_2P(CH_2)_2AsPh_2$; tripod = $MeC(CH_2PPh_2)_3$; triphos = $Ph_2P(CH_2CH_2PPh_2)_2$.

Table 2. Temperature Dependence of $E_{1/2}$ for the Oxidation of Cp_2Fe, Cp^*_2Ru, and $CpIr(CO)(PPh_3)$ in DCE Solvent

Compound	23 °C	40 °C	55 °C	70 °C
$Cp_2Fe^{a,b}$	0.592	0.588	0.593	0.590
$Cp^*_2Ru^{a,b}$	0.683	0.676	0.680	0.680
$CpIr(CO)(PPh_3)^b$	0.484	0.462	0.480	0.476

[a] CV, 100 mV/s; [b] OSWV, 15Hz, 4mV.

Figure Captions

Figure 1. Irreversible cyclic voltammogram (CV, top), symmetrical Osteryoung square wave voltammogram (OSWV, middle), and second harmonic ac voltammogram (SHACV, bottom) for $CpIr(CO)(PPh_2Me)$ in DCE at 23 °C.

Figure 2. Plot of $E_{1/2}$ vs $-\Delta H_{HM}$ for $CpIr(CO)(PR_3)$ complexes.

Figure 3. Plot of $E_{1/2}$ vs $-\Delta H_{HM}$ for the $Mo(CO)_2(L\text{-}L)_2$, $W(CO)_3(PR_3)_3$, $Fe(CO)_3(PR_3)_2$, $CpOs(PR_3)_2X$, $(C_5H_{5-n}Me_n)Ir(COD)$, and $CpIr(CO)(PR_3)$ series of complexes.

Figure 4. Plot of BDE vs $-\Delta H_{HM}$ for the $Mo(CO)_2(L\text{-}L)_2$, $W(CO)_3(PR_3)_3$, $Fe(CO)_3(PR_3)_2$, $CpOs(PR_3)_2X$, $(C_5H_{5-n}Me_n)Ir(COD)$, and $CpIr(CO)(PR_3)$ series of complexes.

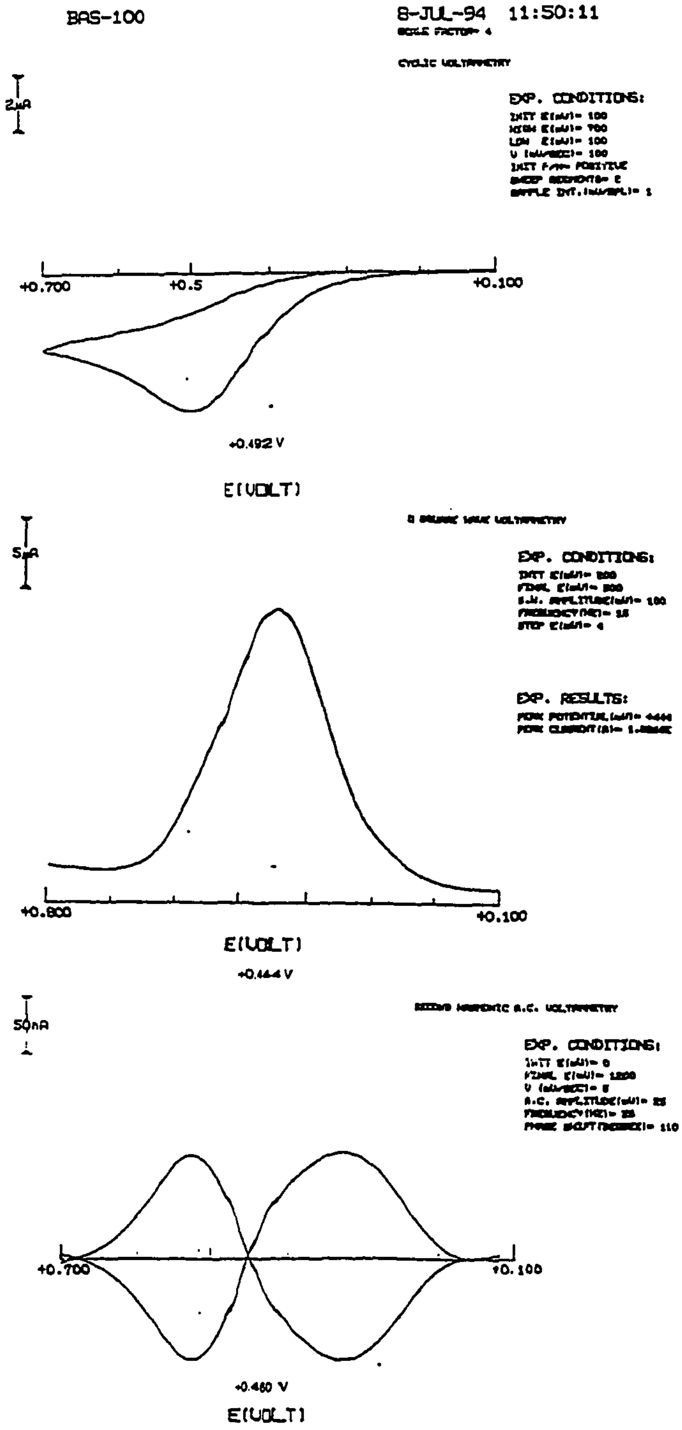

Figure 1. Irreversible cyclic voltammogram (CV, top), symmetrical Osteryoung square wave voltammogram (OSWV, middle), and second harmonic ac voltammogram (SHACV, bottom) for CpIr(CO)(PPh$_2$Me) in DCE at 23 °C.

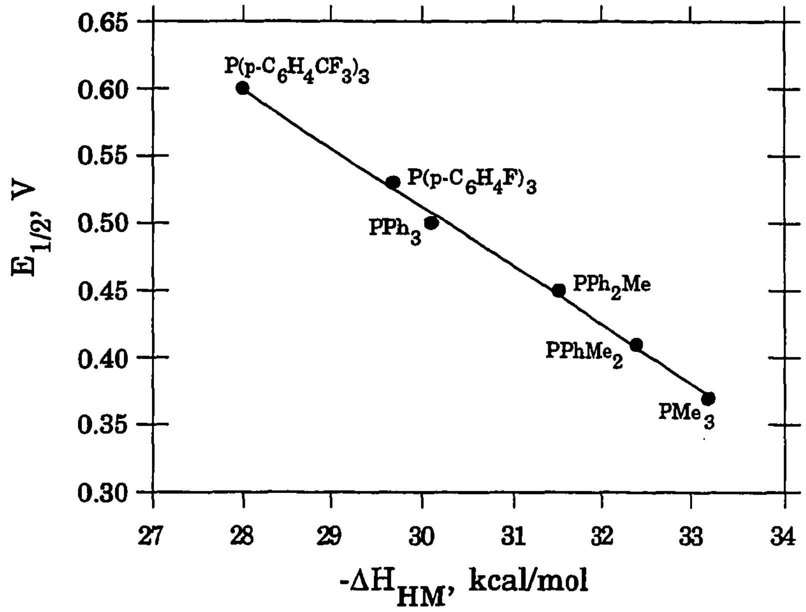

Figure 2. Plot of $E_{1/2}$ vs $-\Delta H_{HM}$ for $CpIr(CO)(PR_3)$ complexes.

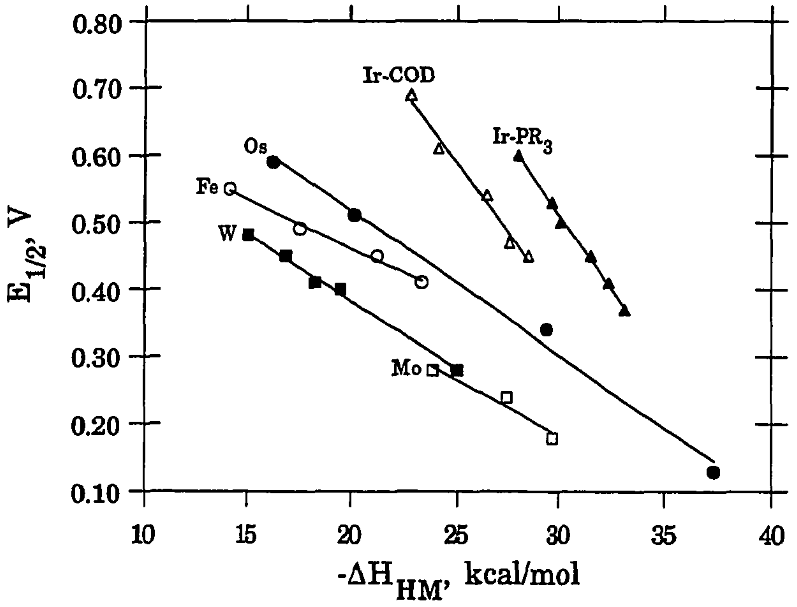

Figure 3. Plot of $E_{1/2}$ vs $-\Delta H_{HM}$ for the $Mo(CO)_2(L\text{-}L)_2$, $W(CO)_3(PR_3)_3$, $Fe(CO)_3(PR_3)_2$, $CpOs(PR_3)_2X$, $(C_5H_{5-n}Me_n)Ir(COD)$, and $CpIr(CO)(PR_3)$ series of complexes.

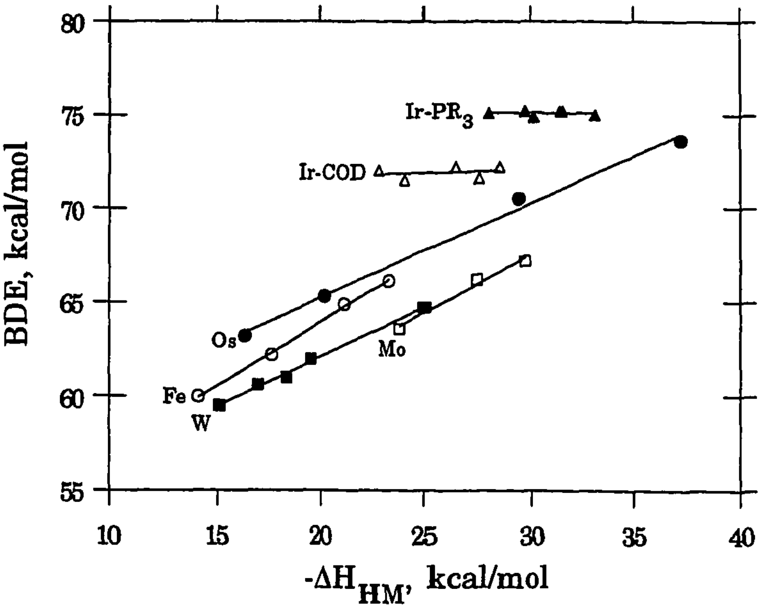

Figure 4. Plot of BDE vs $-\Delta H_{HM}$ for the $Mo(CO)_2(L\text{-}L)_2$, $W(CO)_3(PR_3)_3$, $Fe(CO)_3(PR_3)_2$, $CpOs(PR_3)_2X$, $(C_5H_{5-n}Me_n)Ir(COD)$, and $CpIr(CO)(PR_3)$ series of complexes.

GENERAL SUMMARY

Basicities of the series of complexes CpIr(CO)(PR$_3$) [PR$_3$ = P(*p*-C$_6$H$_4$CF$_3$)$_3$, P(*p*-C$_6$H$_4$F)$_3$, P(*p*-C$_6$H$_4$Cl)$_3$, PPh$_3$, P(*p*-C$_6$H$_4$CH$_3$)$_3$, P(*p*-C$_6$H$_4$OCH$_3$)$_3$, PPh$_2$Me, PPhMe$_2$, PMe$_3$, PEt$_3$, PCy$_3$] have been measured by the heat evolved (ΔH_{HM}) when the complex is protonated by CF$_3$SO$_3$H in 1,2-dichloroethane (DCE) at 25.0 °C. The -ΔH_{HM} values range from 28.0 kcal/mol for CpIr(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$] to 33.2 kcal/mol for CpIr(CO)(PMe$_3$) and are directly related to the basicities of the PR$_3$ ligands in the complexes. The nucleophilicities of the CpIr(CO)(PR$_3$) complexes were established from second order rate constants (k) for their reactions with CH$_3$I to give [CpIr(CO)(PR$_3$)(CH$_3$)]$^+$I$^-$ in CD$_2$Cl$_2$ at 25.0 °C. Values of k range from 0.15 x 10^{-2} M^{-1}s^{-1} for CpIr(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$] to 44 x 10^{-2} M^{-1}s^{-1} for CpIr(CO)(PMe$_3$). There is an excellent linear correlation between the basicities (ΔH_{HM}) and nucleophilicities (k) of the CpIr(CO)(PR$_3$) complexes. Only the complex CpIr(CO)(PCy$_3$) deviates significantly from this correlation, presumably due to the bulkiness of the tricyclohexylphosphine ligand which makes it a much weaker nucleophile than is expected from its basicity. It is also observed that the CpIr(CO)(PR$_3$) complexes are all more nucleophilic than their Co analogs CpCo(CO)(PR$_3$); this difference increases with the bulkiness of the PR$_3$ ligand.

The basicities and nucleophilicities of a series of η^5-pentamethylcyclopentadienyl complexes Cp*Ir(CO)(PR$_3$) (PR$_3$ = P(*p*-C$_6$H$_4$CF$_3$)$_3$, P(*p*-C$_6$H$_4$Cl)$_3$, PPh$_3$, PPh$_2$Me, PMe$_3$) have been determined and compared with values for their CpIr(CO)(PR$_3$) analogs. The -ΔH_{HM} values range from 33.8 kcal/mol for the weakest base Cp*Ir(CO)[P(*p*-C$_6$H$_4$CF$_3$)$_3$] to

38.0 kcal/mol for the strongest $Cp^*Ir(CO)(PMe_3)$. The rate constants vary from 0.048 $M^{-1}s^{-1}$ for the weakest nucleophile $Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$ to 23.4 $M^{-1}s^{-1}$ for the strongest $Cp^*Ir(CO)(PMe_3)$. In general, the pentamethylcyclopentadienyl complexes are 6.2 kcal/mol more basic and react 40 times faster than the cyclopentadienyl analogs. However, the steric size of the Cp* ligand also reduces the nucleophilicities of $Cp^*Ir(CO)(PR_3)$ complexes.

In the course of determining bond dissociation enthalpies (BDE) of fifty-one 18-electron cationic transition metal hydride complexes (L_nMH^+), where $ML_n = Cr(CO)_2(dppm)_2$, $Mo(CO)_2(L\text{-}L)_2$, $W(CO)_3(PR_3)_3$, $W(CO)_2(dppm)_2$, $W(CO)_3$(tripod), $W(CO)_3$(triphos), $Cp^*Re(CO)_2(PR_3)$, $Fe(CO)_3(PR_3)_2$, $Fe(CO)_3(L\text{-}L)$, Cp^*_2Ru, $CpRu(PMe_3)_2I$, $CpRu(L\text{-}L)H$, $CpRu(PPh_3)_2H$, Cp^*_2Os, $CpOs(PR_3)_2Br$, $CpOs(PPh_3)_2Cl$, $CpOs(PPh_3)_2H$, $CpIr(CO)(PR_3)$, $CpIr(CS)(PPh_3)$, $(C_5Me_nH_{5-n})Ir(COD)$, $Cp^*Ir(CO)(PR_3)$, and $Cp^*Ir(CO)_2$, oxidation potentials ($E_{1/2}$) for each of the conjugate Lewis base complexes (L_nM) were measured. Within a family of compounds having the same metal and types of ligands, there is an excellent correlation between the ease of oxidation ($E_{1/2}$) and the basicity ($-\Delta H_{HM}$) of the metal; the more easily oxidized the metal, the more basic it is toward protonation. Because $E_{1/2}$ and $-\Delta H_{HM}$ are used in the calculations of M-H BDE values for the L_nMH^+ complexes, there are also correlations between the BDE and $-\Delta H_{HM}$ values. Thus, within a family of compounds, it is possible to estimate M-H BDE values from $-\Delta H_{HM}$. In all series of compounds, heterolytic cleavage ($-\Delta H_{HM}$) of the M-H bond is much more sensitive to the nature of the ligands in the complex than is homolytic cleavage (BDE).

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