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Basicities of Transition Metal Complexes from Studies of Their Heats of Protonation: A Guide to Complex Reactivity

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Introduction

The concepts of acidity and basicity are fundamental to our understanding of the thermodynamics, rates, and mechanisms of organic reactions. Hammett-type linear free energy correlations of reaction rates or equilibrium constants with basicities (e.g., pK_a) of reactants are used routinely to develop mechanisms and understand trends in reactivity.¹ As in organic systems, one might expect the basicity of the metal in a transition metal complex to be a guide to predicting other reactivities of the metal center such as its nucleophilicity, ability to form hydrogen bonds with alcohols,^{2,3} and tendency to undergo oxidative addition as well as simple oxidation and reduction reactions. Moreover, the acidities of metal hydride intermediates in catalytic hydrogenation reactions markedly influence the course of these reactions.⁴⁻⁸ It is hoped that the quantitative measures of metal complex basicities presented in this Account will be useful to those who seek a guide to a broad range of complex reactivities.

Basicities of metal carbonyl anions, $M(CO)_xL_y^-$, available from pK_a determinations of their protonated forms, are summarized in a very useful review by Kristjánssdóttir and Norton.⁹ These pK_a measurements¹⁰⁻¹² were often performed in $CH_3C\equiv N$ solvent (eq 1) using anilines and other reference bases (B).

Bob Angelici, born in Rochester, MN, on July 29, 1937, received his B.A. degree at St. Olaf College in 1959 and completed the Ph.D. degree in 1962 at Northwestern University, where his major professor was Fred Basolo. He spent a year (1962-1963) as an NSF postdoctoral fellow with E. O. Fischer at the University of Munich and then (1963) joined the faculty at Iowa State University, where he served for four years as chair of the Chemistry Department and is now distinguished professor, as well as senior chemist at the Ames Laboratory. In the ACS, he was chair of the Division of Inorganic Chemistry (1985) and the Organometallic Subdivision (1974). In addition to the investigations described in this Account, his current research includes studies of thiophene transition metal complexes related to hydrodesulfurization, cyaphide ($C\equiv P^-$) and isocyaphide ($C\equiv PR$) complexes, and organometallic chemistry on metal surfaces.



pK_a values of other metal hydride complexes were determined under similar conditions.¹³⁻¹⁵ However, the range of basicities that could be measured was limited by the basicity of the solvent and/or the experimental method used to evaluate concentrations of the species at equilibrium. We sought to extend greatly the range of basicities that could be studied by using titration calorimetry to determine the enthalpies of protonation (ΔH_{HM}) of metal complexes with the strong acid CF_3SO_3H in the relatively non-coordinating, weakly basic 1,2-dichloroethane (DCE)

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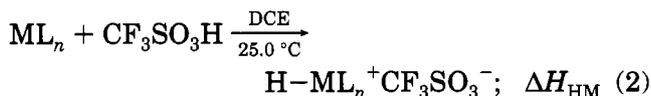
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Table 1. Enthalpies of Protonation (ΔH_{HN} , kcal/mol) of Organonitrogen Bases and Their $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ and $\text{p}K_{\text{a}}(\text{AN})$ Values

	$-\Delta H_{\text{HN}}^a$	$\text{p}K_{\text{a}}(\text{H}_2\text{O})^b$	$\text{p}K_{\text{a}}(\text{AN})^c$
3-bromopyridine	25.7(1)	2.8	
pyridine	29.3(1)	5.2	12.33
morpholine	35.6(4)	8.5	16.61
1,3-diphenylguanidine	36.9(2)	10.1	17.90
triethylamine	39.3(1)	10.8	18.46
tetramethylguanidine (TMG)	43.2(3)	13.6	

^a Reference 28. ^b $\text{p}K_{\text{a}}$ in H_2O at 25.0 °C. Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1972. ^c $\text{p}K_{\text{a}}$ in acetonitrile. Coetzee, J. G.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005.

solvent at 25.0 °C (eq 2). For a series of related ML_n



complexes, the ΔS_{HM} for these reactions should be similar. Thus, relative basicities of two complexes, ML_n and ML'_n , can be estimated from the equilibrium constant K for the reaction in eq 3 from the difference ($\Delta\Delta H_{\text{HM}}$ in kcal/mol) in their ΔH_{HM} values (eq 2) using eqs 4 and 5, assuming that $\Delta\Delta S_{\text{HM}}$ for eq 3 is 0. In the



$$\Delta\Delta H_{\text{HM}} - T(\Delta\Delta S_{\text{HM}}) \approx \Delta\Delta H_{\text{HM}} \approx -RT \ln K = \Delta\Delta G_{\text{HM}} \quad (4)$$

$$\text{at } 25.0\text{ }^\circ\text{C}, \Delta\Delta H_{\text{HM}} \approx -1.36 \log K, \text{ in kcal/mol} \quad (5)$$

few instances where K has been determined experimentally,^{16–18} $\Delta\Delta S_{\text{HM}}$ is slightly negative when $\Delta\Delta H$ is negative; therefore the experimental K is somewhat lower than that estimated from ΔH_{HM} values using eq 5. Nevertheless, K values obtained from eq 5 are useful for approximate comparisons. Since $\Delta\Delta H_{\text{HM}}$ values as large as 30 kcal/mol have been measured, and even larger $\Delta\Delta H_{\text{HM}}$ values are possible, equilibrium constants (K in eq 3) that are 10^{22} or larger can be estimated. Thus, calorimetry can be used to determine basicities of a broad range of complexes.

All of the ΔH_{HM} values reported (Tables 1–4) in this Account were determined in carefully purified DCE with standardized $\text{CF}_3\text{SO}_3\text{H}$ at 25.0 °C (eq 2) under a dry Ar atmosphere using a Tronac Model 458 isoperibol titration calorimeter.^{19,20} All reactions are rapid, occurring within the time of mixing. The acid, with a Hammett acidity H_0 value of -14.2 ,^{21,22} is much stronger than H_2SO_4 and protonates a range of metal complexes, yet does not protonate the DCE solvent.

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Table 2. Enthalpies of Protonation (ΔH_{HP} , kcal/mol) of Monophosphines and Their $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ Values

PR_3	$-\Delta H_{\text{HP}}$, kcal/mol ^a	$\text{p}K_{\text{a}}(\text{H}_2\text{O})$
(<i>p</i> - $\text{CF}_3\text{C}_6\text{H}_4$) ₃ P	13.6(2)	-1.32^b
(<i>p</i> - ClC_6H_4) ₃ P	17.9(2)	1.03 ^c
(<i>p</i> - FC_6H_4) ₃ P	19.6(2)	1.97 ^c
Ph_3P	21.2(1)	2.73 ^d
(<i>o</i> - MeC_6H_4) ₃ P	22.6(2)	3.08 ^c
(<i>p</i> - MeC_6H_4) ₃ P	23.2(3)	3.84 ^c
(<i>p</i> - MeOC_6H_4) ₃ P	24.1(2)	4.57 ^c
MePh_2P	24.7(0)	4.59 ^c
Et_2PhP	27.8(4)	6.25 ^e
Me_2PhP	28.4(2)	6.50 ^d
Me_3P	31.6(2)	8.65 ^d
(<i>c</i> - C_6H_{11}) ₃ P	33.2(4)	9.70 ^d
Et_3P	33.7(3)	8.69 ^d
(<i>t</i> -Bu) ₃ P	36.6(3)	11.4 ^c

^a References 19, 26, and 30. ^b Calculated from eq 9. ^c Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716. ^d Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. ^e Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758.

Table 3. Enthalpies of Protonation (ΔH_{HP1} and ΔH_{HP2})^a of Diphosphines and Their $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ Values ($\text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a2}}$)

phosphine	$-\Delta H_{\text{HP1}}$, ^b kcal/mol	$\text{p}K_{\text{a1}}$ ^d	$-\Delta H_{\text{HP2}}$, ^c kcal/mol	$\text{p}K_{\text{a2}}$ ^d
$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm)	22.0(1)	3.81	14.9(2)	
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dppe)	22.8(2)	3.86	20.2(1)	0.99
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (dppp)	23.4(1)	4.50	22.4(3)	2.53
$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (dppb)	24.6(1)	4.72 ^e	23.8(2)	4.28 ^e
$\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2$ (dppent)	24.8(2)	4.84 ^e	24.5(1)	4.67 ^e
$\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$ (dpph)	25.2(1)	5.05 ^e	24.9(1)	4.89 ^e
<i>cis</i> - $\text{Ph}_2\text{P}(\text{CH}=\text{CH})\text{PPh}_2$ (<i>cis</i> -dppv)	19.9(3)	2.27	10.0(2)	
<i>trans</i> - $\text{Ph}_2\text{P}(\text{CH}=\text{CH})\text{PPh}_2$ (<i>trans</i> -dppv)	21.7(2)	2.74	12.7(1)	
$\text{Ph}_2\text{P}(1,2\text{-C}_6\text{H}_4)\text{PPh}_2$ (dppbz)	21.3(1)	2.91 ^e	10.7(3)	
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$ (arphos)	23.2(4)	3.96 ^e	8.2(1)	
$\text{Me}_2\text{PCH}_2\text{PMe}_2$ (dmpm)	31.0(3)	8.24 ^e	25.8(2)	
$\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ (depe)	31.3 ^e	8.41		5.11
$\text{Cr}(\text{CO})_5(\eta^1\text{-dppm})$	17.1(1)			
$\text{Mo}(\text{CO})_5(\eta^1\text{-dppm})$	18.6(1)			
$\text{W}(\text{CO})_5(\eta^1\text{-dppm})$	19.1(3)			
<i>fac</i> - $\text{Mo}(\text{CO})_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$	22.3(2)			
<i>fac</i> - $\text{Mo}(\text{CO})_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$	23.0(1)			
<i>fac</i> - $\text{W}(\text{CO})_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$	23.1(1)			

^a References 30 and 31. ^b For protonation with 1 equiv of $\text{CF}_3\text{SO}_3\text{H}$ in DCE solvent at 25.0 °C. ^c For addition of a second equivalent of $\text{CF}_3\text{SO}_3\text{H}$ in DCE solvent at 25.0 °C. ^d In H_2O . Berners-Price, S. J.; Norman, R. E.; Sadler, P. J. *J. Inorg. Biochem.* **1987**, *31*, 197. ^e Calculated from eq 9.

The CF_3SO_3^- anion of the protonated product is weakly coordinating²³ and therefore less likely to give side reactions in which CF_3SO_3^- displaces ligands in reactant or product complexes; each reaction is examined spectroscopically to ensure that CF_3SO_3^- is not coordinated. The low dielectric constant (10.46) of DCE means that the $\text{H}-\text{ML}_n^+\text{CF}_3\text{SO}_3^-$ products probably occur as ion pairs.^{19–24} While there must be an ion-pairing energy associated with their formation, attempts^{25,26} to determine the effect of ion pairing on trends in ΔH_{HM} values suggest that the effects are small, at least for a family of similar complexes. Other studies also indicate that non-hydrogen-bonding sol-

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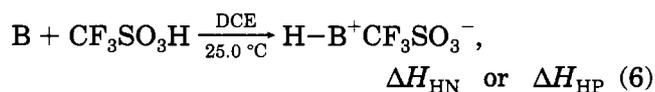
Table 4. Enthalpies of Protonation (ΔH_{HM}) of Transition Metal Complexes^{a,b} with CF_3SO_3H in DCE Solvent at 25.0 °C

compd	$-\Delta H_{HM}$	compd	$-\Delta H_{HM}$
Chromium			
<i>cis</i> -Cr(CO) ₂ (dppm) ₂	25.5(1) ^f		
Molybdenum			
<i>cis</i> -Mo(CO) ₂ (dppp) ₂	19.0(2) ^f	<i>cis</i> -Mo(CO) ₂ (dppm) ₂	29.7(3) ^f
<i>cis</i> -Mo(CO) ₂ (arphos) ₂	23.8(4) ^f	<i>cis</i> -Mo(CO) ₂ (dmpe) ₂	38.7(5) ^f
<i>cis</i> -Mo(CO) ₂ (dppe) ₂	27.4(2) ^f		
Tungsten			
<i>fac</i> -W(CO) ₃ [MeC(CH ₂ PPh ₂) ₃]	10.5(1) ^{d,e}	<i>fac</i> -W(CO) ₃ (η^2 -bpy)(PPh ₂ Me)	18.8(2) ^f
<i>fac</i> -W(CO) ₃ (PMePh ₂) ₃	15.1(3) ^{d,e}	<i>fac</i> -W(CO) ₃ (PMe ₃) ₃	19.5(3) ^f
<i>fac</i> -W(CO) ₃ [PhP(CH ₂ CH ₂ PPh ₂) ₂]	16.7(1) ^{d,e}	<i>fac</i> -W(CO) ₃ (PET ₃) ₃	25.0(3) ^f
<i>fac</i> -W(CO) ₃ (PEtPh ₂) ₃	16.9(3) ^f	<i>cis</i> -W(CO) ₂ (dppe) ₂	25.1(2) ^f
<i>fac</i> -W(CO) ₃ (PMe ₂ Ph) ₃	17.5(2) ^f	<i>cis</i> -W(CO) ₂ (dppm) ₂	31.5(2) ^f
<i>fac</i> -W(CO) ₃ (PEt ₂ Ph) ₃	18.3(1) ^e		
Rhenium			
Cp*Re(CO) ₂ (PMe ₂ Ph)	18.3(4) ^f	Cp*Re(CO) ₂ (PMe ₃)	20.1(3) ^f
Iron			
Fe(CO) ₃ (PPh ₃) ₂	14.1(1) ^g	Fe(CO) ₃ (dppe)	23.2(1) ^h
Fe(CO) ₃ [P(<i>p</i> -MeOC ₆ H ₄) ₃] ₂	16.2(3) ^g	Fe(CO) ₃ (PMe ₃) ₂	23.3(3) ^g
Fe(CO) ₃ (PMePh ₂) ₂	17.6(4) ^g	Fe(CO) ₃ (dppbz)	23.4(2) ^h
Fe(CO) ₃ (dppb)	20.1(2) ^h	Fe(CO) ₃ (dppm)	24.0(2) ^h
Fe(CO) ₃ (dppp)	21.1(2) ^h	Fe(CO) ₃ (diars)	26.5(3) ^h
Fe(CO) ₃ (PMe ₂ Ph) ₂	21.2(3) ^g	Fe(CO) ₃ (dcpe)	28.4(2) ^h
Fe(CO) ₃ (arphos)	22.6(1) ^g	Fe(CO) ₃ (dmpm)	30.2(4) ^h
Fe(CO) ₃ (<i>cis</i> -dppv)	23.1(3) ^h		
Ruthenium			
Cp* ₂ Ru	19.0(1) ^f	CpRu(dppe)H	29.0(1) ^j
CpRu(PMe ₃) ₂ I	20.6(2) ⁱ	CpRu(dppp)H	29.6(1) ^j
CpRu(PMe ₃) ₂ Br	20.9(3) ^j	CpRu(PPh ₃) ₂ H	29.7(2) ^j
CpRu(PMe ₃) ₂ Cl	21.2(4) ^j	Cp* ₂ Ru(PMe ₃) ₂ Cl	30.2(2) ^j
CpRu(dppm)H	28.9(2) ^j	Cp* ₂ Ru(PPh ₃) ₂ H	35.2(2) ^j
Osmium			
CpOs(PPh ₃) ₂ I	14.1(1) ⁱ	Cp* ₂ Os	26.6(2) ^f
CpOs(PPh ₃) ₂ Br	16.3(1) ⁱ	(H) ₄ Os(PPhMe ₂) ₃	27.7(1) ^j
CpOs(dppm)Br	17.5(4) ⁱ	CpOs(PMe ₃) ₂ Br	29.4(4) ^j
CpOs(PPh ₃) ₂ Cl	19.7(2) ^j	CpOs(PPh ₃)[P(OEt) ₃]H	33.6(3) ^j
CpOs(PPh ₂ Me) ₂ Br	20.0(2) ^j	<i>cis</i> -(H) ₂ Os(P(OEt) ₃) ₄	34.2(2) ^j
CpOs(dppp)Br	20.1(4) ^j	<i>cis</i> -(H) ₂ Os(PPh(OEt) ₂) ₄	37.2(2) ^j
(H) ₄ Os(PPh ₂ Me) ₃	23.9(3) ^j	CpOs(PPh ₃) ₂ H	37.3(1) ^j
CpOs(PPh ₃)(PMe ₃)Br	25.6(4) ^j	<i>cis</i> -(H) ₂ Os(PPh ₂ Me) ₄	38.8(2) ^j
CpOs(PPhMe ₂) ₂ Br	26.2(1) ⁱ	CpOs(PPh ₂ Me) ₂ H	39.2(3) ^j
CpOs(PMe ₃) ₂ I	26.6(4) ^j	<i>cis</i> -(H) ₂ Os(PPhMe ₂) ₄	43.3(3) ^j
Iridium			
CpIr[P(OPh) ₃](H) ₂	11.9(2) ^j	Cp*Ir(COD)	28.5(2) ^k
CpIr(AsPh ₃)(H) ₂	19.4(1) ^j	CpIr(CO)[P(<i>p</i> -ClC ₆ H ₄) ₃]	29.2(2) ^g
CpIr(PPh ₃)(H) ₂	19.7(2) ^j	(indenyl)Ir(CO)(PPh ₃)	29.8(3) ^g
Cp*Ir(CO) ₂	21.4(1) ^g	CpIr(CO)(PPh ₃)	30.1(2) ^g
CpIr(COD)	22.8(2) ^k	CpIr(CO)(PMePh ₂)	31.5(1) ^g
(C ₅ MeH ₄)Ir(COD)	24.1(1) ^k	CpIr(CO)(PMe ₂ Ph)	32.4(3) ^g
(1,2,3-C ₅ Me ₃ H ₂)Ir(COD)	26.4(2) ^k	CpIr(CO)(PMe ₃)	33.2(5) ^g
CpIr(CS)(PPh ₃)	26.51(1) ^g	(H)Ir(CO)(PPh ₃) ₃	38.8(4) ^j
(C ₅ Me ₄ H)Ir(COD)	27.5(2) ^k		

^a For each metal, complexes are listed in order of increasing basicity ($-\Delta H_{HM}$). ^b Ligand abbreviations are given in Table 3 or are as follows: 1,2-(Me₂As)₂C₆H₄ (diars), (c-C₆H₁₁)₂PCH₂CH₂P(c-C₆H₁₁)₂ (dcpe), η^5 -C₅H₅ (Cp), η^5 -C₅Me₅ (Cp*), 1,5-cyclooctadiene (COD). ^c Reference 28. ^d Reference 47. ^e Reference 26. ^f Reference 31. ^g Reference 20. ^h Reference 25. ⁱ Reference 18. ^j Reference 63. ^k Reference 16.

vents have little effect on *relative* basicities of metal complexes⁹ or organonitrogen and -sulfur compounds.²⁷

Before discussing enthalpies of protonation of metal complexes, it is worth considering the relationship between ΔH for protonation (eq 6) of simple bases (B) and pK_a values of their protonated forms (HB⁺). For



the amines in Table 1, which span a range of 10.8 pK_a -

(H₂O) units in water, there is an excellent correlation (eq 7, $r = 0.997$)²⁸ between the enthalpy of protonation

$$-\Delta H_{HN} = 1.64 pK_a(H_2O) + 21.0, \text{ in kcal/mol} \quad (7)$$

(eq 6) ($-\Delta H_{HN}$) and the $pK_a(H_2O)$ (Figure 1) despite the substantial differences in solvent properties of 1,2-dichloroethane and water. There are fewer known $pK_a(AN)$ values for amines in acetonitrile solvent (Table 1), but there is likewise a satisfactory correlation (eq 8, $r = 0.989$) between ΔH_{HN} and $pK_a(AN)$. By replacing $-\Delta H_{HN}$ with $-\Delta H_{HM}$, this correlation may

(27) Abboud, J.-L. M.; Notario, R.; Berthelot, M.; Claramunt, R. M.; Cabildo, P.; Elguero, J.; El Ghomari, M. J.; Bouab, W.; Mokhlisse, R.; Guihéneuf, G. *J. Am. Chem. Soc.* **1991**, *113*, 7489.

(28) Sowa, J. R., Jr.; Bonanno, J. B.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1992**, *31*, 1370.

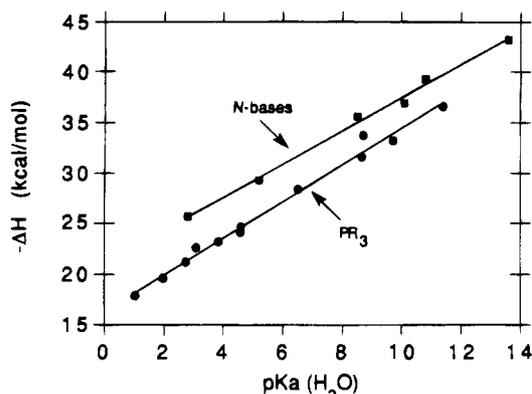


Figure 1. Correlations of $-\Delta H_{\text{HM}}$ for organonitrogen and phosphine bases with their $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ values.

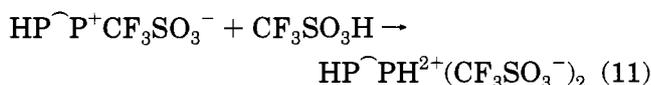
$$-\Delta H_{\text{HN}} = 1.52 \text{ p}K_{\text{a}}(\text{AN}) + 10.4, \quad \text{in kcal/mol} \quad (8)$$

be of use for estimating $-\Delta H_{\text{HM}}$ values (eq 2) for cationic metal hydride complexes whose $\text{p}K_{\text{a}}(\text{AN})$ values are known.^{9,13,15,29} However, it is important to realize inherent shortcomings in using eq 8 for estimating ΔH_{HM} . These are illustrated by a comparison of ΔH vs $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ correlations for amines and phosphines. Like the correlation for amines (eq 7), there is an excellent linear relationship (eq 9, Figure 1) between the enthalpy of protonation (eq 6) ($-\Delta H_{\text{HP}}$) and the $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ of the protonated phosphine (HPR_3^+).¹⁹

$$-\Delta H_{\text{HP}} = 1.82 \text{ p}K_{\text{a}}(\text{H}_2\text{O}) + 16.3, \quad \text{in kcal/mol} \quad (9)$$

However, amines and phosphines (Figure 1) do not follow the same correlation (eqs 7 and 9, Figure 1), which is not surprising given the different solvation and hydrogen-bonding abilities of DCE and H_2O toward nitrogen and phosphorus bases. However, acetonitrile and DCE are likely to have more similar solvent effects than DCE and H_2O , which suggests that eq 8 may be used tentatively for estimating ΔH_{HM} and $\text{p}K_{\text{a}}(\text{AN})$ values for the protonation of neutral complexes.

Diphosphines may be protonated at both phosphorus atoms (eqs 10 and 11). The enthalpy of protona-



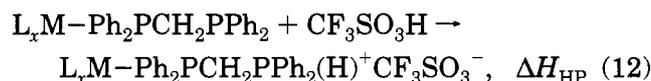
tion for the addition of the first equivalent of $\text{CF}_3\text{SO}_3\text{H}$ is ΔH_{HP1} while that for the second equivalent is ΔH_{HP2} .³⁰ The $-\Delta H_{\text{HP1}}$ values for ligands whose $\text{p}K_{\text{a}1}(\text{H}_2\text{O})$ values are known (Table 3) follow the same correlation (eq 9) as that for monophosphines. As compared with $-\Delta H_{\text{HP}}$ for Ph_2PMe (24.7 kcal/mol), $-\Delta H_{\text{HP1}}$ for dppm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$, 22.0 kcal/mol) is small, which suggests that the PPh_2 group in dppm is electron-withdrawing as compared with H in Ph_2PMe . As the PPh_2 groups are distanced from each other in the $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ series of ligands, $-\Delta H_{\text{HP1}}$ increases to about 24.7 kcal/mol at $n = 4$ and remains at that value for larger n values.

(29) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077.

(30) Sowa, J. R., Jr.; Angelici, R. *J. Inorg. Chem.* **1991**, *30*, 3534.

The $-\Delta H_{\text{HP1}}$ value (22.0 kcal/mol) for dppm is much larger than $-\Delta H_{\text{HP2}}$ (14.9 kcal/mol), which reflects the strongly electron-withdrawing character of the $\text{Ph}_2(\text{H})\text{P}^+$ group in $\text{Ph}_2(\text{H})\text{PCH}_2\text{PPh}_2^+$. However, as n increases from 1 to 5 in the $\text{Ph}_2(\text{H})\text{P}(\text{CH}_2)_n\text{PPh}_2^+$ compounds, the difference between $-\Delta H_{\text{HP1}}$ and $-\Delta H_{\text{HP2}}$ decreases to 0. For n -values of 5 and larger, the $-\Delta H_{\text{HP1}}$ and $-\Delta H_{\text{HP2}}$ values are all the same within experimental error as $-\Delta H_{\text{HP}}$ for Ph_2PMe (24.7 kcal/mol); thus, the Ph_2P groups at the ends of the $-(\text{CH}_2)_n-$ chains behave as independent P-donors. While ΔH_{HP1} and ΔH_{HP2} values are substantially different for dppm, they also differ by large amounts (~ 10 kcal/mol) in diphosphines in which the Ph_2P groups are separated by unsaturated linkages such as a double bond (*cis*-dppv, *trans*-dppv) or an aryl group (dppbz) (Table 3); in these cases the unsaturated linkages readily transmit the electron-withdrawing effect of the $\text{Ph}_2(\text{H})\text{P}^+$ group.

We have also examined³¹ the effect of metal complexes (ML_x) coordinated at one end of dppm on the basicity (Table 3) of the dangling PPh_2 group (eq 12).



For the complexes where ML_x is $\text{Cr}(\text{CO})_5$ (17.1 kcal/mol), $\text{Mo}(\text{CO})_5$ (18.6), or $\text{W}(\text{CO})_5$ (19.1), the dangling PPh_2 group is less basic than in dppm (22.0 kcal/mol) itself but is considerably more basic than $\text{Ph}_2(\text{H})\text{PCH}_2\text{PPh}_2^+$ (14.9 kcal/mol). The $\text{M}(\text{CO})_3(\text{N}^{\wedge}\text{N})$ groups are not electron-withdrawing at all and may even slightly increase the basicity of the dangling PPh_2 group as detected in the following $-\Delta H_{\text{HP}}$ values: $\text{Mo}(\text{CO})_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ (22.3 kcal/mol), $\text{Mo}(\text{CO})_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ (23.0), $\text{W}(\text{CO})_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ (23.1). Since the metal in these complexes must act as a σ -bonding electron acceptor, any increase in electron density on the dangling PPh_2 group presumably occurs as a result of metal-to-P π back-bonding.

The overall effect of H^+ and WL_x complexes on dangling PPh_2 basicity is summarized in the following trend in $-\Delta H_{\text{HP}}$: $\text{H}(\text{dppm})^+$ (14.9 kcal/mol) < $\text{W}(\text{CO})_5(\eta^1\text{-dppm})$ (19.1) < dppm (22.0) < $\text{W}(\text{CO})_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ (23.1). The observation that the $\eta^1\text{-dppm}$ complexes are protonated at the dangling PPh_2 rather than at the metal suggests that the metal is the less basic site, even in the most electron-rich complex $\text{W}(\text{CO})_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$. This was confirmed for *fac*- $\text{W}(\text{CO})_3(\eta^2\text{-bpy})(\text{PPh}_2\text{Me})$, which has a $-\Delta H_{\text{HM}}$ value (18.8 kcal/mol) that is 4.3 kcal/mol less basic than the dangling PPh_2 in $\text{W}(\text{CO})_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$.

Effects of Monophosphine Ligands on Metal Basicity

Phosphines are common ligands in transition metal complexes; there is evidence^{9,13} that the basicity of the metal in these complexes increases as the basicity of its phosphine ligands increases. We have determined ΔH_{HM} values (Table 4) for four series of complexes, $\text{CpIr}(\text{CO})(\text{PR}_3)$,²⁰ $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$,²⁰ $\text{CpOs}(\text{PR}_3)_2\text{Br}$,¹⁸ and *fac*- $\text{W}(\text{CO})_3(\text{PR}_3)_3$,²⁶ where PR_3 is PPh_3 , PPh_2Me , PPhMe_2 , or PMe_3 . For these protonation reactions (eqs 13,²⁰ 14,²⁰ 15,²⁰ and 16²⁶), $-\Delta H_{\text{HM}}$ increases as

(31) Rottink, M. K.; Angelici, R. *J. Inorg. Chem.* **1993**, *32*, 2421.

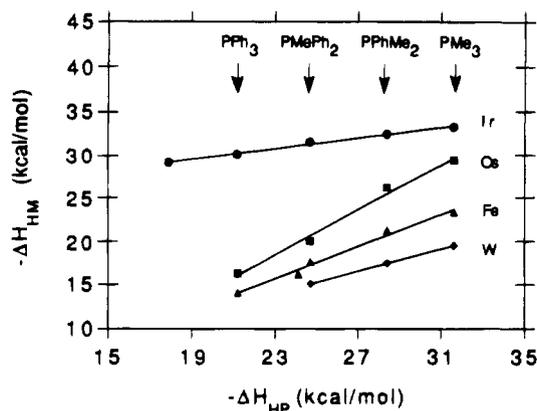
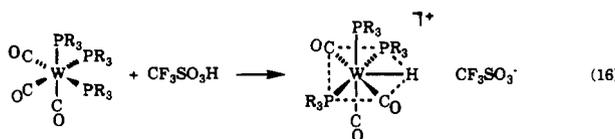
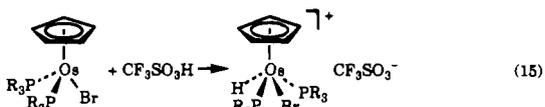
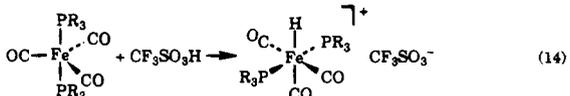


Figure 2. Correlations of metal basicity ($-\Delta H_{HM}$) with phosphine basicity ($-\Delta H_{HP}$) for $\text{CpIr}(\text{CO})(\text{PR}_3)$, $\text{CpOs}(\text{PR}_3)_2\text{Br}$, $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$, and *fac*- $\text{W}(\text{CO})_3(\text{PR}_3)_3$ (eqs 13–20).

the basicity ($-\Delta H_{HP}$) of the phosphine increases. Plots



of $-\Delta H_{HM}$ vs $-\Delta H_{HP}$ (Figure 2) for these complexes are linear and are represented by eqs 17,²⁰ 18,²⁰ 19,¹⁸ and 20²⁶ (all values in kcal/mol). Since $-\Delta H_{HP}$ and

$$-\Delta H_{HM} = -0.298\Delta H_{HP} + 23.9, \quad \text{for } \text{CpIr}(\text{CO})(\text{PR}_3) \quad (17)$$

$$-\Delta H_{HM} = -0.916\Delta H_{HP} - 5.36, \quad \text{for } \text{Fe}(\text{CO})_3(\text{PR}_3)_2 \quad (18)$$

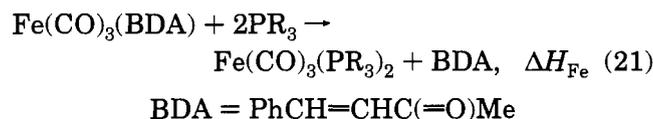
$$-\Delta H_{HM} = -1.31\Delta H_{HP} - 11.6, \quad \text{for } \text{CpOs}(\text{PR}_3)_2\text{Br} \quad (19)$$

$$-\Delta H_{HM} = -0.638\Delta H_{HP} - 0.645, \quad \text{for } \text{W}(\text{CO})_3(\text{PR}_3)_3 \quad (20)$$

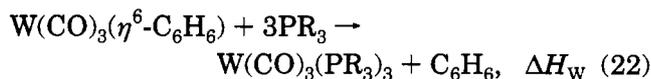
$\text{p}K_a(\text{H}_2\text{O})$ for the phosphines are correlated (eq 9), plots of $-\Delta H_{HM}$ vs $\text{p}K_a(\text{H}_2\text{O})$ are also linear. The coefficient for the $-\Delta H_{HP}$ term in eqs 17–20 gives the change in metal basicity with a change of 1.0 kcal/mol in PR_3 basicity. Since several of the complexes involve replacement of more than one PR_3 ligand, a comparison of ligand effects is most useful if the coefficient of the $-\Delta H_{HP}$ term is divided by the number of PR_3 ligands. This gives the following metal basicity change parameters: $\text{CpIr}(\text{CO})(\text{PR}_3)$ (0.298), $\text{Fe}(\text{CO})_3$ -

$(\text{PR}_3)_2$ (0.916/2 = 0.458), $\text{CpOs}(\text{PR}_3)_2\text{Br}$ (1.31/2 = 0.65), $\text{W}(\text{CO})_3(\text{PR}_3)_3$ (0.638/3 = 0.213). It is clear that the metal basicity change parameter is different for each series of complexes. Given the widely differing structures of the reactants and products in each series, many factors contribute to the different parameters for each set of complexes. The relative insensitivity of the $\text{CpIr}(\text{CO})(\text{PR}_3)$ complexes to a change in PR_3 basicity has been rationalized²⁰ by noting that the Cp in the related $\text{CpRh}(\text{CO})_2$ is an excellent π -accepting ligand,³² the Cp in $\text{CpIr}(\text{CO})(\text{PR}_3)$ could partially remove electron density from the Ir donated to it by the more basic phosphines. One might expect the CO groups in the $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$ complexes to play the same role; yet the change in metal basicity per phosphine (0.456) is substantially greater than that (0.298) in $\text{CpIr}(\text{CO})(\text{PR}_3)$. The very low sensitivity (0.213) of ΔH_{HM} in the *fac*- $\text{W}(\text{CO})_3(\text{PR}_3)_3$ complexes could be due to the π -accepting CO groups; however, it is evident that steric factors are also involved since complexes of the more bulky Et ligands (PEtPh_2 , PEt_2Ph , and PEt_3) are more basic than those of PMePh_2 , PMe_2Ph , and PMe_3 .²⁶ Complexes of the bulky ligands presumably favor protonation because crowding in the starting *fac*- $\text{W}(\text{CO})_3(\text{PR}_3)_3$ complexes is relieved by rearrangement to a meridional-type structure in the protonated product (eq 16). Steric effects of PR_3 ligands are also likely to contribute to the high sensitivity (0.65) of $-\Delta H_{HM}$ to phosphine basicity in the $\text{CpOs}(\text{PR}_3)_2\text{Br}$ complexes. In this case, the steric effect plays in the opposite direction with the more bulky ligands such as PPh_3 disfavoring the addition of another ligand (H^+) to the Os. Thus, $\text{CpOs}(\text{PPh}_3)_2\text{Br}$ is especially weakly basic compared to $\text{CpOs}(\text{PMe}_3)_2\text{Br}$ not only because PPh_3 is a much weaker base than PMe_3 but also because of steric crowding in the product. Evidence of this steric effect is seen in the $-\Delta H_{HM}$ (25.6 kcal/mol) of the mixed ligand complex $\text{CpOs}(\text{PPh}_3)(\text{PMe}_3)\text{Br}$, which is not intermediate between that of $\text{CpOs}(\text{PPh}_3)_2\text{Br}$ (16.3 kcal/mol) and $\text{CpOs}(\text{PMe}_3)_2\text{Br}$ (29.4); it is only 3.8 kcal/mol less basic than $\text{CpOs}(\text{PMe}_3)_2\text{Br}$ but 9.3 kcal/mol more basic than $\text{CpOs}(\text{PPh}_3)_2\text{Br}$. An argument based on the electronic properties of PPh_3 and PMe_3 does not readily account for this result; however, the substitution of one PPh_3 in $\text{CpOs}(\text{PPh}_3)_2\text{Br}$ by PMe_3 would substantially reduce crowding in the protonated product and make protonation much more favorable for $\text{CpOs}(\text{PPh}_3)(\text{PMe}_3)\text{Br}$ than for $\text{CpOs}(\text{PPh}_3)_2\text{Br}$.

In the metal carbonyl systems, $\text{CpIr}(\text{CO})(\text{PR}_3)$, $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$, and *fac*- $\text{W}(\text{CO})_3(\text{PR}_3)_3$, the $-\Delta H_{HM}$ values correlate linearly with $\nu(\text{CO})$ frequencies of the complexes,^{20,26} but there is not a broader correlation among the different types of complexes. Thus, $\nu(\text{CO})$ values are not a general predictor of $-\Delta H_{HM}$ values. There are, however, correlations between $-\Delta H_{HM}$ and the donor abilities of the $\text{PMe}_x\text{Ph}_{3-x}$ phosphines as measured by enthalpies of the following reactions:



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The correlation between $-\Delta H_{\text{HM}}$ for the reaction in eq 14 with ΔH_{Fe} (eq 21³³) is given in eq 23 while that between $-\Delta H_{\text{HM}}$ for the reaction in eq 16 and ΔH_{W} (eq 22^{34,35}) is shown in eq 24.

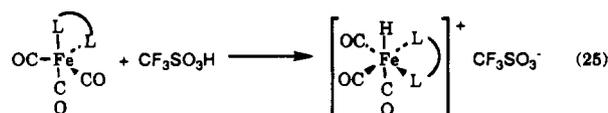
$$-\Delta H_{\text{HM}} = -0.741\Delta H_{\text{Fe}} - 6.4, \quad \text{in kcal/mol}, \\ r = 0.972 \quad (23)$$

$$-\Delta H_{\text{HM}} = -0.365\Delta H_{\text{W}} - 4.6, \quad \text{in kcal/mol}, \\ r = 0.999 \quad (24)$$

In addition to phosphine ligand effects on metal basicity, there are a few comparisons of phosphines with olefins and CO. The $-\Delta H_{\text{HM}}$ of $\text{Cp}^*\text{Ir}(\text{CO})_2$, where $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, is 21.4 kcal/mol, whereas the $-\Delta H_{\text{HM}}$ of the 1,5-cyclooctadiene (COD) analog $\text{Cp}^*\text{Ir}(\text{COD})$ is 28.5 kcal/mol.^{17,18} Thus, the diolefin ligand makes the iridium 7.1 kcal/mol more basic than the two CO ligands. However, the iridium in $\text{CpIr}(\text{COD})$ (22.8 kcal/mol) is 7.3 kcal/mol less basic than that in $\text{CpIr}(\text{CO})(\text{PPh}_3)$ (30.1 kcal/mol). Thus, the basicity of the metal in $\text{Cp}^*\text{Ir}(\text{L})(\text{L}')$ complexes increases with the $(\text{L})(\text{L}')$ ligand set in the following order: $(\text{CO})_2 < \text{COD} < (\text{CO})(\text{PPh}_3)$. The 14.4 kcal/mol difference between the $(\text{CO})_2$ and $(\text{CO})(\text{PPh}_3)$ ligand groups corresponds (eq 5) to a 4×10^{10} ratio of their equilibrium protonation constants. Dramatic increases in basicities of $\text{M}(\text{CO})_x^-$ anions when a CO ligand is replaced by a phosphine are also found in studies⁹ of $\text{p}K_{\text{a}}(\text{AN})$ and $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ values of $\text{HM}(\text{CO})_x(\text{L})_y$ complexes. Despite the weak donor character of CO as a ligand, CS is even weaker, as indicated by the $-\Delta H_{\text{HM}}$ values for $\text{CpIr}(\text{CO})(\text{PPh}_3)$ (30.1 kcal/mol) and $\text{CpIr}(\text{CS})(\text{PPh}_3)$ (26.5 kcal/mol).²⁰

Chelating Phosphine Ligand Effects on Metal Basicity

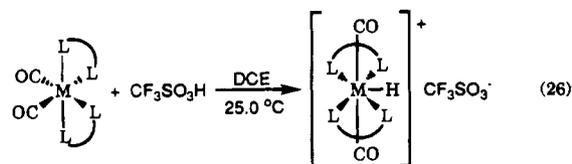
The ring size of diphosphine chelating ligands is known to influence a variety of properties of metal complexes including their structures,^{36,37} catalytic activities,^{36,38,39} rates of CO insertion,⁴⁰ oxidation potentials,⁴¹ and ³¹P NMR chemical shifts.⁴² The first study²⁵ to identify a chelate effect on metal complex basicity was that of the $\text{Fe}(\text{CO})_3(\text{bidentate phosphine})$ complexes (eq 25). It established that all of the chelated complexes $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$ are more basic than the monodentate phosphine analog $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PMe})_2$ (eq 14) and that the metal basicity increases as the size of the chelate ring decreases. The



$-\Delta H_{\text{HM}}$ values (Table 3) increase in the order following: $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PMe})_2$ (17.6 kcal/mol) $<$ $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)$ (20.1) $<$ $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)$ (21.1) $<$ $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ (23.2) $<$ $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ (24.0). The difference (6.4 kcal/mol) in $-\Delta H_{\text{HM}}$ values between the most basic complex $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ and the least basic $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PMe})_2$ represents a difference in equilibrium protonation constants (eq 5) of approximately 5×10^4 . A similar difference (6.9 kcal/mol) between $-\Delta H_{\text{HM}}$ for $\text{Fe}(\text{CO})_3(\text{Me}_2\text{PCH}_2\text{PMe}_2)$ (30.2 kcal/mol) and $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$ (23.3) is also observed.²⁵ In order to understand these substantial differences in $-\Delta H_{\text{HM}}$, one might consider the effect of the different product structures in eqs 14 and 25. The protonated monodentate product $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PMe})_2(\text{H})^+$ has *trans* Ph_2PMe ligands (eq 14), which is presumably the most stable arrangement of the P-donor ligands since there is no evidence for the *cis* structure. The *cis* P-donor arrangement in the chelated products $\text{Fe}(\text{CO})_3(\text{L}^-\text{L}')(\text{H})^+$ would therefore be less stable and the driving force for their formation (eq 25) should be less than that in eq 14. This argument leads to the conclusion that $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PMe})_2$ should be more basic than $\text{Fe}(\text{CO})_3(\text{L}^-\text{L}')$, which is opposite to the experimental results.

The reactant structures, however, are also different in the monodentate (eq 14) and bidentate (eq 25) complexes. The diaxial structure of $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PMe})_2$ is presumably the most stable because it is the one that is observed, and extended Hückel MO calculations⁴³ support this as the most stable geometry with the strongest π -accepting ligands (CO) in the equatorial positions. Thus, distortions from the diaxial phosphine arrangement will increase the energy of the complex, thereby increasing the exothermicity of its protonation. X-ray structures of the $\text{Fe}(\text{CO})_3(\text{L}^-\text{L}')$ complexes show that the P-Fe-P angle⁴⁴ decreases in the same order as the basicity increases: $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)$ (92.4°) $>$ $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)$ (91.5°) $>$ $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ (84.1°) $>$ $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ (73.5°). Thus, the greater the distortion from the most stable diaxial P-donor arrangement (180°) in $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PMe})_2$, the higher the basicity.

Results of the $\text{Fe}(\text{CO})_3(\text{L}^-\text{L}')$ studies suggest that distortion of a reactant by a chelating ligand from its most stable geometry, i.e., that adopted by monodentate ligands, will increase its basicity. Such a trend is also observed in ΔH_{HM} studies (eq 26) of the *cis*- $\text{M}(\text{CO})_2(\text{L}^-\text{L}')_2$ complexes, where M = Mo or W. In



this system $-\Delta H_{\text{HM}}$ also increases as the chelate ring

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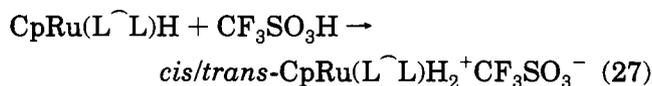
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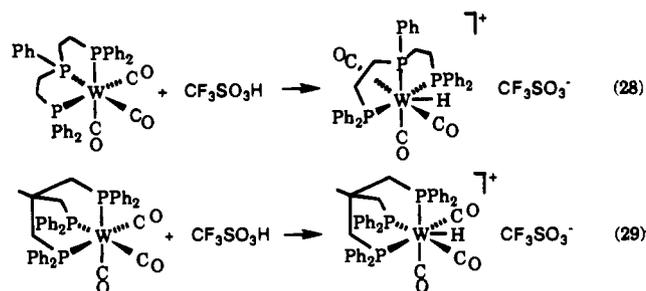
size decreases:²⁸ $\text{Mo}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2$ (19.0 kcal/mol) < $\text{Mo}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2$ (27.4) < $\text{Mo}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$ (29.7). The analogous *cis*- $\text{W}(\text{CO})_2(\text{L}^-\text{L})_2$ complexes follow the same $-\Delta H_{\text{HM}}$ trend: $\text{W}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2$ (25.1) < $\text{W}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$ (31.5). As for the $\text{Fe}(\text{CO})_3(\text{L}^-\text{L})$ complexes, these increasing basicities parallel decreasing P–M–P bond angles as the chelate ring size decreases; this decrease in P–M–P angles is illustrated by the series of $\text{Mo}(\text{CO})_4(\text{L}^-\text{L})$ complexes:⁴⁵ $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)$ (91.65°) > $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)$ (89.74°) > $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ (80.2°) > $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ (67.3°). Thus, complexes with P–M–P angles that are much smaller than 90° have the highest basicities. The effect on $-\Delta H_{\text{HM}}$ is very large in the $\text{Mo}(\text{CO})_2(\text{L}^-\text{L})_2$ series, where $\text{Mo}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$ is 10.7 kcal/mol more basic than $\text{Mo}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2$; in terms of their equilibrium constants (eq 5) for protonation, $\text{Mo}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$ is 7×10^7 times more basic than $\text{Mo}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2$. Thus, chelate ring effects on metal basicity can be very large.

In contrast, very small differences in $-\Delta H_{\text{HM}}$ (eq 27¹⁸) have been noted for the series of complexes $\text{CpRu}(\text{L}^-\text{L})\text{H}$: $\text{CpRu}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{H}$ (29.6 kcal/mol) > $\text{CpRu}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)\text{H}$ (29.0) > $\text{CpRu}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{H}$ (28.9). While these $-\Delta H_{\text{HM}}$ values are nearly



within experimental error of each other, equilibrium constant measurements⁴⁶ for protonations of these complexes show that the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ complex is indeed the weakest base, which is opposite to the trend for the $\text{Fe}(\text{CO})_3(\text{L}^-\text{L})$ and *cis*- $\text{Mo}(\text{CO})_2(\text{L}^-\text{L})_2$ series of complexes. In the $\text{CpRu}(\text{L}^-\text{L})\text{H}$ system, the structure of the product contains either *cis* or *trans* P-donor groups, depending on the bidentate ligand. Complexes $\text{CpRu}(\text{L})_2(\text{H})_2^+$ with monodentate phosphine ligands have the *trans* structure, as does $\text{CpRu}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{H})_2^+$. Since the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligand does not permit a *trans* structure, $\text{CpRu}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\eta^2\text{-H}_2)^+$ has *cis* P-donor groups and an $\eta^2\text{-H}_2$ ligand.⁴⁶ This is presumably a higher energy structure than the *trans*- $\text{CpRu}(\text{L})_2(\text{H})_2^+$ geometry adopted by monodentate ligands. Therefore, protonation of $\text{CpRu}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{H}$ to give the less stable *cis* structure is less favorable than protonation of $\text{CpRu}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{H}$, which yields the stable *trans* product. The $\text{CpRu}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)\text{H}_2^+$ complex is an intermediate situation since it exists as a mixture of *cis* and *trans* isomers. Thus, the basicities of the $\text{CpRu}(\text{L}^-\text{L})\text{H}$ complexes are determined by the length of the $-(\text{CH}_2)_n-$ link between the P-donors; those links that permit formation of the more stable *trans* structure upon protonation are the most basic.

Structural effects of tridentate ligands are observed in the $-\Delta H_{\text{HM}}$ value for *fac*- $\text{W}(\text{CO})_3[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$ (16.7 kcal/mol) (eq 28), which is much more basic than *fac*- $\text{W}(\text{CO})_3[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]$ (10.5 kcal/mol) (eq 29).^{26,47} Like *fac*- $\text{W}(\text{CO})_3(\text{PPh}_2\text{Me})_3$ (15.1 kcal/

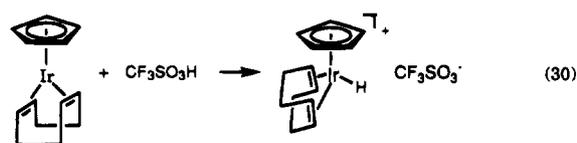


mol, eq 16), both of the tridentate complexes have *facial* structures. Upon protonation, $\text{W}(\text{CO})_3(\text{PPh}_2\text{Me})_3$ rearranges⁴⁸ to a structure in which two CO groups are *trans* to each other and the three PPh_2Me ligands are approximately coplanar with the tungsten (eq 16). The protonated tridentate tungsten complex $\text{W}(\text{CO})_3[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2](\text{H})^+$ has a similar structure, and its $-\Delta H_{\text{HM}}$ value (16.7 kcal/mol) is similar to that (15.1 kcal/mol) of $\text{W}(\text{CO})_3(\text{PPh}_2\text{Me})_3$. The much lower $-\Delta H_{\text{HM}}$ value (10.5 kcal/mol) for $\text{W}(\text{CO})_3[\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3]$ presumably results from the inability of the $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ ligand to give a protonated product with the stable structure in which the three P-donor groups are approximately coplanar with the tungsten. Thus, the higher energy structure of the protonated $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ complex makes ΔH_{HM} much less exothermic for the reaction in eq 29 than those in eqs 16 and 28.

From the studies discussed in this section, it is evident that multidentate ligands may increase or decrease the basicities of metal complexes by distorting the reactants or products from their most stable structures, that is, structures that are preferred by the metal center with monodentate ligands.

Methylcyclopentadienyl Ligand Effects on Metal Basicity

There has been much interest⁴⁹ in the electronic^{50,51} and steric effects⁵² of the cyclopentadienyl ligand and its methyl-substituted derivatives on the properties of transition metal complexes. For the protonation reaction in eq 30,¹⁶



$-\Delta H_{\text{HM}}$ increases regularly by 1.1 kcal/mol for each CH_3 group introduced into the Cp ring, as noted for the following complexes: $(\text{C}_5\text{H}_5)\text{Ir}(\text{COD})$ (22.8 kcal/mol) < $(\text{C}_5\text{MeH}_4)\text{Ir}(\text{COD})$ (24.1) < $(1,2,3\text{-C}_5\text{Me}_3\text{H}_2)\text{Ir}(\text{COD})$ (26.4) < $(\text{C}_5\text{Me}_4\text{H})\text{Ir}(\text{COD})$ (27.5) < $(\text{C}_5\text{Me}_5)\text{Ir}(\text{COD})$ (28.5). The 5.7 kcal/mol higher $-\Delta H_{\text{HM}}$ value for $\text{Cp}^*\text{Ir}(\text{COD})$ as compared with $\text{CpIr}(\text{COD})$ corresponds (eq 5) to an equilibrium constant (*K*) for

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protonation that is 1.5×10^4 higher for the Cp* compound. For the only other pairs of Cp*ML_x compounds (Cp' = Cp* or Cp) for which $-\Delta H_{\text{HM}}$ values have been determined, the Cp* compound is the more basic by the amount indicated: Cp'Ru(PPh₃)₂H (5.5 kcal/mol) < Cp'Ru(PMe₃)₂Cl (9.0).¹⁸ The greater basicity increase in Cp'Ru(PMe₃)₂Cl upon replacing Cp by Cp* may be due to the poorer π -accepting ability of PMe₃, which makes the Ru in this complex more sensitive to changes in the donor ability of the Cp' ligand. It is also possible that Cp* crowding in the Cp*Ru(PPh₃)₂H complex makes its protonation less favorable than it would have been without this steric consideration. The η^5 -indenyl ligand has the same effect as Cp since the $-\Delta H_{\text{HM}}$ values of (η^5 -indenyl)-Ir(CO)(PPh₃) (29.8 kcal/mol) and CpIr(CO)(PPh₃) (30.1) are the same within experimental error;²⁰ on the basis of results from other studies,⁵³ the η^5 -indenyl ligand has been described as a stronger donor than Cp.

Hydride and Halide Ligand Effects on Metal Complex Basicity

The influence of hydride and halide ligands (X⁻) on $-\Delta H_{\text{HM}}$ was determined in protonations of the CpM(PR₃)₂X complexes (eq 31).¹⁸ For the CpOs(PPh₃)₂X



complexes, $-\Delta H_{\text{HM}}$ increases with X⁻ in the order I⁻ (14.1 kcal/mol) < Br⁻ (16.3) < Cl⁻ (19.7) < H⁻ (37.3). There are two notable trends in these results. First, the H⁻ complexes are enormously more basic than any of the halide analogs. Second, the basicity of the metal increases with the halide in an order, I⁻ < Br⁻ < Cl⁻, that is opposite to that expected on the basis of their electronegativities. Both of these results can be understood in terms of the donor abilities of the X⁻ ligands. As we showed for phosphine ligands, $-\Delta H_{\text{HM}}$ values of complexes increase as the basicities of their PR₃ ligands increase. For the X⁻ ligands, we choose the gas-phase proton affinities (PA) of the X⁻(g) ions as measures of their basicities; their PA values increase as follows: I⁻ (314.3 kcal/mol) < Br⁻ (323.6) < Cl⁻ (333.3) < H⁻ (400.4).^{54,55} These values are in the same order as the $-\Delta H_{\text{HM}}$ values for the CpOs(PPh₃)₂X complexes; moreover, there is an excellent correlation (eq 32,¹⁸ $r = 0.9995$) between $-\Delta H_{\text{HM}}$ and PA. Since PA values are known⁵⁴ for a large number

$$-\Delta H_{\text{HM}} = 0.2698(\text{PA}) - 70.64, \text{ in kcal/mol} \quad (32)$$

of other X⁻(g) ions, eq 32 should be useful for predicting basicities of other CpOs(PPh₃)₂X complexes, including those of CH₃, NR₂, and SR, where $-\Delta H_{\text{HM}}$ cannot be measured because protonation either occurs on X⁻ or leads to removal of the X⁻ ligand as HX.

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The trend in $-\Delta H_{\text{HM}}$ values for the CpOs(PPh₃)₂X complexes could also be interpreted in terms of the size of the X⁻ ligand; the smaller the X⁻, the more favorable the protonation because there would be less steric crowding in the product. To test this possibility, $-\Delta H_{\text{HM}}$ values for the analogous CpOs(PPh₂Me)₂X complexes with the less bulky PPh₂Me ligand were measured. Here, too, the H⁻ complex (39.2 kcal/mol) is much more basic (19.2 kcal/mol) than the Br⁻ analog (20.0). Since the difference between the H⁻ and Br⁻ complexes is somewhat smaller in the PPh₂Me complexes (19.2 kcal/mol) than in the more crowded PPh₃ complexes (21.0 kcal/mol), steric effects may account for a small portion of the large difference in basicities between the H⁻ and Br⁻ complexes; however, it cannot be the primary factor. In the CpOs(PPh₃)₂X halide series, where the differences in ΔH_{HM} are relatively small, the size of the halide ligand may play a role. This is supported by the observation that $-\Delta H_{\text{HM}}$ (eq 31) depends only slightly on the halide in the less crowded series of CpRu(PMe₃)₂X complexes, where $-\Delta H_{\text{HM}}$ increases as follows: I⁻ (20.6 kcal/mol) < Br⁻ (20.9) < Cl⁻ (21.2).¹⁸ Another interpretation⁵⁶ of the trend in $-\Delta H_{\text{HM}}$ values with different halide (X⁻) ligands considers that both σ - and π -donation of electron density from X⁻ contribute to the increasing basicity of the metal in the order I⁻ < Br⁻ < Cl⁻. Evidence for halide π -donation has been reported in other Ru complexes,⁵⁷ although the effect must be small in the CpRu(PMe₃)₂X complexes, where $-\Delta H_{\text{HM}}$ changes very little with X⁻.

The very large difference between $-\Delta H_{\text{HM}}$ values for the CpOs(PR₃)₂X hydride and halide complexes suggests that the electron density on the Os is much higher in the H⁻ complex. This difference between CpOs(PPh₃)₂H and CpOs(PPh₃)₂I is 23.2 kcal/mol; in terms of equilibrium constants (K , eq 5), the H⁻ complex is 1.1×10^{17} more basic. To put this large difference in K values in the context of other large changes in K , we note that Ryan, Tilset, and Parker^{15,58,59} estimated pK_a values from electrochemical studies for a series of metal hydride complexes HML_x and the corresponding HML_x⁺ cations. The cationic complexes are approximately 21 pK_a units more acidic than the neutral analogs. For specific pairs of neutral and cationic complexes, the differences in pK_a units are as follows: CpRu(CO)(PPh₃)₂H (23), CpCr(CO)₃H (22.8), Cp*Cr(CO)₃H (23.3), CpCr(CO)₂(PPh₃)H (23.9), CpMo(CO)₃H (19.9), CpW(CO)₃H (19.1), CpW(CO)₂(PMe₃)H (21.5). Choosing 21 pK_a units, i.e., $K = 10^{21}$, as a representative difference between neutral (0) and cationic (H) complex acidities, our difference of 10^{17} between the basicities of the H⁻ and I⁻ complexes of CpOs(PPh₃)₂X is nearly as large as occurs upon one-electron oxidation. If Os is considered to be in the +2 oxidation state in CpOs(PPh₃)₂I, then the effective oxidation state of Os in CpOs(PPh₃)₂H is only slightly higher than +1. This means that the H behaves as a H atom ligand and the electrons in the Os-H bond are nearly equally shared by the two atoms.

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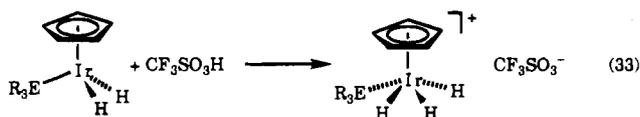
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The remarkable ability of H^- to increase the basicity of a metal complex affects significantly the chemistries of its complexes compared to those of the corresponding halide derivatives. While the above $-\Delta H_{\text{HM}}$ measurements are only for the $\text{CpOs}(\text{PR}_3)_2\text{X}$ system, qualitative results suggest that, in general, hydride complexes are surprisingly basic toward protons even when the metal is in a high formal oxidation state, e.g., $\text{ReH}_5(\text{PPh}_3)_3$,⁶⁰ $\text{OsH}_4(\text{PPhMe}_2)_3$ ⁶¹ (see next section), and many others.^{13a,62} In contrast, halide complexes with the metal in a high oxidation state cannot be protonated; even in low oxidation states, halide compounds are not often protonated. The high basicity of hydride complexes is important in catalytic systems involving hydrogenation (H_2) of a substrate. The degree of protonation of hydride intermediates will be strongly influenced by the presence of hydride or halide ligands. In general, the hydride ligand imparts quite different properties to a metal complex than a halide does despite the fact they are both considered as formally -1 ligands.

Effects of Isoelectronic Ligand Groups on Metal Complex Basicities

Since many transition metal complexes follow the 18-electron rule, one ligand or set of ligands may be replaced by an isoelectronic set of ligands to give a new complex that also obeys the 18-electron rule. In the studies described in this section, we sought to understand how such isoelectronic ligand replacements affect the basicities ($-\Delta H_{\text{HM}}$) of metal complexes. We compare complexes with the isoelectronic series of ligands: $(\text{H})_2$, CO , and PR_3 . In another series, basicities of complexes with the ligand sets Cp and $(\text{H})(\text{PR}_3)_2$ are compared. While the interpretation of differences in $-\Delta H_{\text{HM}}$ values for complexes with isoelectronic ligand sets is inherently risky because of the different structures of reactants and products, the results may allow us to estimate basicities of a broader range of complexes.

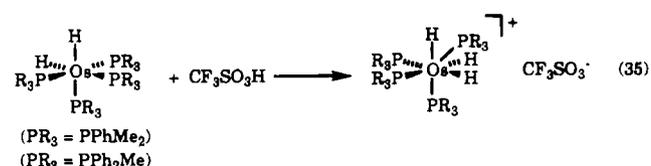
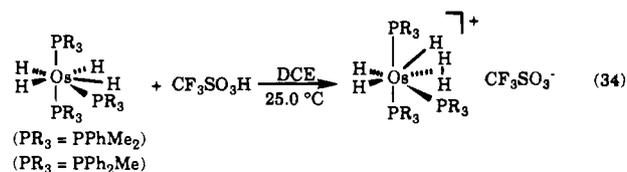
For the $(\text{H})_2$ and CO ligand sets, we determined $-\Delta H_{\text{HM}}$ values for the protonation (eq 33⁶³) of $\text{CpIr}(\text{PPh}_3)(\text{H})_2$ (19.7 kcal/mol) and $\text{CpIr}(\text{PPh}_3)(\text{CO})$ (eq 13, 30.1 kcal/mol). The 10.4 kcal/mol lower basicity of the



dihydride complex indicates that, despite the strong donor ability of the H^- ligand as compared with the halides, the strongly π -accepting CO ligand nevertheless gives the most basic complex. Formally, the oxidation state of the Ir is $+3$ in the $(\text{H})_2$ complex but only $+1$ in the CO compound. It was noted in the previous section that a one-electron oxidation causes an approximately 10^{21} decrease in the protonation equilibrium constant. The 10.4 kcal/mol reduction in basicity observed upon replacing CO by $(\text{H})_2$ in the

$\text{CpIr}(\text{PPh}_3)$ system corresponds to a decrease in the protonation equilibrium constant (eq 5) of only 4.4×10^7 , which is substantially lower than the 10^{21} decrease expected for even a one-electron oxidation. Thus, while the $-\Delta H_{\text{HM}}$ values suggest that the electron density on Ir in $\text{CpIr}(\text{PPh}_3)(\text{H})_2$ is lower than that in $\text{CpIr}(\text{PPh}_3)(\text{CO})$, the difference is *much* smaller than would be expected for a formal oxidation of Ir from $+1$ to $+3$.

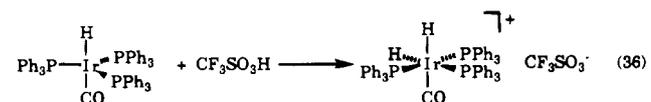
The effect on $-\Delta H_{\text{HM}}$ of replacing $(\text{H})_2$ by PPhMe_2 was studied in protonations of $(\text{H})_4\text{Os}(\text{PPhMe}_2)_3$ (eq 34)^{63,64} and $(\text{H})_2\text{Os}(\text{PPhMe}_2)_4$ (eq 35).⁶³ As replace-



ment of $(\text{H})_2$ by CO increased the basicity of the metal in the $\text{CpIr}(\text{PPh}_3)$ complexes, the substitution of $(\text{H})_2$ in $(\text{H})_4\text{Os}(\text{PPhMe}_2)_3$ (27.7 kcal/mol) by PPhMe_2 to give $(\text{H})_2\text{Os}(\text{PPhMe}_2)_4$ (43.3 kcal/mol) also increases the basicity of the Os; this increase (15.6 kcal/mol) is somewhat larger than observed for $(\text{H})_2$ replacement by CO (10.4 kcal/mol). Thus, the increase in metal basicity with these isoelectronic ligands follows the trend $(\text{H})_2 < \text{CO} < \text{PR}_3$. It should be emphasized that these comparisons are qualitative because of the substantial differences in reactant and product structures.

It is rather remarkable that $(\text{H})_4\text{Os}(\text{PPhMe}_2)_3$ (27.7 kcal/mol) is nearly as basic as pyridine (29.3 kcal/mol) despite the $+4$ oxidation state of the Os. The dihydride complex $(\text{H})_2\text{Os}(\text{PPhMe}_2)_4$ (43.3 kcal/mol) is even more basic than Et_3N (39.3 kcal/mol). These results illustrate again the strong donor ability of H^- ligands.

Structural differences in reactants and products make interpretations of $-\Delta H_{\text{HM}}$ values for complexes of the Cp and $(\text{H})(\text{PR}_3)_2$ isoelectronic ligand sets even more speculative. Replacement of Cp in $\text{CpIr}(\text{PPh}_3)(\text{CO})$ (30.1 kcal/mol) by $(\text{H})(\text{PPh}_3)_2$ in $(\text{H})(\text{PPh}_3)_2\text{Ir}(\text{PPh}_3)(\text{CO})$ (eq 36,⁶³ 38.8 kcal/mol) increases the Ir basicity by 8.7 kcal/mol. On the other hand, replace-



ment of Cp in $\text{CpOs}(\text{PPh}_2\text{Me})_2\text{H}$ (39.2 kcal/mol) by $(\text{H})(\text{PPh}_2\text{Me})_2$ in $(\text{H})(\text{PPh}_2\text{Me})_2\text{Os}(\text{PPh}_2\text{Me})_2(\text{H})$ (eq 35, 38.8 kcal/mol) slightly *decreases* the basicity of Os by 0.4 kcal/mol. Thus, $-\Delta H_{\text{HM}}$ differences between related Cp and $(\text{H})(\text{PR}_3)_2$ complexes are not sufficiently consistent to be useful for estimating $-\Delta H_{\text{HM}}$ values for these types of complexes.

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Replacement of Cp* in Cp*RuCp* (19.0 kcal/mol) by (H)(PPh₃)₂ to give (H)(PPh₃)₂RuCp* (eq 31, 35.2 kcal/mol) increases the basicity of the Ru by 16.2 kcal/mol. Replacement of both Cp* ligands in Cp*₂Os (26.6 kcal/mol) by two (H)(PPh₂Me)₂ sets to give H₂Os(PPh₂Me)₄ (38.8 kcal/mol) increases the Os basicity by 12.2 kcal/mol.

For the multihydride complexes described in this section, we also observed that $-\Delta H_{\text{HM}}$ for the protonation (eq 33) of CpIr(ER₃)(H)₂ increases with ER₃ in the order P(OPh)₃ (11.9 kcal/mol) < AsPh₃ (19.4) ~ PPh₃ (19.7).⁶³ For the *cis*-(H)₂Os(PR₃)₄ complexes, the basicities (eq 35, $-\Delta H_{\text{HM}}$) increase with the PR₃ ligand in the order P(OEt)₃ (34.2 kcal/mol) < PPh(OEt)₂ (37.2) < PPh₂Me (38.8) < PPhMe₂ (43.3).⁶³

Effects of Different Metals within the Same Group

With few exceptions, the basicities of transition metal complexes reported in the literature⁹ increase as the metal is replaced by successively heavier metals from the same group. The same general trend is observed in systems where ΔH_{HM} has been determined. Thus, for the following pairs of Os and Ru complexes, $-\Delta H_{\text{HM}}$ of the Os derivative is more positive than that of the Ru analog by the amount (kcal/mol) indicated in parentheses: CpM(PMe₃)₂I (6.0 kcal/mol), CpM(PPh₃)₂H (7.6), Cp*₂M (7.6), CpM-(PMe₃)₂Br (8.5). These results indicate that replacement of Ru by Os increases the basicity of the complex by 6.0–8.5 kcal/mol, with an average value of 7.4 kcal/mol.

For the *cis*-M(CO)₂(Ph₂PCH₂PPh₂)₂ series of complexes, the $-\Delta H_{\text{HM}}$ values increase as the group 6 metal becomes heavier in the following order: Cr (25.5 kcal/mol) < Mo (29.7) < W (31.5). However, for the closely related *cis*-M(CO)₂(Ph₂PCH₂CH₂PPh₂)₂ complexes, $-\Delta H_{\text{HM}}$ is larger for Mo (27.4 kcal/mol) than W (25.1); this is one of the few exceptions⁹ to the normal trend.

Conclusion and Trends

From these ΔH_{HM} results, we can extract the following conclusions that might be of use to chemists whose applications of organometallic complexes depend on knowing something about the basicity or electron richness of a metal complex. These guidelines may be useful for estimating basicities ($-\Delta H_{\text{HM}}$) of complexes related by the substitution of one ligand for another; by using eq 5, differences in protonation equilibrium constants (*K*) can be approximated:

(1) The $-\Delta H_{\text{HM}}$ of a complex depends linearly on the basicity ($-\Delta H_{\text{HP}}$ or $\text{p}K_{\text{a}}$) of its phosphine ligands. Replacement of a PPh₃ ligand by PMe₃ increases the basicity of the metal by 3.1–6.6 kcal/mol.

(2) Chelating phosphines can increase the basicity of a complex by distorting the structure of the reactant from its most stable geometry. Chelate-induced distortions of the protonated product decrease the basicity of the complex.

(3) Replacement of Cp by Cp* increases the basicity of the complex by 5.5–9.0 kcal/mol.

(4) For the CpM(PR₃)₂X complexes (M = Ru, Os), the basicity increases in the order I⁻ < Br⁻ < Cl⁻ <<< H⁻. The $-\Delta H_{\text{HM}}$ values correlate with the proton affinities (PA) of the X⁻ ligands. The H⁻ complex is approximately 20 kcal/mol more basic than the halide analogs.

While these guidelines are useful for complexes that are modifications of compounds whose basicities are known, the only way to determine basicities of other types of complexes is to measure them experimentally. We still have much to learn about the factors that influence the basicities of metal complexes.

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